

CHEMICAL PROPERTIES AND ANALYSIS OF REFRACTORY COMPOUNDS

ХИМИЧЕСКИЕ СВОЙСТВА И МЕТОДЫ АНАЛИЗА ТУГОПЛАВКИХ СОЕДИНЕНИЙ

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# CHEMICAL PROPERTIES AND ANALYSIS OF REFRACTORY COMPOUNDS


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## PREFACE

This collection sets out the results of various investigations into the chemical properties of refractory compounds and refractory-base alloys used in various fields of modern technology, together with original methods of analysis.

The book is intended for analytical chemists, engineers, workers in scientific-research establishments and industrial laboratories, graduates, and students of the senior courses in chemical and metallurgical higher-education institutions.

# CONTENTS

Interaction of the Carbides of Group IV and V Transition Metals with Various Acids E. E. Kotlyar and T. N. Nazarchuk . . . . .	1
Method of Quantitative X-ray Analysis for Determining the Amount of Free Carbon in Boron Carbide M. I. Sokhor and G. V. Sofronov . . . . .	6
Method of Separating and Determining the Free Carbon in Materials Containing Refractory Compounds L. A. Mashkovich and A. F. Kuteinikov . . . . .	14
Stability of Boron–Carbon Compounds in Oxygen at High Temperatures L. E. Pechentkovskaya and T. N. Nazarchuk . . . . .	20
Certain Chemical Properties of Boron Carbonitride L. E. Pechentkovskaya and T. N. Nazarchuk . . . . .	25
Oxidation of Boron, Gallium, and Indium Phosphides in Air L. L. Vereikina . . . . .	29
High-Temperature Oxidation Resistance of Refractory Silicon Nitride–Silicon Carbide Materials I. N. Godovannaya and O. I. Popova . . . . .	33
Production and Chemical Stability of the Hydrides of Group IV and V Transition Metals M. M. Antonova . . . . .	36
Chemical Analysis of the Reaction Products of Boron with Arsenic and Phosphorus A. A. Reshchikova and Z. S. Medvedeva . . . . .	42
Complexometric Analysis of Molybdenum Alloys L. N. Kugai, O. F. Galadzhii, and V. I. Kornilova . . . . .	48
Analysis of Titanium, Zirconium, Hafnium, and Tantalum Germanides G. T. Kabannik and O. I. Popova . . . . .	54
Some Data Relating to the Chemical Properties of Germanides O. I. Popova . . . . .	57
Analysis of the Selenides of the Rare–Earth Elements V. A. Obolonchik and T. M. Mikhlina . . . . .	61
Complexometric Analysis of Alloys of the Rare–Earth Oxides with the Oxides of Group II Elements and Chromium S. F. Boremskaya and G. T. Kabannik . . . . .	64

Separation of Alloyed Chromium Carbides of the $\text{Cr}_2\text{C}$ (Metastable) and $\text{Cr}_{23}\text{C}_6$ or $\text{Cr}_7\text{C}_3$ Types Isolated from Steels and Alloys L. V. Zaslavskaya, N. V. Ivanova, and N. F. Lashko . . . . .	68
Chemical and Electrochemical Methods of Separating the Carbides $\text{MeC}$ and the Carbonitrides $\text{Me}(\text{C}, \text{N})$ of Group IV and V Metals G. G. Georgieva, N. F. Lashko, and K. P. Sorokina . . . . .	72
Electrolytic Isolation of the $\sigma$ Phase from Heat-Resistant Steels and the Determination of Its Composition E. F. Yakovleva, I. M. Dubrovina, and L. V. Stegnukhina . . . . .	77
Interaction of Refractory Group V Metals with Zinc A. P. Obukov, V. N. Gurin, I. R. Kozlova, Z. P. Terent'eva, and T. I. Mazina . . . . .	81
Determination of Tungsten in Binary Tungsten-Molybdenum Alloys Z. S. Mukhina, L. I. Il'ina, and N. S. Kondukova . . . . .	86
Determination of Molybdenum in the Presence of Tungsten V. G. Shcherbakov, Z. K. Stegendo, and R. A. Antonova . . . . .	91
Photometric Determination of Boron in Nickel and Titanium Borides Using Magnezona I in an Alkaline Medium E. I. Nikitina . . . . .	94
Spectrophotometric Study of the Formation of Compounds between Niobium and the Reagent PAN V. I. Kornilova . . . . .	100
Determination of Arsenic in High-Purity Molybdenum V. G. Shcherbakov and G. V. Onuchina . . . . .	103
Chemical Phase Analysis of Mixtures of Borides, Carbides, and Borocarbides N.V. Vekshina and L. Ya. Markovskii . . . . .	106
Interaction of Borides with Carbon and Carbides L. Ya. Markovskii, N. V. Vekshina, and E. T. Bezruk . . . . .	114
Chemical Properties and Analysis of Certain Transition Metal Sulfides S. V. Radzikovskaya and V. F. Bukhanevich . . . . .	119
Analysis of the Silicides of Group IV to VI Transition Elements V. P. Kopylova and T. N. Nazarchuk . . . . .	123

# INTERACTION OF THE CARBIDES OF GROUP IV AND V TRANSITION METALS WITH VARIOUS ACIDS

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The interaction of the carbides of Group IV and V transition metals with acids and alkalis has hitherto mainly been studied in order to secure qualitative or semiquantitative data relating to their chemical stability; no attention has been paid to the composition of the gaseous decomposition products [2].

The aim of the present investigation was to study the interaction of carbides with phosphoric, sulfuric, and nitric acids, to establish the composition of the gaseous decomposition products, and to use the results in discussing the nature of the chemical bond in the carbides.

The interaction of the carbides with concentrated phosphoric, sulfuric, and nitric acids was studied in an inert-gas (nitrogen) atmosphere, heating being carried out in the apparatus illustrated in Fig. 1.

