

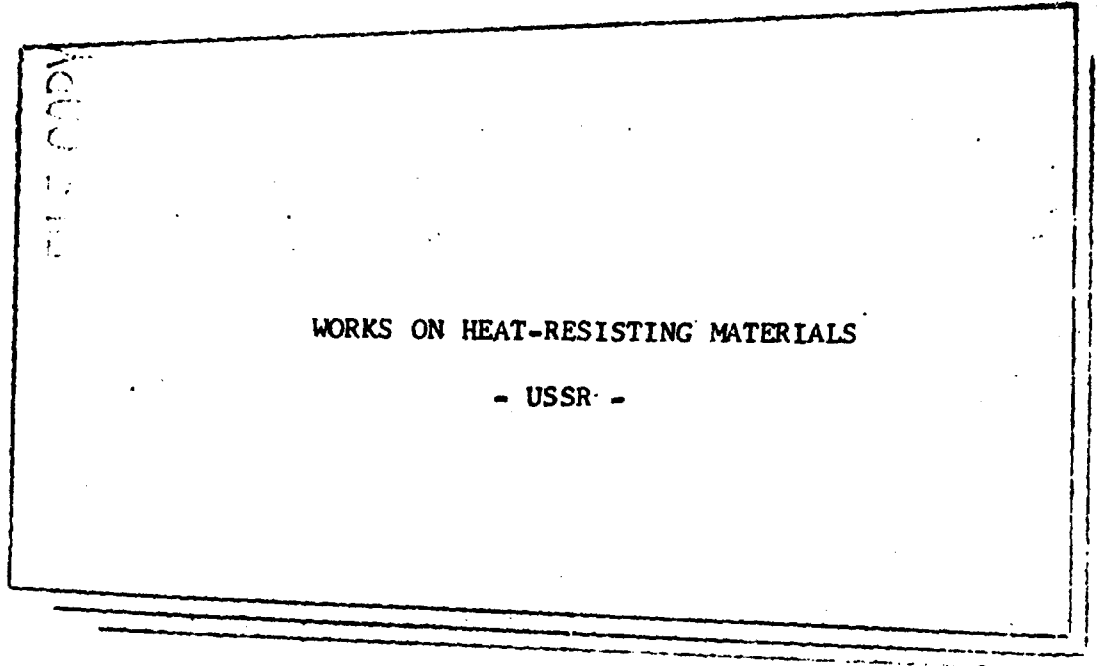
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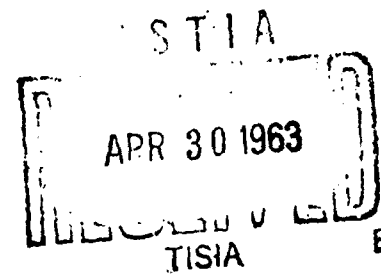
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WORKS ON HEAT-RESISTING MATERIALS

- USSR -



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WORKS ON HEAT-RESISTING MATERIALS

- USSR -

Following is a translation of "Works of the Seminar on Heat-Resisting Materials 13-17 June 1958" published in the Russian-language periodical Byulleten' Institut metallokeramiki i spetsial'nikh splavov (Bulletin. Institute of Metal Ceramics and Special Alloys), No 5, Academy of Sciences, Ukrainian SSR, Kiev, 1960, pages 1-65.

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FOREWORD

This collection of works is dedicated to the physical properties and the technology of preparation of refractory metals and their metalloid borides, carbides, nitrates and silicides.

It reports the results of investigations on absorption spectra and emission spectra of columbium and chromium compounds, the results of research into the processes of joint co-diffusion of two elements into metals, the data on the phenomenological study of the physical properties of the metalloid phases.

The basic principles for production of powders and articles from rare metals and refractory compounds are examined for the various fields of contemporary engineering.

The collection includes a number of reports which illuminate individual problems of the powder metallurgy of ordinary metals and alloys.

It is intended for engineers, scientists, students of polytechnical schools specializing in refractory metals and their compounds, in powder metallurgy, electronics, mechanical engineering and in the metallurgical science.

PREFACE

Recently, more and more attention is being paid to refractory metals and heat-stable compounds in connection with their use in the manufacture of heat-resisting alloys, of special fire-proof hard alloys for metal working, of corrosion-resistant parts for chemical apparatuses as well as with their use in electronics, electric engineering, automation, and so on.

In the USSR, the conditions of obtaining the properties and applying these groups of metals and compounds were successfully investigated in many scientific research organizations, engineering bureaus, factory and school laboratories.

At the Seminar, conducted in Kiev on 13-17 June 1958, the results of a rather large bulk of work were expounded. The works were made in the Institute of Metal Ceramics and Special Alloys of the Academy of Sciences USSR, the Government Institute of Applied Chemistry (Leningrad), the Kharkov Polytechnical Institute, the Institute of Metals Physics, the Sverdlovsk Government University, the All-Union Institute of Aviation Material, the Central Scientific Research Institute of Ferrous Metallurgy, the All-Union Scientific Research Institute of Abrasives and Polishing, the Institute of Metallurgy of the Academy of Sciences USSR, the All-Union Scientific Research Institute of Fuel Recovery, the Scientific Research Institute of the Government Committee of Radio Engineering and Electronics, the Moskva Combine of Hard Alloys, the Gor'skiy Polytechnical Institute, the Moskva Electric Lamp Factory.

The editorial board was unanimous in considering it proper to publish in the present collection that part of the Seminar's material which pertains to the physical properties and crystal structure of the electronic arrangement of refractory compounds, since this part is interesting in itself, and includes a few theoretical questions of major importance.

PHYSICAL PROPERTIES OF METALLOID COMPOUNDS

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AN USSR

The metalloïd compounds include borides, carbides, nitrides and silicides of the transition metals (with closed electronic d- and f-levels).

The criteria of metalloïd compounds are:

- 1) high degree of hardness reaching 3000 kg/mm^2 ;
- 2) metallic shine and in the majority, metallic conductivity, at least at normal temperature;
- 3) high degree of thermal stability; as a rule, the melting or dissociation temperatures of these compounds are very high (up to 3500°C), and frequently above the melting temperatures of the most refractory metals and oxides;
- 4) brittleness and absence of plastic deformation at a temperature in the order of $0.85 - 0.95 T_{\text{melt}}$.

Crystal Chemistry of Metalloid Compounds

According to structure, the metalloid compounds can be divided into two kinds.

The first group includes the intrusion structures with closely packed metal atoms, i.e., the carbides and nitrides of the transition metals subjected to the law of Hagg:

$$r_x : r_{Me} \leq 0.59$$

where r_x and r_{Me} are the corresponding atomic radii of the metalloid and the metallic components.