A 0.1-0.3 g sample of carbide was placed in a Wurtz flask, into which 30-40 ml of acid were poured. In order to study the interaction of the carbides with the sulfuric acid, 50 ml of 80% isopropyl alcohol solution were poured into the first washing bottle to absorb the  $\text{SO}_3$  [4] and 50 ml of 2% iodine solution into the second to absorb the  $\text{SO}_2$ , while in studying the interaction of the carbides with nitric acid both washing bottles were filled with 1:1 sulfuric acid in order to remove the nitrogen oxides. Then the whole system was connected as indicated in Fig. 1.

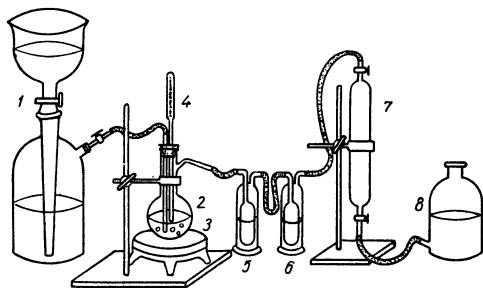


Fig. 1. Apparatus for studying the interaction of carbides with acids: 1) Gas-holder with nitrogen; 2) Wurtz flask; 3) electric plate; 4) thermometer; 5) bottle containing 80% isopropyl alcohol for absorbing  $\text{SO}_3$ ; 6) bottle containing 2% iodine solution for absorbing  $\text{SO}_2$ ; 7) gas burette; 8) pressure-head bottle.

In order to displace the air before the beginning of the reaction, nitrogen was passed slowly through the whole system for 2-2.5 h (3-4 bubbles per second), after which the reaction mixture was heated (with the tap open in the gas burette) and the gases evolved were collected. When the reaction had finished, the solution was analyzed for metal content, while the undissolved residue was analyzed for carbide and free carbon. The gas mixture was analyzed chromatographically. The carbon material balance was determined to an accuracy of 3-5%.

TABLE 1. Composition of the Products of the Interactions between Group IV and V Transition Metal Carbides and Sulfuric, Phosphoric, and Nitric Acids

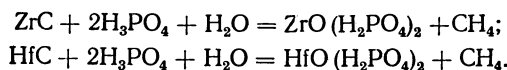
Products of the interaction	Reaction temperature, °C	Reaction time, h	Decomposing carbide, %	Amorphous carbon, %	Composition of gas mixture (chromatographic method)			
					CH <sub>4</sub>	CO	CO <sub>2</sub>	H <sub>2</sub>
ZrC+H <sub>3</sub> PO <sub>4</sub> (d=1.7 g/cm <sup>3</sup> )	260-270	1	100.0	—	91.4	—	7.8	0.8
	250-255	1	100.0	—	87.3	—	12.0	0.7
HfC+H <sub>3</sub> PO <sub>4</sub> (d=1.7 g/cm <sup>3</sup> )	230-240	1.5	77.0	—	62.1	—	35.2	3.0
	250	1	100.0	—	77.2	—	19.3	3.4
	250-270	1.5	100.0	—	69.3	—	28.9	1.7
TiC+H <sub>2</sub> SO <sub>4</sub> (d=1.84 g/cm <sup>3</sup> )	240-250	2	74.5	57.0	—	18.0	8.0	2.0
	250-270	2	76.0	33.0	—	6.3	92.4	1.3
	315-320	1	100.0	25.7	—	5.5	92.0	1.5
ZrC+H <sub>2</sub> SO <sub>4</sub> (d=1.84 g/cm <sup>3</sup> )	260	1	100.0	14.2	48.2	—	48.2	3.0
	200-235	1.5	100.0	7.0	71.0	—	26.5	2.5
HfC+H <sub>2</sub> SO <sub>4</sub> (d=1.84 g/cm <sup>3</sup> )	264-268	1	100.0	16.1	64.2	—	31.8	4.0
	290-300	1	100.0	6.3	16.2	—	81.3	2.4
VC+H <sub>2</sub> SO <sub>4</sub> (d=1.84 g/cm <sup>3</sup> )	260	1.5	—	—	—	20.0	78.0	2.0
	300	1	—	—	—	—	96.4	3.6
NbC+H <sub>2</sub> SO <sub>4</sub>	260	1.5-2	93.0	36.3	—	19.7	79.0	1.3
	280	1.5	92.0	47.0	—	24.3	73.8	1.9
	290-310	1	100.0	—	—	13.7	82.9	3.4
	265	1.5	81.0	13.0	—	5.4	92.3	2.3
TaC+H <sub>2</sub> SO <sub>4</sub>	255	1.5	75.0	10.0	—	2.2	96.0	1.6
	276	1.0	86.0	6.0	—	6.0	92.3	1.7
ZrC+HNO <sub>3</sub>	110-120	0.5	100.0	—	Trace	—	95-97	2-3
HfC+HNO <sub>3</sub>	110-120	0.5	100.0	—	Trace	—	95-97	2-3
NbC+HNO <sub>3</sub> +NH <sub>4</sub> F	110-120	0.5	100.0	—	—	Trace	95-97	2-3
TaC+HNO <sub>3</sub> +NH <sub>4</sub> F	110-120	0.5	100.0	—	—	Trace	95-97	2-3

At 230-260°C, concentrated phosphoric acid (d = 1.7) only decomposes zirconium and hafnium carbides. Decomposition starts at 230-240°C, and at 250° the dissolution proceeds very energetically; on boiling for 30-40 min these carbides decompose completely. Titanium, vanadium, niobium, and tantalum carbides are unaffected by phosphoric acid, even on heating to 300°C.

The main gaseous decomposition product resulting from the interaction of hafnium and zirconium carbides with phosphoric acid is methane (70-90 vol.%). Apart from this, the products include hydrogen (1-3%) and CO<sub>2</sub> (Table 1).