In these compounds, the metalloid atoms are located in the interstices of the cubic or hexagonal close-pack of metal atoms, and they do not form bonds with each other. The bonds between the atoms of metal and metalloid bear a directional character which conditions high-grade hardness and brittleness of the compounds, and they have an octahedral configuration to which the hybridization of the bonding d_{2sp_3} orbitals correspond [1]. Here, the d-electrons of the metal participate in the creation of the bond. This causes a decrease in magnetic susceptibility and a change in electric conductivity of the metals at the formation of metalloid compounds [2]. The maximum electric density (electron density) in the bond directions is here somewhat dislocated sideward to the metal atoms, owing to the incomplete structure of their d-shell and, consequently, to an incomplete shielding of the nuclear charge by the electrons of this shell [3,4].

The degree of dislocation of the electron cloud depends also

upon the strength of the metalloid electrons bond, i.e., to a first approximation upon its ionizing potential, being diminished with the increase of the latter. Since the ionisation potential of nitrogen is higher than that of carbon, the dislocation of the electron cloud to the metallic atoms is less in the Me - N bonds than in the Me - C bonds. It is possible that, owing to its considerable electronegativity, which brings the nitrides close to the oxides, in the first case the electron cloud is even dislocated toward the nitrogen.

On Fig.1 we indicated the emission spectra of the K-series of titanium in TiO_2 , TiN , TiC , TiH_2 and Ti [B].

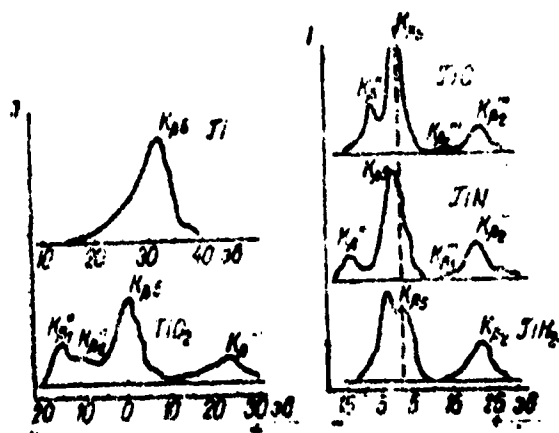


Fig.1. Emission spectra of the K-series of titanium in TiO_2 and metalloid compounds.

(Abscissa: eV = electron volts)

It can be seen that to the extent of the electronegativity and the ionizing potential of the metalloid, the long-wave constituent of the $K\beta$ σ -line is gradually strengthened with the latter, and it disappears in titanium hydride and metallic titanium, which probably is related to the gradual translation of the density maximum of electron cloud in the above quoted series of compounds to the metal, and also related to an increase in the density of the occupied states in the d-band of the metal, but the latter reduces the probability of patternless transitions. In the Me - X bonds, not all electrons of the two components are apparently occupied, which conditions the presence of free electric-current carriers, and the metallic conductivity of the intrusion phases.

The second type of metalloid compounds includes compounds with more complicated structure in which, parallel with the Me - X bonds, there are bonds between the metalloid atoms themselves. The possibility of the formation of such structures requires a mutual overlap of the bonding orbits of metalloid atoms, and it depends upon the relative sizes of the metal and metalloid atoms and upon the ease of excitation of the metalloid valency states.

The tendency toward the formation of complicated structures increases in this order: -- nitrides, carbides, borides, and silicides.

The carbides of complex structures are formed in case of

$r_X : r_{Me} > 0.59$ (chromium, manganese, elements of the iron triad).

The borides and silicides do not form simple intrusion structures at any value of $r_X : r_{Me}$. In these phases, to the extent of the metalloïd content, the ground of the metalloïd bonds is intensified, and single and double chains, two-dimensional grids, and three-dimensional structural frames appear in the lattice, formed by metalloïd bonds with one another, which can be seen on Fig.2.

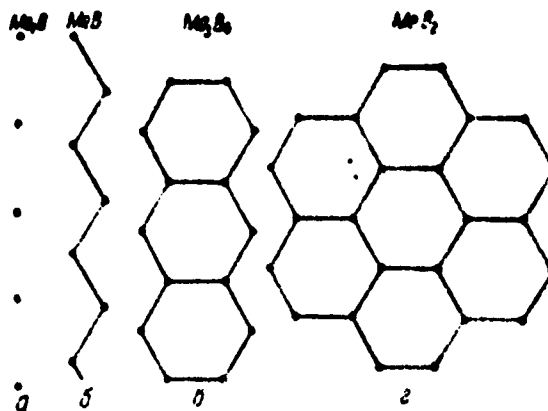


Fig.2. Diagram of the mutual bonds of boron with borides of different composition.
(Letters at bottom: a,b,v,g... indicating a,b,c,d)

In the majority of cases, the distance X - X is close to the doubled common covalent radius of the metalloïd atoms. Apparently, the Me - X bonds in all metalloïd compounds are close by nature, which results in a qualitative similarity of their physical properties.

Electrophysical Properties

The electronic structure of the metalloïd compounds is the most clearly reflected in their electrophysical properties. G.V. Samsonov [6] observed that the electric resistance of the transition metals regularly increases with the increase of the acceptor capacity of the metal atoms (Fig.3). The latter can be evaluated to a first approximation by the criterion

$$\xi = 1/Nn$$

where N ... is the main quantum number of the partially filled d-shell; n ... is the number of d-electrons. The significance of magnitude ξ (Greek χ) is therein that the small N and n are, i.e., the larger ξ becomes, the less the shielding is of the nuclear charge of the metal atom, and the more the atomic core is able to act as an acceptor of supplementary electrons [6].

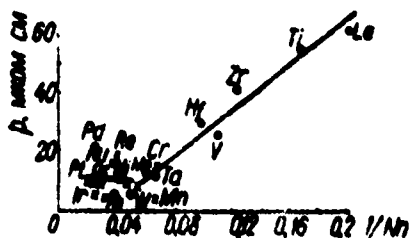


Fig.3. Relation of electric resistance of transition metals to their acceptor capacity (ξ).
(On ordinata: r micro-ohm cm).

Increase in the acceptor capacity leads to supplementary electron scattering at the lattice points occupied by the transition metal atoms, and consequently to an increase in electric resistance. Comparison of the value of electric resistance of the metalloid compounds with the magnitude ξ of the metals shows (Fig.4) that the resistances of borides, carbides and nitrides regularly decrease with the increase of the metal's ξ .