The resultant solutions are dense and transparent; on heavily diluting with water, amorphous white precipitates appear, and, after heating, these transform into pyrophosphates Zr<sub>2</sub>P<sub>2</sub>O<sub>7</sub> and Hf<sub>2</sub>P<sub>2</sub>O<sub>7</sub>. According to Brauer [5], the acid zirconium and hafnium phosphates (biphosphates) ZrO(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>, HfO(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> in the freshly precipitated state dissolve in a mixture of phosphoric, oxalic, and sulfuric acids with the formation of soluble complexes. Evidently these complexes are also formed in the presence of a large excess of concentrated phosphoric acid. Diluted with water, i.e., on reducing the concentration of phosphoric acid, they transform into poorly-soluble middle phosphates and are precipitated.

The decomposition of the hafnium and zirconium carbides by phosphoric acid may be represented by the equations



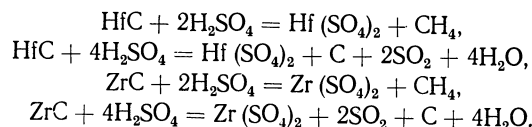


Concentrated sulfuric acid decomposes all the carbides between 200 and 300°C. The decomposition of hafnium and zirconium carbides starts at 200–220°C; at 230–250°C they are dissolved very energetically, and decompose completely in 30–40 min. The titanium, niobium, and tantalum carbides decompose by 70–80% on boiling for 1.5 h at 250–260°C, and decompose completely after boiling for 1.5–2 h at 290–310°C. The decomposition of all the carbides is accompanied by the release of amorphous carbon, which gives the solution a chestnut color in the finely-dispersed state. At the beginning of the interaction the solution and the walls of the vessel show amorphous carbon flakes; at the end of the reaction the solution clears and at 290–310°C it becomes transparent.

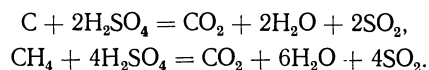
The precipitation of amorphous carbon was observed by Greenwood and Osborne [6] when lanthanum dicarbide interacted with 4 N sulfuric acid. The solution of 2% iodine in the washing bottle becomes much lighter during the reaction; frequently it is completely decolorized by the evolving SO<sub>2</sub>.

It follows from the tabulated data that the interaction of zirconium and hafnium carbides with sulfuric acid differs from that of titanium, vanadium, niobium, and tantalum carbides, not only in respect of the temperature range of decomposition and the period of dissolution, but also in respect of the composition of the gaseous products. The gaseous products of the decomposition of zirconium and hafnium carbides contain methane (50–70 vol.%), CO<sub>2</sub> (30–50 vol.%), and hydrogen (2.5–4%). The ratio of methane, CO<sub>2</sub>, and amorphous carbon depends on the temperature.

The principal reaction governing the decomposition of hafnium and zirconium carbides by sulfuric acid may be expressed as follows:



Secondary reactions:

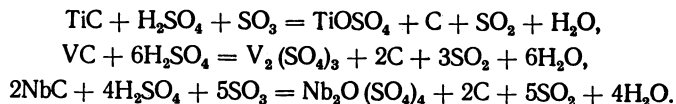


The interaction of titanium, vanadium, niobium, and tantalum carbides with concentrated sulfuric acid results in the precipitation of amorphous carbon. The amount of amorphous carbon relative to the whole of the decomposing carbon in the titanium carbide is 57–33% between 240 and 270°C; in the case of niobium carbide the figures are 47–36%. Vanadium carbide decomposes partly, with the formation of vanadium sulphate (green solution) and a poorly soluble yellow precipitate, which, according to analysis, has the formula composition V<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>; in all other cases the solutions are viscous and transparent after decomposition, and no precipitates are formed on diluting with water. Hydrolysis of the solutions only occurs after prolonged standing. It thus follows that titanium, niobium, and tantalum carbides decompose with the formation of oxysulphates stable in concentrated H<sub>2</sub>SO<sub>4</sub> [1].

The composition of the gaseous products includes carbon monoxide (5–25%), carbon dioxide (70–90%), and hydrogen (1.5–3.0%). No methane is found in the gas phase at any temperature.

The ratio of the amorphous carbon, carbon monoxide, and carbon dioxide depends on the temperature. This would suggest that the CO and CO<sub>2</sub> are not the direct products of the decomposition of the carbides but are formed as a result of the oxidation of the amorphous carbon by the concentrated sulfuric acid.

The decomposition of the titanium, niobium, and tantalum carbides by fuming sulfuric acid is represented by the equations:

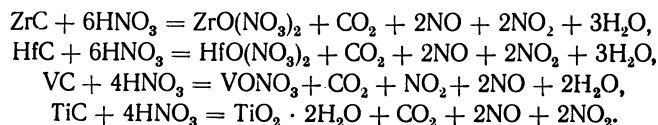


Nitric acid ( $d = 1.43$ ) and nitric acid (1:1) decompose zirconium, hafnium, titanium, and vanadium carbides at 100–110°C. No carbon is precipitated in the decomposition; after the dissolution of the vanadium, zirconium, and hafnium carbides, the solutions are transparent, i.e., the interaction involves the formation of soluble nitrates. Titanium carbide is decomposed completely with the precipitation of titanium hydroxide  $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ .

In the decomposition of zirconium and hafnium carbides, the gas fraction incorporates 95–97% of  $\text{CO}_2$ , 2–3% of hydrogen, and traces of methane. In the decomposition of vanadium and titanium carbides, the gas products contain hydrogen (2–3%) and traces of carbon monoxide as well as  $\text{CO}_2$ .

Niobium and tantalum carbides are decomposed by nitric acid at 100–120°C in the presence of a 5% solution of ammonium fluoride. After decomposition the solutions are transparent, no precipitation of amorphous carbon taking place. The gaseous products include carbon dioxide (95–97%), hydrogen (2–3%), and traces of carbon monoxide.

The interaction of the carbides with nitric acid may be represented by the equations:



It follows from the foregoing data that only zirconium and hafnium carbides are decomposed by phosphoric and sulfuric acids with the evolution of methane (as the principal gaseous product), i.e., the carbon in these carbides is present in the form of  $\text{C}^4$  groups possessing the stable  $\text{sp}^3$  electron configuration. The even bonds of the carbon are symmetrical and identical; they form covalent polarized bonds with the metal, and this leads to considerable polarization of the  $\text{ZrC}$  and  $\text{HfC}$  molecules, although clearly the ionic bond is not the predominant one in these carbides, since they are not decomposed by water and dilute acids like carbides of the ionic type such as  $\text{ScC}$ ,  $\text{YC}$ , and others. The absence of methane from the composition of the gaseous products in the decomposition of titanium, vanadium, niobium, and tantalum carbides indicates that the ionic  $\text{Me}-\text{C}$  bond is either entirely absent from these carbides or at any rate contribute very little.