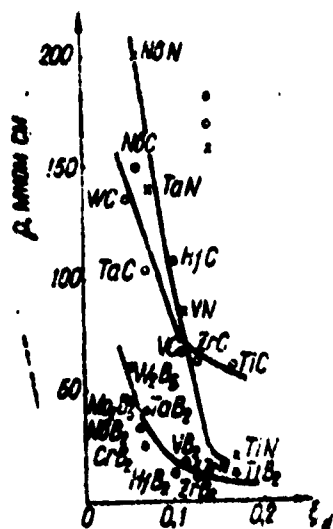


Fig.4. Relation of electric resistance of metalloid compounds to the acceptor capacity (ξ) of the metal components: ... borides; o... carbide; x... nitride. (On ordinata: r micro-ohm cm)

This tendency is also observed for silicides, but it is less clearly expressed. The cause of such a relationship is given by the following. The increase in the acceptor capacity of metal atoms leads to

greater dislocation of the electron cloud in the Me - X bond directions toward the metal atom cores, which provokes a statistical decrease in the electron defect of their d-shell; consequently, its acceptor capacity and the scattering effect upon the conductivity electrons decreases. The latter in its turn leads to a reduction in electric resistance. The strength of interatomic bonding in the metalloid compounds also happens to increase, as it will be indicated below. Consequently, the effective cross-section of the phonons (lattice-vibration quanta) is reduced which seem to be also a source of the scattering conductivity electrons. Due to this, with the growth of ξ_1 , a reduction in the electric resistance of metalloid compounds occurs sharply.

For the hexaborides of fd- transitional metals with a CaB_6 type of structure, the growth in electric resistance was found to run parallel with the enlargement of the atomic number of the metallic component in the series $LaB_6 - CaB_6 - \dots SmB_6$, which is related to the reduction in effective concentration of the current's carriers (the free electrons), as a result of the elevation of the stability of the (4f)-state in this series and the difficulties of the $f \rightarrow d$ transition [28, 29].

Jointly with N.V. Kolomoits, G.V. Samsonov, and S.A. Semenkovich [7], we have investigated the thermal relation of electric resistance of a number of metalloid compounds (Fig. 5 - 8). The draw-

ings make it clear that for borides and carbides, the metallic conductivity corresponds at all the examined temperature intervals, and their resistance linearly increases with the temperature, which points to an independence of the number of the current's carriers from the temperature [8] and to a sufficiently full overlapping of the band of valency electrons with the band of conductivity.

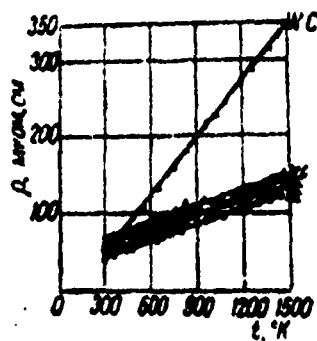


Fig.5. Temperature relation of electric resistance of carbides. (Ordinata: r micro-ohm cm).

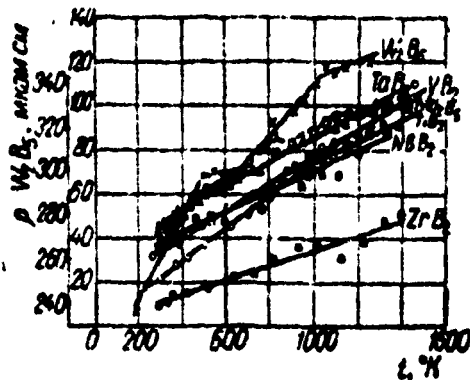


Fig.6. Temperature relation of resistance in borides. (Ordinata: r W_2B_5 microohm cm).

Silicides and nitrides only show similar character of conductivity at definite temperatures above which the dependence of their resistance upon temperature diminishes, which can be related only to a change in the mechanism of conductivity, since, at the examined temperature range [9], no phasic transformations are observed for these substances.

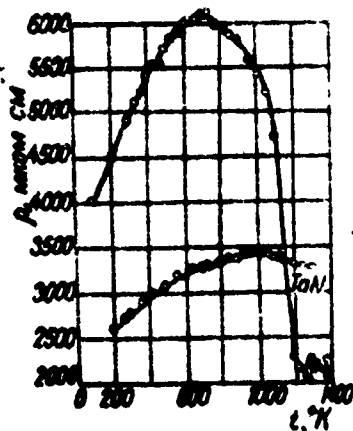


Fig. 7. Temperature relation of electric resistance of nitrides.
(Ordinata: r microhm cm)

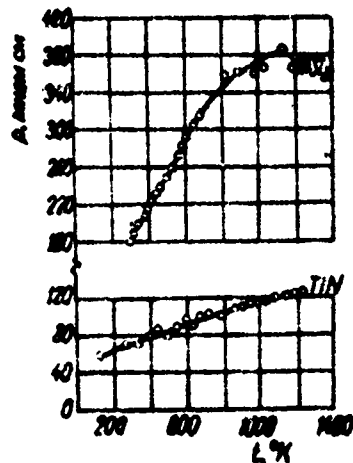


Fig. 8. Temperature relation of electric resistance of silicides.
(Ordinata: r microhm cm).

The reduction in resistance with the temperature growth is related to a noticeable increase in the number of the current's carriers under the influence of warming-up, which is characteristic for semiconductors [8]. The cause of change in the conductivity mechanism in case of the examined silicides and nitrides* is apparently found in a slight overlapping of the energy bands of the valency and conductivity electrons, which at increased temperature causes the appearance of energy gaps between them, as a result of the increase of interlaminar distances in the crystals. An analogous relation of resistance to temperature was detected by L.N. Gusev and V.I. Ovechkin for chromium disilicide [10].

* ([NOTE]: For titanium nitride, a deviation of the thermal relation of resistance from linearity was only detected. Apparently, the temperature obtained by us is not enough to cause a divergence of the valency and conductivity zones .)

In this manner, the borides and carbides of transition metals must belong to metal-type substances with substantial overlapping of the bands of the valency and conductivity electrons, while the nitrides and silicides apparently belong to semimetals with a slight overlap of these bands.

The thermoelectromotive force arising in the metalloids compounds is not large, reaching the order of a few dozen microvolts by grade, i.e., it has the same order as also in case of metals [11,12]. Some silicides (CrSi_2 [1C], MnSi and FeSi_2 [13,14]) are excluded. Their thermoelectromotive force has the order of 10^2 micro-V/ $^\circ\text{C}$, which emphasizes their intermediate position between metals and semi-conductors. With the elevation of temperature, the thermoelectromotive force of borides, nitrides, and silicides is increased (Fig.9 - 1C), which points to the vacancy character of their conductivity ($+\alpha/\text{dT}$), and for the carbides it decreases, which corresponds with the electron-type conductivity ($-\alpha/\text{dT}$) [7]. Here the α designates the thermoelectromotive force for 1°K .