As we have found, the carbides of the group IV transition metals (particularly zirconium and hafnium) are chemically much less stable than the group V carbides; the chemical stability of the group IV carbides diminishes with increasing atomic number of the transition metal (from titanium carbide to hafnium carbide), and this may be explained, as indicated in the foregoing, by the increase in the proportion of ionic bond in the same order. The chemical stability of the group V carbides, on the other hand, increases with increasing atomic number, from vanadium carbide to tantalum carbide.

In respect of its chemical properties, tantalum carbide resembles the carbides of the covalent type. This is evidently due to the fact that, in the carbides of group V metals, the covalent bonds between the atoms of the transition metals are particularly sharply expressed; the proportion of the covalent  $\text{Me}-\text{Me}$  bond increases with diminishing acceptor capacity of the metal, from vanadium carbide to tantalum carbide [3].

### Conclusions

Concentrated phosphoric acid only decomposes zirconium and hafnium carbides at 230–250°C with the evolution of methane (70–90 vol.%). Titanium, vanadium, niobium, and tantalum carbides are not decomposed by phosphoric acid, even at 300°C.

Concentrated sulfuric acid decomposes all the carbides between 200 and 300°C. Zirconium and hafnium carbide decompose at 200–230°C with the formation of amorphous carbon and the evolution of methane as the principal gaseous product (50–70 vol.%). Titanium, vanadium, niobium, and tantalum carbides decompose at 250–300°C with the formation of amorphous carbon. The gaseous products include hydrogen, CO, and CO<sub>2</sub>. Nitric acid, as a strong oxidizing agent, decomposes titanium, niobium, zirconium, and vanadium carbides with the evolution of carbon dioxide. Niobium and tantalum carbides are decomposed by nitric acid in the presence of ammonium fluoride.

The results of our analysis of the gaseous products obtained in the decomposition of the carbides by phosphoric and sulfuric acids confirm the corresponding chemical-stability data and lead to the conclusion that zirconium and hafnium carbides possess a considerable proportion of an ionic Me–C bond.

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# METHOD OF QUANTITATIVE X-RAY ANALYSIS FOR DETERMINING THE AMOUNT OF FREE CARBON IN BORON CARBIDE

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The method principally employed at the present time for determining the amount of free carbon in boron carbide is chemical analysis. There are two well-known chemical methods: the direct determination of  $C_{\text{free}}$ , and an indirect determination based on the overall composition ( $B_{\text{tot}}$  and  $C_{\text{tot}}$ ). The direct chemical analysis for  $C_{\text{free}}$  is based on treating the boron carbide with a chromic mixture and plotting a graph of the amount of  $\text{CO}_2$  evolved against the period of oxidation. However, in treating the sample with the chromic mixture partial oxidation of the boron carbide itself occurs, and the results of the chemical analysis for  $C_{\text{free}}$  may therefore be too high. Furthermore, it is assumed in both chemical methods that the boron carbide is always of the same composition given by the formula  $\text{B}_4\text{C}$ , while the  $C_{\text{free}}$  is the proportion of the carbon actually free [5]. The assumption as to the constant composition of the carbon and boron carbide leads to a second assumption, namely, that the properties of the two phases, and in particular their oxidizability, remain constant.

However, there is no certain evidence as to the constancy of the properties of the carbon and boron carbide in different samples. Earlier investigations (1957-1961) showed that the free carbon in boron carbide was frequently not pure graphite, but that it contained boron in the form of a solid solution of varying concentration; boron carbide had a wide range of compositions, from  $\text{B}_4\text{C}$  to  $\text{B}_{6.75}\text{C}$  [3, 8].

These doubtful assumptions underlying the existing chemical methods of quantitatively determining the amount of free carbon  $C_{\text{free}}$  in boron carbide have made it desirable to develop an x-ray method of quantitative determination, allowing for the composition and structural state of the boron carbide and the carbon phase [9].

Figure 1 presents the Debye photographs of single-phase samples of boron carbide and graphite and a sample of commercial boron carbide containing free carbon. The x-ray method under consideration is based on determining the intensity of the (002) line of graphite relative to the intensity of the (110) line of boron carbide. The choice of these lines is due to the fact that the amount of free carbon in the commercial boron carbide is usually no greater than a few percent, so that the graphite phase appearing on the x-ray diffraction patterns of the commercial boron carbide will usually only be represented by the single, very strong graphite (002) line, with  $\theta_{\text{Co}} \approx 15^\circ$ , the intensity of this line on the x-ray diffraction patterns being similar to that of the neighboring (110) line of the boron carbide phase with  $\theta_{\text{Co}} \approx 18.5^\circ$  (Fig. 2).

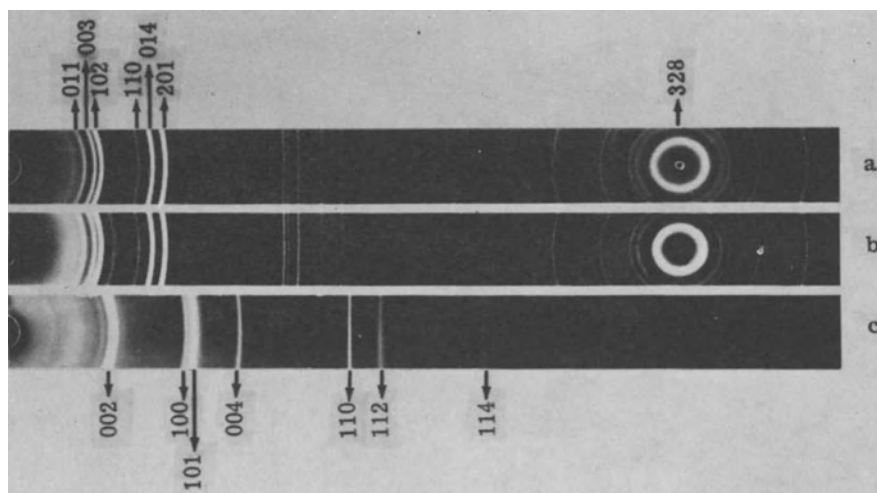


Fig. 1. Debye photographs of single-phase boron carbide  $B_{4.78}C$  (a), commercial boron carbide containing the nominal compound together with 2% of free carbon (b), and ARV graphite (c).  $Co K_{\alpha}$  radiation.