Together with Samsonov and Rudintsev, we investigated the thermoemission parameters of the borides and transition metals [15].

It was shown that the work function of electrons from d-transition

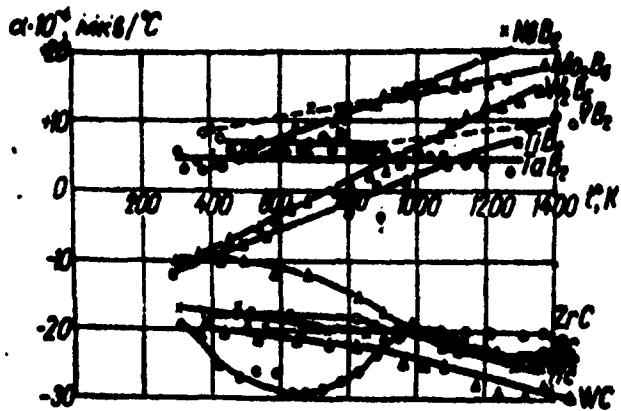


Fig.9. Temperature relation of the thermoelectromotive force of carbides and borides.
 (At top, left: microvolt/ $^\circ\text{C}$; at top right: Nb equals Ob).



Fig.10. Temperature relation of thermoelectromotive force of nitrides and silicides.
 (On ordinata: microvolt/ $^\circ\text{C}$).

metals decreases with the growth of the acceptor capacity (i.e., with the reduction of the degree of shielding) of their atoms (Fig.11). This

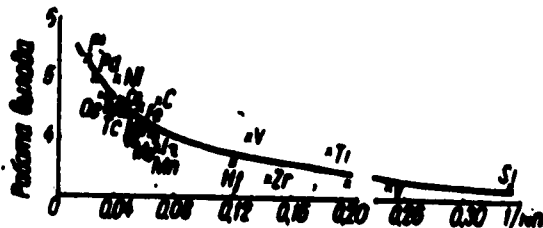


Fig.11. Relation of the work function of electrons from transition metals to the acceptor capacity (ξ). (Ordinata: work function).

is related to the growth of the perturbation effect of atomic cores upon electron conductivity, and thus to an elevation of the level of the chemical potential. On the contrary, for the borides of the d-transition metals, as it can be seen on Fig.12, the work function of electrons increases with the growth of the acceptor capacity of the d-shell of metal atoms, which -- as it was already indicated above -- is related to the rise in the degree of dislocation of the electron cloud of binding toward the atomic cores of metal, also related to the statistical filling of the d-state with these electrons. The latter leads to a lowering of the chemical potential of elec -

trons in the boride lattices, which is manifested by an increase in the work function of electrons.

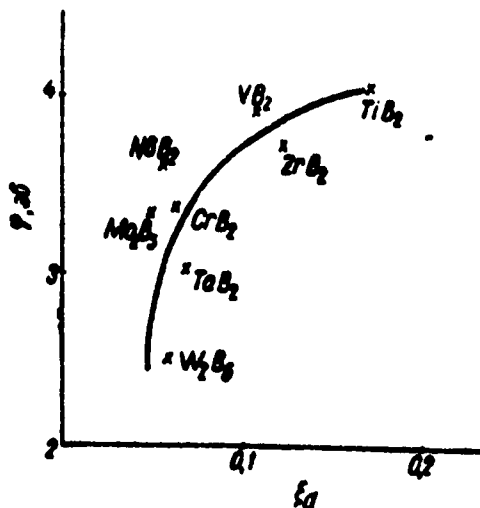


Fig.12. Relation of work function of electrons of borides of transition metals to the acceptor capacity (ξ_0) of the metals.
(Ordinata: $\varphi, 3b$; on graph: Nb = Cr)

G.A.Kudintsev and V.M.Tsarev [27] established that the work function of electrons from the hexaborides of the rare-earth (f-d-transitional) metals is almost monotonously growing from LaB_6 to EuB_6 , and in case of GdB_6 it has a clearly expressed minimum, then again it increases toward DyB_6 , and further on, it drops smoothly from DyB_6 toward LuB_6 . As in case of the electric conductivity, too, this relation is connected with the $f \rightarrow d$ transition's probability [28].

Interatomic interaction energy and the bond strength
in metalloid compounds

The high-grade hardness, the heat resistance, and the chemical resistance of metalloid compounds prove the considerable strength of bondings between the atoms in crystals.

G.A. Samsonov and the author [16,17,26] have computed the interatomic interaction power according to the method proposed by H.S. Sarkisov [18], and also the Debye characteristic temperature and the amplitude of the atomic thermal vibrations according to the data of experiments and literature on the thermal expansion coefficients by the method suggested by the author [19]. The obtained results are in the Table.

At considering the changes in interatomic interaction energy in case of transition from one metalloid compound to another, and the changes of the physical properties of these compounds also, it is easy to see that the interatomic interaction energy and the physical characteristics, indirectly connected with this quantity (hardness, characteristic temperature) are lowered at transition from a compound of titanium to a compound of tantalum and wolframium (Fig.13).

The interatomic interaction energy of borides does not change here monotonously, in distinction from the carbides and nitrides, which is related to the marked heterodesmia of the crystal structure of borides. Such a nature of regularity in the change of interatomic

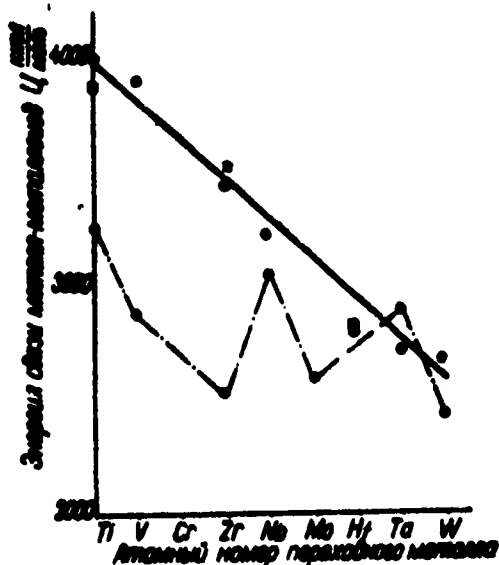


Fig.13. Change of energy of the Me - X bond with the change of the position of the metallic components in the periodic system:—o— carbides; -.-o- borides; •••■••• nitrides.

(Ordinate: Energy of the metal-metalloid bond, kcal/mol. Abscissa: Atomic number of transition metal).

interaction energy convincingly indicates that the unfilled d-shell of the metal atoms plays a decisive role in the structure of metalloid compounds.