We developed the x-ray quantitative analysis of the  $C_{free}$  content on the basis of Palatnik's superposition technique [4].

The superposition method is based on comparing the x-ray diffraction patterns of the systems under analysis with standard superposition x-ray diffraction patterns obtained by x-ray photographing the single-phase constituents of the two-phase system on a single film. By varying the ratio of the exposures of the individual components we may vary the ratio of the line intensities on the superposition photographs, which is equivalent to varying the concentration of the components in the mixture.

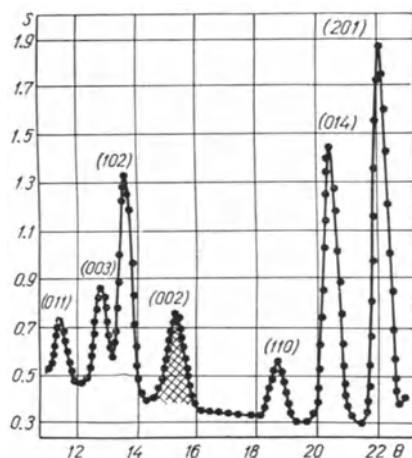


Fig. 2. Microphotometer recording of the front section of the Debye photograph of commercial boron carbide containing free carbon. (Six forward lines of boron carbide and the (002) line of graphite are illustrated.)  $Co K_{\alpha}$  radiation.

In order to obtain the superposition Debye photographs, a special Debye camera (D-85) 85 mm in diameter had to be developed and constructed so as to facilitate the successive photographing of two or more samples on the same film without unloading the camera [6]. The form of the camera (with an indication of the individual units) is shown in Fig. 3. In contrast to the usual Debye cameras, the D-85 has interchangeable holding units for the cylindrical sample, enabling the sample to be adjusted outside the camera by means of a special adjusting device (Fig. 4). The holder with its duly adjusted sample is placed in the already loaded camera. The camera records lines corresponding to reflection angles  $\theta$  between 7 and 87.5° [2]. The sample is provided with rotation during the exposure.

Different carbon-containing materials are characterized by fine differences in the degree of perfection of their crystal lattices and the shape and size of the graphite crystals. These differences are reflected in the Debye photographs (Fig. 5). A particular feature is the fact that the structural state of the carbon phase changes the fine

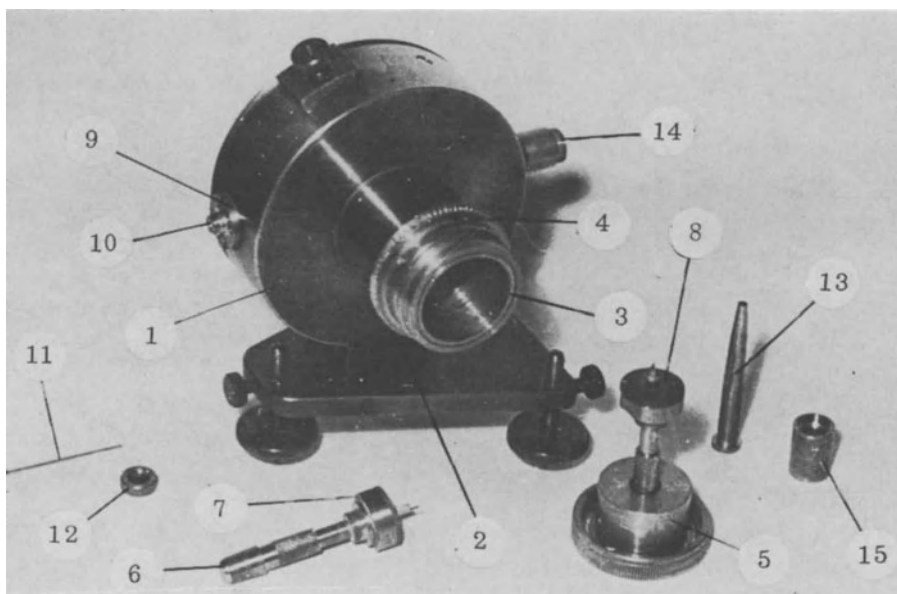


Fig. 3. The D-85 camera in dismantled form: 1) Body; 2) support connecting the body to the base of the camera; 3) sliding bearing with a conical socket for the sample holder; 4) pulley attached to bearing 3; 5) conical socket with the sample holder unit installed; 6) conical rod of the sample holder; 7) permanent magnet press-fitted to the rod 6; 8) soft iron disc with sample attached (the sample is adjusted by moving the disc with the magnet 7); 9) insertion piece guiding the collimator 10; 11) needle entering into the collimator 10 and cutting out a beam of x rays 0.5–0.8 mm in diameter [7]; 12) nut for setting the filter and fixing the trap (this is screwed on to the insertion piece 9); 13) primary-beam trap; 14) insertion piece for siting the trap 13; 15) nut with fluorescent screen (screwed on to the insertion piece 14).

structure and absolute intensity of the strongest line, the (002), which is used to determine the  $C_{\text{free}}$  content of the sample. Figure 6 shows the dependence of the (002) line intensity of petroleum coke on the temperature of graphitization as obtained experimentally. The intensity of the (002) line of ARV graphite is arbitrarily taken as 100%. We see that the intensity of the (002) line of petroleum coke increases with increasing graphitization temperature. However, the x-ray pictures show that the diffuseness of the edges of the (002) line remains unaltered. For graphites of the ARV or Acheson type the (002) line is sharp and clear with a high intensity and no splitting. Natural graphite gives a split (002) line due to the texture of the sample.

Many years of experience in microscope and x-ray diffraction work carried out in our Institute (by V. G. Kondakov and A. A. Kalinina) in relation to various types of commercial boron carbide have shown that the structural state of the carbon phase in boron carbide may vary considerably, being determined by the manufacturing conditions. In high-quality boron carbide the free carbon occurs in the form of a finely-dispersed phase, often forming a eutectic with the boron carbide and constituting a solid solution of boron in graphite. In relation to the x-ray effect, this kind of finely-dispersed graphite in boron carbide may be formally likened to carbon material with a low degree of graphitization, for example, petroleum coke roasted at 1550°C. In products obtained from melts of commercial boron carbide, and very frequently in

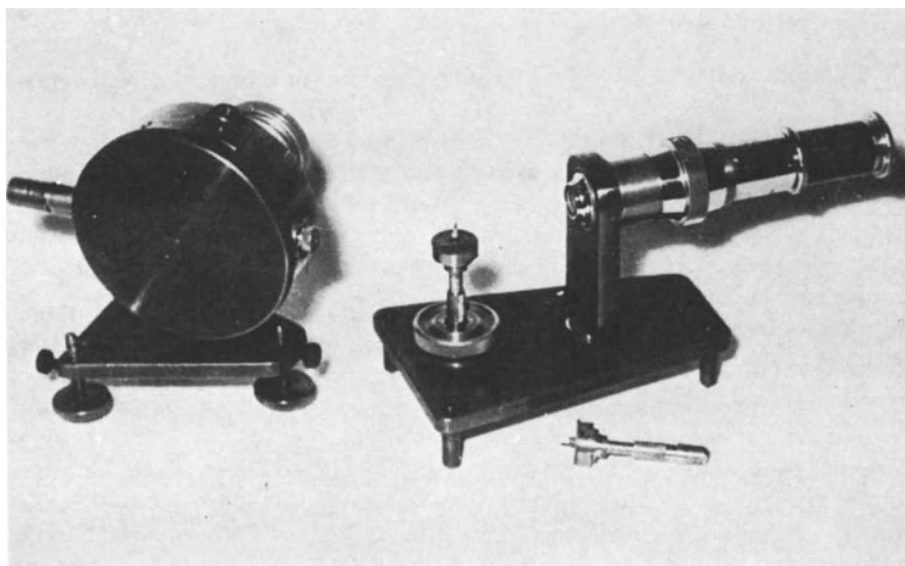


Fig. 4. D-85 camera in assembled form and adjusting attachment enabling the sample to be adjusted outside the camera.

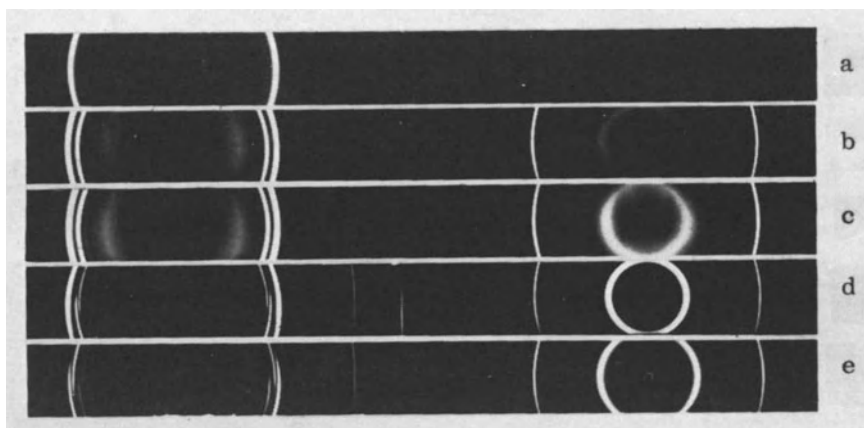


Fig. 5. Debye photographs of various carbon-containing materials. a) Petroleum coke roasted at  $1550^{\circ}$  for 1.5 h; b) Acheson graphite; c) ARV graphite; d) natural graphite; e) graphite extracted from contaminated boron carbide. Cr radiation.

pressed boron-carbon alloys, we encounter graphite in the form of larger precipitates also. This graphite gives an x-ray diffraction pattern similar to that of ARV or Acheson graphite. In some cases of boron-carbon alloys prepared by repeated hot pressing, or in graphitized fused boron carbide in which the boron carbide decomposes, the graphite separates in the form of perfect petal-like crystals, giving a texture during the preparation of the sample. The x-ray diffraction patterns of this kind of graphite are similar to those of natural graphite as regards the relative intensity and fine structure of the lines (Fig. 5e), although an increase in the lattice constants  $a$  and (particularly)  $c$  relative to those of natural graphite is often indicated, this

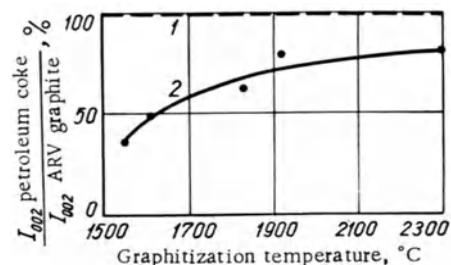


Fig. 6. Intensity of the (002) line of petroleum coke as a function of graphitization temperature: 1) ARV graphite; 2) petroleum coke.

being due to the dissolution of boron in the graphite separated during the decomposition of the boron carbide.

In order to obtain a series of superposition Debye photographs, we used original components consisting of ARV graphite (0.05% moisture, 0.16% ash, 0.95% volatile materials) and boron carbide corresponding to the composition  $B_{4.78}C$ , not containing any free carbon (according to chemical analysis) and only giving the lines of boron carbide on the x-ray picture.