An increase in the degree of shielding (or a reduction in the acceptor capacity) at transition from the top to the bottom elements in the groups of the periodic system, or generally at a sequence along the series Ti - V - Cr - Zr - Nb - Mo - Hf - Ta - W,

leads to an increase in the electron energy in the Me - X bonds, and so to a loosening of this bond, which is expressed by a reduction in interatomic interaction energy.

On Fig.14, we publish the graphs of change in the bonding energy, the characteristic temperature and the frequency of atomic vibrations in carbides, in relation to the criterion of the acceptor capacity ξ of the metals.

Although this relation does not seem to be monotonous, yet the tendency toward an elevation of the bonding strength with the growth of ξ is rather clearly expressed. The symbasic change in the calculated values of bond energy and in the characteristics of the tem-

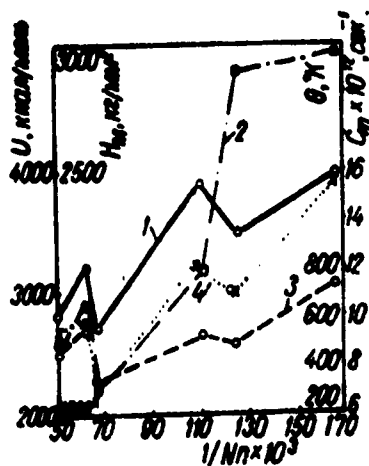


Fig.14. Relation of bond energy, hardness, characteristic temperature and frequency of atomic vibrations in carbides to the acceptor capacity (ξ) of the metals.
(Ordinata: kcal/mol; right vertical line or second ordinata: $\text{cm} \times 10^{12} \cdot \text{sec}^{-1}$).

perature and the frequency of vibrations, extracted from experimental quantities, calls attention upon itself.

The energy of the Me - X bonding in carbides and nitrides, which have simple interstitial intrusion structure, has a roughly identical value whereas in the borides which are characterized by a marked heterogeneity of the bondings these magnitudes are less, which probably is caused so that part of the valency electrons in the Me - B bonding is connected with the boron atom.

In some publications [20,21], the atomization heat is accepted as a measure for the strength of bonding in metalloid compounds, which in our opinion is not correct, since this magnitude represents in itself merely the difference of enthalpy of the components in phase and in free state of a monatomic gas, and it does not directly characterize the energy of interaction between the atoms in a solid body. From Fig.15 it can be seen that the atomization heat per one g-at(gram-atom) of the metalloid is monotonically reduced with the increase of the metalloid content in phase(the graphs are given for borides and silicides of molybdaenum), i.e., with the growth of the ground for metalloid bondings in the crystals of the compounds.

An extrapolation for a 100-per cent. content of metalloids gives the heat of their atomization. This is pointing to a decrease in the difference in enthalpy of metalloid components at elementary state, and of metalloid compounds, with increase of the number of L bondings between the metalloid atoms in phases.

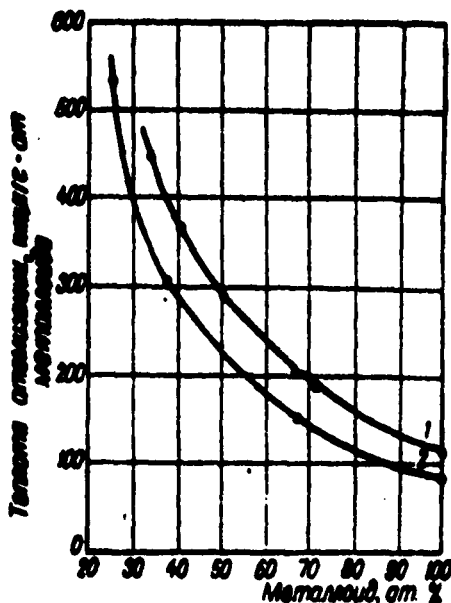


Fig. 15. Relation of atomization heat per 1 g-at. of the metalloid in borides(1), and silicides(2) of molybdenum to the metalloid content in phase.
 (Ordinata: atomization heat of metalloid, kcal/g-at.;
 Abscissa: Metalloid, at. per cent.)

Physico-mechanical characteristics of metalloid compounds

The basic laws of the physico-mechanical properties of metalloid compounds have been formulated by the author and G.V. Samsonev in the publication [17].

The most characteristic property of the metalloid compounds seems to be their high-grade hardness (See Table), related to the directional character and the high energy strength of the interatomic

bond⁸. As it can be seen from the Table and from Fig.16, the microhardness of metalloid compounds decreases with the increase in the atomic number of the metal components in the groups, and according to the diagonal of the field of the periodic system occupied by the transition metals, which is related to the reduction of the acceptor capacity of the d-shell of atoms of the transition metals. On Fig.14, the relation is shown between the microhardness of carbides to the criterion of the acceptor capacity ξ . It can be seen that the microhardness is growing with the growth of ξ in the same direction as the interatomic interaction energy and the characteristic temperature.

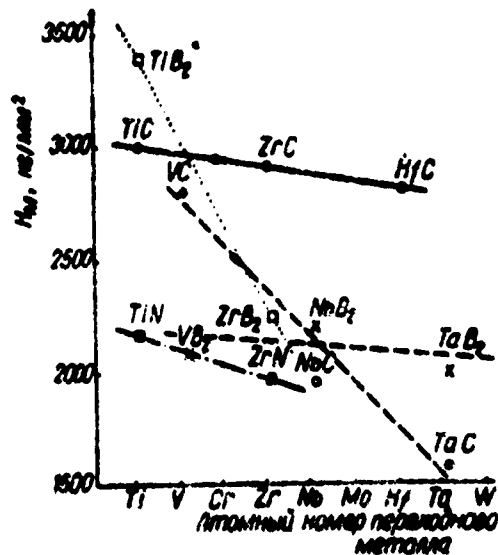


Fig.16. Relation of microhardness of metalloid compounds to the position of the metal components in the periodic system.

(Ordinata: Pressure, kg/mm². Abscissa: Atomic number of transition metal. On diagram: Nb = Cb).

Moreover, to a substantial degree, the strength of interatomic bond, the microhardness of metalloid compounds depends upon their crystal structure.

From the Table it is evident that at transition from the cubic monocarbides CbC and TaC to hexagonal carbides Cb_2C and Ta_2C there is an increase in hardness, without any regard to the fact that the bonding energy for the Me_2C carbides is less than for the MeC monocarbides.

In this, structure seems to have an effect upon the hardness, -- the cubic carbides have two slippage planes: (111) and (001), whereas the hexagonal carbides have only one (001). This makes difficult a plastic deformation, and it increases the hardness of these carbides.

Apparently, an analogous phenomenon takes place for the hexagonal diborides of transition metals. By comparing the microhardness of carbides and borides of the same metals, it can be seen that in those cases where the interatomic bonding energies of borides and carbides are close to the value ($U_{\text{MeB}_2} / U_{\text{MeC}} > 0.8$), in case of the dislocation stress of the hexagonal boride lattice whose rigidity is also elevated by the chains of boron atoms with each other, difficulties will lead to an overshoot of the hardness of borides above the hardness of carbides.

But in case of $U_{\text{MeB}_2} / U_{\text{MeC}} < 0.8$, the structural factor can not compensate for the weakening of lattice strength. In this case, the

hardness of borides shows a substantially lesser hardness than the corresponding carbides (ZrC and ZrB_2 ; TaC and TaB_2).

The hardness of the $MeSi_2$ disilicides is considerably less than the hardness of the borides and carbides, due to both the lesser energy lattice strength and the laminar character of structure in case of a comparatively weak bonding between the metallic layers (in comparison with borides) [22], which facilitates their dislocation stress.

Attention is called to the high values of the modulus of normal elasticity and of the modulus of dislocation of the metalloid compounds (See Table), which corresponds with a greater strength of interatomic bond.

SOME PHYSICAL CHARACTERISTICS OF TRANSITION METALS AND THEIR METALLOID COMPOUNDS

Phase	T_{melt} °C	H_{r} , kg/mm ²	Poisson's ratio	E , kg/mm ²	G , kg/mm ²	θ , °K	$\sqrt{D_{290}^2}$	U , kcal/mol	$\alpha \cdot 10^6$, g./rad-1
Ti	1725	157	0,36	10630	3870	350	0,140	—	8,5
TiC	3140	2988	0,41	39000	11364	741	0,067	3980	7,42
TiN	2680	2100	0,45	26400	8821	517	0,091	3900	9,26
TiB ₂	2900	3370	0,42	37400	13167	615	0,073	3280	6,30
TiSi ₂	1460	870	—	—	—	—	0,087	—	—
Zr	1830	97	0,37	6870	2540	280	0,136	—	8,9
ZrC	3630	2925	0,43	36500	12369	490	0,074	3470	6,74
ZrN	2680	1988	—	—	—	—	—	3540	—
ZrB ₂	3040	2352	0,42	35000	12334	481	0,072	2540	6,23
ZrSi ₂	1700	1030	—	—	—	—	0,087	—	—
Hf	2130	206	0,37	8500	3100	213	0,127	—	6,1
HfC	3250	2800	—	—	—	—	—	2800	—
HfN	—	—	—	—	—	—	—	2840	—
HfB ₂	3250	—	—	—	—	—	—	—	5,3
HfSi ₂	1750	—	—	—	—	—	—	—	—
V	1700	65	0,35	15000	5500	413	0,124	—	9,7
VC	2830	2004	0,45	27600	9530	531	0,008	3900	—
VN	2300	—	—	—	—	—	—	3630	—
VB ₂	2400	2044	—	—	—	—	—	2880	—
VSi ₂	1750	1090	—	—	—	—	—	—	—
Nb	2500	—	0,35	16000	6000	301	0,124	—	7,1
NbC	3500	1961	0,44	34300	11946	470	0,076	3216	—
Nb ₂ C	—	2123	—	—	—	—	—	2570	—
NbB ₂	3000	2200	—	—	—	—	—	3060	—
NbSi ₂	1980	1060	—	—	—	—	—	—	—
Ta	2850	108	0,35	18820	7000	245	0,111	—	6,5
TaC	3680	1599	0,45	29100	10358	318	0,082	2770	8,2
Ta ₂ C	3400	1714	—	—	—	—	—	2380	—
TaB ₂	3100	2800	—	—	—	—	—	2940	—
TaSi ₂	2300	1560	—	—	—	—	0,073	—	—
Mo	2622	192	0,31	33630	12200	380	0,098	—	6,0
Mo ₂ C	2690	1499	0,34	54400	20268	461	0,055	2280	4,4
Mo ₂ B	2142	1790	—	—	—	—	—	2630	—
MoSi ₂	2030	1230	—	—	—	—	0,076	—	5,1
W	3377	350	0,3	41520	15140	310	0,086	—	4,4
WC	2900	1780	0,37	61300	22405	453	0,088	2780	3,9
W ₂ C	2700	3000	0,38	42800	15484	299	0,082	2000	—
WB	2770	2350	—	—	—	—	—	2470	—
WSi ₂	2165	1090	—	—	—	—	0,073	—	—

Note: Here, N_{m} is microhardness; E is modulus of normal elasticity; G is modulus of dislocation; θ is characteristic temperature; $\sqrt{D_{290}^2}$ is the amplitude of heat variation at normal temperature; U is bonding energy; and α is the coefficient of expansion.

With this difference in the elasticity moduli of transition metals and their metalloid compounds, it decreases with the decrease of the acceptor capacity of the metal atoms, which is caused by the weakening of the interatomic bonding in the compounds.

The metalloid phases are very fragile, moreover their brittleness is related to the directional character, and to a much greater rigidity of the interatomic bonds, which makes it difficult for the elastic stresses in the material to relax. The author and G.V. Samsonov have shown [23, 24] that the tendency of the metalloid compounds to expand under the effect of elastic and thermal stresses is reduced with the increase of the amplitudes of atomic thermal vibrations in their crystal lattices, i.e., with the reduction of the bonding rigidity.

Together with G.V. Samsonov and L.M. Khrenov, we made a detailed investigation of the microfragility of a larger number of metalloid compounds on the PMT-3 apparatus for the determination of microhardness [25]. Moreover, in difference from publication [26], in this case not only the rate of rise of the degree of breakage (crack) of impressions was taken into account with the increase of load, but also the character of the cracks (See the address of V.S. Neshpor after the report of Frantsevich and Pilyankevich). It was established that the brittleness of these compounds increases in the sequence of silicide -- boride -- nitride -- carbide, with increase in the rigidity of the interatomic bond.

The results of this work are in good qualitative agreement with the results obtained earlier by the method of studying the packing speed of the powders of hard compounds upon pressing [23].

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THE L_{β_2} AND L_{γ_1} EMISSION BANDS OF COLUMBIUM IN CbN , CbC AND CbB_2

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For the explanation of the change of valency electrons of columbium at the formation of CbC , CbN and CbB_2 , we investigated the emission L-spectra of columbium, and its indicated compounds [See Note]

([Note]: Specimens for the investigations were given to us by G. V. Samsonov.)

We expound here the preliminary results of the experiments.