The foregoing differences in the structural state of the carbon phase in different samples of commercial boron carbide necessitated the photographing of a further series of superposition x-ray diffraction patterns with other samples of carbon-containing materials as components. Thus in addition to ARV graphite we used natural graphite and petroleum coke roasted at  $1550^{\circ}C$ . In order to allow for the influence of the composition of the boron carbide on the intensity of its lines, we studied  $B_{6.75}C$  as well as  $B_{4.78}C$ .

Figure 7 shows the forward sections of the superposition Debye photographs of boron carbide  $B_{4.78}C$  and ARV graphite taken with different exposure ratios of the components. The exposure time for the boron carbide samples in the superposition Debye photographs was as follows: for  $B_{4.78}C$  2.5 h and for  $B_{6.75}C$  5 h. The exposure time for the carbon component varied from 1 to 60 min. The exposure was maintained by reference to the clock in the URS-70 x-ray equipment. Exact maintenance of the minute exposures was ensured by connecting an RV time relay to the cut-off circuit of the high-voltage supply of the URS-70; this automatically disconnected the high voltage when the exposure time had expired, the accuracy being  $\pm 0.05$  min.

The operating conditions of the URS-70 were kept constant by stabilizing the voltage on the primary winding of the high-voltage transformer by means of an SN-1 stabilizer ( $127 \pm 0.5$  V). We used  $Co K_{\alpha}$  radiation.

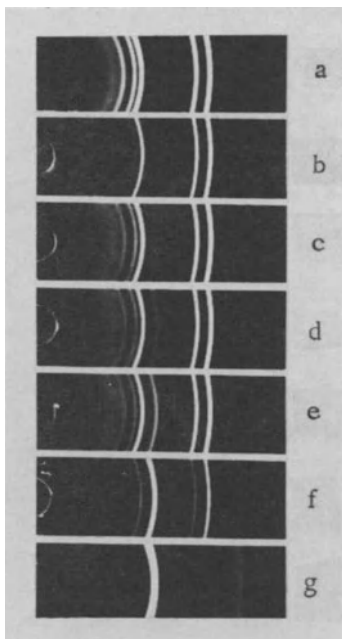


Fig. 7. Forward part of the superposition Debye photographs of boron carbide  $B_{4.78}C$  and ARV graphite taken with different exposure ratios of the components. a) Boron carbide  $B_{4.78}C$ ; b-f) boron carbide + graphite; g) graphite. Exposure ratio graphite/boron carbide: b) 0.03; c) 0.05; d) 0.08; e) 0.13; f) 0.5.  $Co K_{\alpha}$  radiation.



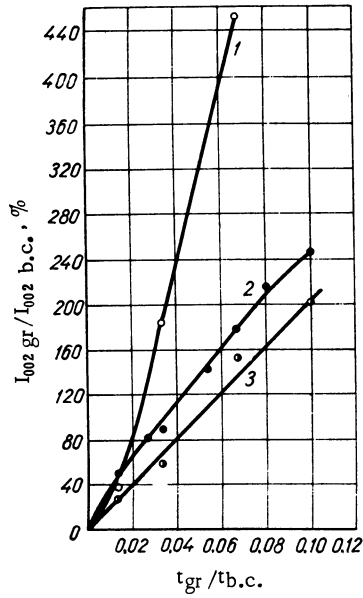


Fig. 8. Calibration curves plotted from series of superposition Debye photographs of various boron carbides and carbon materials: 1)  $B_{6.75}C$  + ARV graphite; 2)  $B_{4.78}C$  + ARV graphite; 3)  $B_{4.78}C$  + petroleum coke roasted at  $1550^{\circ}C$ .

In practice, the quantitative determination of the  $C_{free}$  in boron carbide from the superposition Debye photographs amounted to the following. First a series of superposition Debye photographs of boron carbide and graphite was taken in the D-85 camera with various exposure ratios  $t_{gr} / t_{b.c.}$ ; for each photograph the intensity ratio of the graphite and boron carbide lines  $I_{002\text{ gr}} / I_{110\text{ b.c.}}$  was determined, and a calibration curve  $I_{002\text{ gr}} / I_{110\text{ b.c.}} = f(t_{gr} / t_{b.c.})$  was plotted.

Allowing for the multitude of possible structural states of  $C_{free}$  in the boron carbide and also the wide range of possible phase compositions (from  $B_4C$  to  $B_{6.75}C$ ), it is also essential to construct calibration curves for a number of combinations of boron carbides of different composition with different carbon-containing materials. Then the sample to be analyzed is photographed in the D-85 or some other Debye camera. By examining the fine structure (profile, width, intensity distribution) of the (002) line of the graphite lattice, it is decided which graphite is closest as regards the structural state of the free carbon to the sample in hand. By analyzing the lattice parameters (angle  $\Theta_{328}$ ), the composition of the boron carbide is determined [3]. Then the photometric densities of the (002) line of graphite and the (110) of boron carbide are measured by determining the areas of the peaks on the angular-distribution curve of the photometric density. The ratio of the densities  $S_{002} / S_{110}$  is found, and this equals the intensity ratio  $I_{002\text{ gr}} / I_{110\text{ b.c.}}$ , if the work is conducted in the range of photometric densities  $\leq 1$ .

By referring to the calibration curve plotted from the superposition Debye photographs of boron carbide and the carbon-containing material, with due regard to the structural state of the corresponding phases in the sample under analysis, the exposure ratio  $t_{gr} / t_{b.c.}$  corresponding to the value of  $I_{002} / I_{110}$  so found is determined (Fig. 8). From the ratio  $t_{gr} / t_{b.c.}$  on the calculated curve of  $C_{free} = f(t_{gr} / t_{b.c.})$  plotted for boron carbide of the same composition as that in the sample under analysis,  $C_{free}$  is found (Fig. 9).