Spectra of the L-series of roentgen rays were obtained on a powerfully transmitting roentgen spectrograph according to the method of Johann with the aid of a bent quartz crystal ($d_{100} = 4246.02 \text{ \AA}$) of a radius of $R = 1000 \text{ mm}$.

In the spectrograph, a specially constructed roentgen fluorescence tube was mounted with replaceable plates.

To get a great intensity of the characteristic radiation of the matter of the primary plate mirror, the cathode beam was emitted under a small angle of inclination (about 28°).

During the work of the tube, the vacuum in the spectrograph (about $10 - 5 \text{ mm Hg}$) was maintained by M - 1000 and MM - 40 - A

L pumps.

The primary and secondary plates were cooled with running water. The temperature of the secondary plate did not exceed 25°C.

The mirror of the primary plate was made of silver. The fluorescent L-spectra of Cb were excited by the characteristic radiation of the L-series of Ag.

In the L-spectra of Cb, the L lines with subscripts $\alpha_{1,2}$, β_1 , β_2 , β_3 , β_4 , β_5 , β_6 and γ_1 as well as groups of satellite lines L_{α} and L_{β_1} were obtained.

On Fig.1, the microphotogram of the region of the L-series of Cb is represented, including the L emission lines with subscripts β_1 , β_2 , β_3 , β_4 , β_5 , β_6 and γ_1 and the reference line $K_{\alpha}S$.

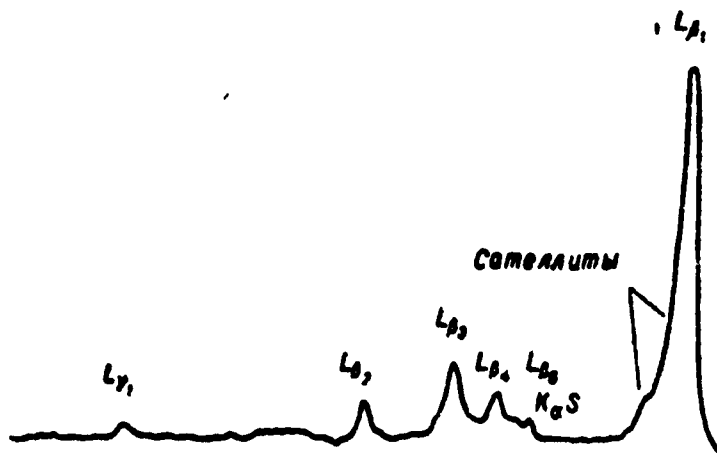


Fig.1. (On graph: Satellites).

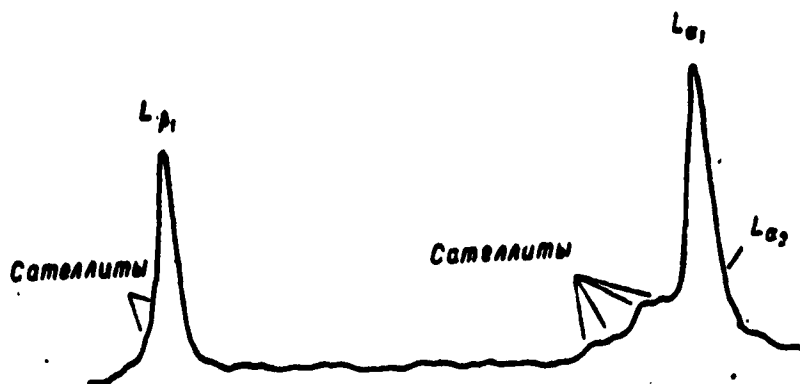


Fig. 2.
(Russian word on graph: Satellites)

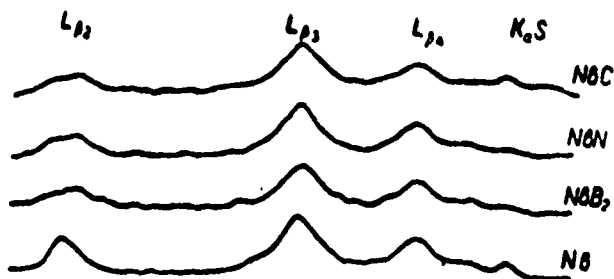


Fig. 3 (Nb = Cb)

On Fig. 2, the region of the same spectrum is given between L_{α_1} and L_{β_1} . Analogous spectrograms were obtained for the L-series of Cb in the compounds CbC, CbN and CbB₂.

From the comparison of the obtained spectrograms it can be

seen that, at transition of Cb into a compound, different parts of the spectrum change. The shape and the intensity of the individual spectral lines and satellite lines change.

The emission bands of $L\beta_2$ and $L\gamma_1$ were more thoroughly studied.

On Fig.3, microphotograms of spectral regions $L\beta_4 - L\beta_2$ (at identical scale) of the indicated compounds and Cb were compared.

The times of exposure were so selected (for Cb...14 h, for CbC and CbN...16 h, and for CbB₂...17 h) that $L\beta_4$ lines were received of identical intensity.

The sharp changes in the form and intensity of band $L\beta_2$ are clearly seen. In case of pure Cb, it has a normal form of spectral line with an asymmetry index of $a = 1.4$. In case of CbC and CbN, it has the shape of a wide two-humped line. In case of CbB₂, it is markedly asymmetrical, with a very gentle drop at the short-wave side.

For the exact study of the character of changes which occurred to the $L\beta_2$ band, the microphotograms of pure Cb and of the compounds were combined.

Since the relative intensities of spectral lines changed, the question arose about the selection of a line ("reference line") which should be combined with superimposition of the microphotograms.

It seemed for us that in the given case the most appropriate is to conduct the comparison by line $L\beta_4$.

1. At the transition from Cb to its compounds, changes occur in the joint band N_{IV}, N_V, O_I of Cb. On this account, the relative intensity is changed for the lines which represent transitions concurrent with transitions $L_{III} \rightarrow N_{IV}, V, O_I$. Therefore, the lines $L\alpha_{1,2}, L\beta_4, L\beta_6$ and others cannot be used as reference lines.

2. From the non-concurrent transitions $L_I \rightarrow M_{II, III}$ and $L \rightarrow N_{I, III}$ the $L\beta_4$ line itself represents a transition between the deepest levels, owing to which it should be the least adversely influenced by the changes in the outer shell.

Therefore, we combined the spectra of Cb and its compounds on line $L\beta_4$



Fig. 4

On Fig. 4, the combined region of the spectra of $Cb_4 - CbN$ is presented in the region of the lines $L\beta - L\beta_2$ / (See Note 7) (the dotted line indicates the contour of the non-coincident regions of the microphotographs of pure Cb; the striping shows the portion of the band which "slipped" away from Cb).

(Note 7: The combination of microphotograms at a given L region of the spectra was carried out by way of selection of their

[posure time, and not by way of re-calculation for equal intensity.]

As it can be seen, in case of Cb and CbN, lines $L\beta_4$ coincide along their entire contour, but line $L\beta_2$ keeps its form, and slightly differs in regard to intensity (about 7 percent.)

The changes which occur to band $L\beta_3$ have different character. Band $L\beta_2$ of Cb in CbN completely enters into the lower part of the contour of band $L\beta_2$ of pure Cb. The change of band $L\beta_2$ has the same aspect as given also on Fig.4, but without the striped region, while it disappears at the nitride formation.

This permits to explain the processes, which occur at the formation of CbN, by the departure of a part of the electrons which are in N_{IV}, N_V, O_I states of the Cb atoms.

Analogous combinations were also made for the microphotograms of Cb - CbC and Cb - CbE₂. The combined regions of these bands are shown on Fig.5 (the dotted line refers to pure Cb; the striping is

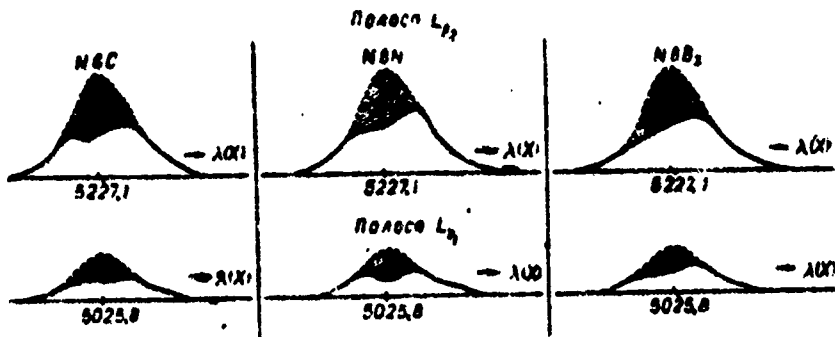


Fig.5

(On diagram, Russian word: Band; Nb = Cb)

for the band parts "slipped" away from columbium). As it is seen, in all examined compounds, the $L\beta_2$ bands enter into the lower part of the contour of the emission band of pure Cb.

In this manner, in borides and carbides and nitrides, the change of the $L\beta_2$ band has the character of disappearance of a part of the emission band. It is interesting to remark that in the different compounds different regions of the band vanish. Thus, in case of CbB_2 , preferably the short-wave part vanishes. In carbide and nitride, preferably the central part disappears.

Since the emission band seems to be complex, expressing the states N_{IV} , N_V and O_I , such changes can attest that, in the different compounds, electrons of different states take part in different ways in bonding.

In Table 1, the numbers are given which characterize the changes of band $L\beta_2$ in pure Cb and its compounds.

TABLE 1.

Таблица 1		
1 Вещество	r^*	$1-r$
NbN	0,715	0,285
NbC	0,729	0,271
NbB ₂	0,685	0,315

(Column heads: 1...Substance; 2(Note): r is equal to the ratio of the area of $L\beta_2$ of the compound and of columbium)

Analogous changes occur also in band $L\gamma_1$. In Fig.6, we present the combined $L\gamma_1$ band of the compounds and pure Cb (as in case of band $L\beta_2$, the combination also was made at identical intensity of line $L\beta_4$).

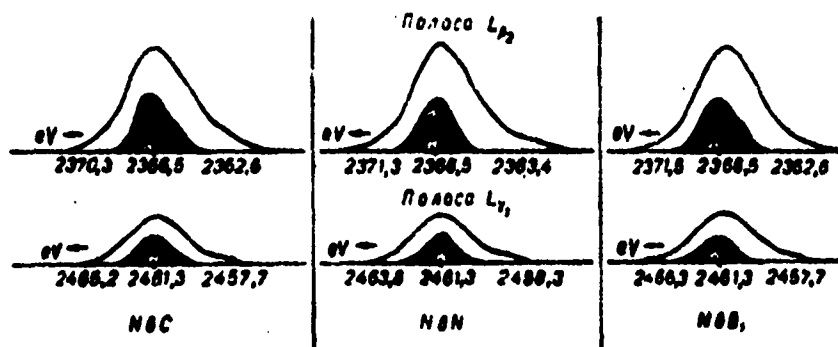


Fig.6

(Russian word on diagram: Band;
Nb = Cb)

It can be seen that the change in band $L\gamma_1$ is similar to the changes in band $L\beta_2$, i.e., there seems to be a departure of its various parts.

In Table 2, we give the numbers which characterize the change in band $L\gamma_1$ for pure Cb and its compounds.

The comparison of the slipping part of bands $L\beta_2$ and $L\gamma_1$ is also presented on Fig.6.

The data of Table 1 and 2 as well as Fig.6 show that in concrete substance the changes in bands $L\beta_2$ and $L\gamma_1$ are not entirely similar.

TABLE 2.

1 Вещество	r	$1-r$
NbN	0.703	0.297
NbC	0.789	0.271
NbB ₂	0.740	0.260

2. r равно отношению площадей L_{γ_1} соединения и нитрида.

(Column headings: 1...substance; 2... r is equal to the ratio of the area of L_{γ_1} of the compound and of Cb).

This difference seems to result apparently so that L_{β_2} is caused by transition into the states $S_{1/3}, d_{3/2},$ and $d_{5/2}$, but for L_{γ_1} only by transition into $S_{1/3}$ and $d_{3/2}$.

It should be assumed that the different form of bands L_{β_2} and L_{γ_1} in the different compounds of Cb, is due to the fact that the specific weight of states $d_{3/2}$ and $d_{5/2}$ in the common band are different.

The specific weight of states $d_{3/2}$ and $d_{5/2}$ in the common band can be limited by the assumption that the part of transitions to state $S_{1/3}$ in emission bands L_{β_2} and L_{γ_1} is small in comparison with $d_{3/2}$ and $d_{5/2}$ (in the heavier atoms the intensities of lines L_{β_7} and L_{γ_9} form not more than 2 percent. of the intensities of lines L_{β_2} and L_{γ_1}).

In the supposition that the intensities of lines L_{β_2} and L_{γ_1} satisfy the formula:

$$I\beta_2 : I\beta_{1,5} : I\gamma_1 = 6 \frac{N_{5/2}}{N_{3/2}} = 1:5 .$$

where $N_{5/2}$ is the number of $d_{5/2}$ states; $N_{3/2}$...the number of the $d_{3/2}$ states, from the experimental data for the ratio of intensities of the $L\beta_1$ and $L\gamma_1$