The calculated curves of Fig. 9 are plotted [4] in accordance with the system of equations

$$\frac{C_{gr}}{C_{b.c.}} = \frac{(\mu/\rho)_{b.c.} t_{gr}}{(\mu/\rho)_{gr} t_{b.c.}},$$

$$C_{gr} + C_{b.c.} = 100\%,$$

where  $C$  are the weight concentrations of graphite and boron carbide,  $t$  is the exposure of the graphite and boron carbide samples on the superposition photographs, and  $\mu/\rho$  are the mass-

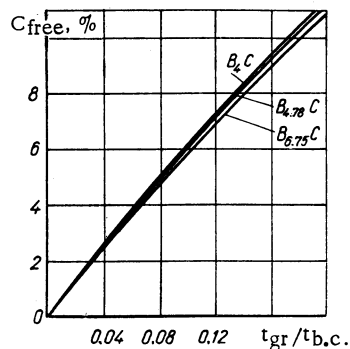


Fig. 9. Calculated curves for determining the amount of free carbon in boron carbide by the superposition method.

absorption coefficients of graphite and boron carbide. In Co K radiation the mass-absorption coefficients for the corresponding components are [1]:

Phase	Graphite	$B_4C$	$B_{4.78}C$	$B_{6.75}C$
$\mu/\rho$	8.5	5.5	5.4	5.2

If the composition of the boron carbide differs from the compositions  $B_4C$ ,  $B_{4.78}C$ , or  $B_{6.75}C$ , for which the calculated curves have been plotted, the amount of  $C_{free}$  is found by extrapolation.

If the series of superposition Debye photographs contains a large number of photographs differing by small degrees of exposure, then without measuring the photometric densities we may visually select one particular x-ray superposition photograph for which the intensity ratio of the lines under analysis is approximately equal to that characterizing the x-ray diffraction pattern under test. For greater accuracy of selection it is recommended that the intensity of the (002) line of graphite should always be estimated by reference to all six of the first lines of boron carbide.

The method has been developed for analyzing samples containing up to 10% free carbon. Quantitative analysis of samples with greater  $C_{free}$  contents may be carried out in an analogous manner; however, the (002) line of graphite should then be compared not with the (110) line of boron carbide but with one of the stronger lines: (102), (014), or (201).

The main advantages of the superposition method should be emphasized [4]:

1. There is no need to prepare standard mixtures or introduce additional phases into the sample;
2. The method is independent of chemical analysis (it is only necessary to be confident of the purity and single-phase nature of the components used for obtaining the superposition Debye photographs);
3. The method may be applied to very small quantities of material.

In our own investigations the advantages of the superposition method proved especially valuable in connection with the very small quantities of single-phase boron carbide samples not containing graphite at our disposal, such materials being very rarely achieved in practice.

It was found from the superposition Debye photographs that the lower level of sensitivity for observing free carbon in boron carbide was around 0.15% if its structural state was analogous to Acheson graphite, and 0.3% if the carbon in the boron carbide was extremely finely-dispersed or had a nonequilibrium, poorly-shaped crystal lattice, i.e., if the fine structure of the (002) line of carbon in the sample was the same as in low-graphitized petroleum coke.

The error in parallel determinations based on the superposition Debye photographs is 6% (relative). The reliability of the x-ray analysis is determined by the extent to which the structural state of the free carbon in the sample under analysis agrees with that of the standard materials used for taking the Debye photographs in the superposition series from which the calibration curves are plotted.

The method thus developed may be used for analyzing samples of boron carbide not containing boron nitride in which the carbon phase is finely-dispersed and in an equilibrium state [7], and also in research work associated with the analysis of phase diagrams, in improving the results of chemical analysis, and so on. In particular, the method gives excellent results in the analysis of boron-carbon alloys made by hot pressing.

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# METHOD OF SEPARATING AND DETERMINING THE FREE CARBON IN MATERIALS CONTAINING REFRACTORY COMPOUNDS

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The various forms of carbon at present in existence are distinguished from each other by a number of properties, including their relationship to chemical reagents. The so-called amorphous carbon (soot, highly active coals) is easily oxidized by a 30% solution of hydrogen peroxide [10] and adsorbs several dyes (bromothymol blue, etc.) [9], whereas according to our present data graphite remains unaffected by these reagents. In order to conduct a systematic investigation into the chemical properties of various carbon materials and establish their phase relationship, we studied two ways of separating free carbon from refractory compounds: the removal of free carbon by roasting in a muffle furnace at 850°C, and the "wet" oxidation technique.

The first method only proved possible for the SiC-graphite system. In the presence of other carbides, polyfluorethylene resin, or even boron dissolved in silicon, this method was quite unsuitable; in addition to the combustion of free carbon, the carbides were also oxidized, the second process prevailing over the first [6], while polyfluorethylene resin was burnt completely in advance of the carbon at 600-700°C.

In order to choose the conditions for the complete oxidation of various forms of carbon we tried a number of mixtures: 10 ml H<sub>2</sub>SO<sub>4</sub> + 10 ml HNO<sub>3</sub> + 5 ml HClO<sub>4</sub> + 20 ml K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>; H<sub>2</sub>SO<sub>4</sub> + K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> + HClO<sub>4</sub> (with various ratios of the components); H<sub>2</sub>SO<sub>4</sub> + HClO<sub>4</sub>; HClO<sub>4</sub> + K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>; H<sub>2</sub>SO<sub>4</sub> + K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>; HIO<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub>; H<sub>3</sub>PO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub> + HClO<sub>4</sub> [1, 3, 7, 8, 11].

The oxidizing effect of the mixtures was verified for graphites of various types (PROG-2400, PG-50, AG-1500, etc.), soots (gas channel, thermal, PG-33), and cokes (KNPS, cracking, pitch, aryl resin, etc.). The experiments showed that the forms of carbon studied were only oxidized completely by mixtures Nos. 5 and 2 (ratio of the components 2:2:1). It was found that the presence of perchloric acid (mixture No. 2) worsened the oxidizing power of the mixture, increasing the oxidation time. Subsequently the whole work was carried out with mixture No. 5, comprising a concentrated solution of sulfuric acid and a 5% aqueous solution of potassium bichromate taken in 1:1 ratio.

The mechanism of the oxidation of carbon by the H<sub>2</sub>SO<sub>4</sub> + K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> mixture is expressed by the equation

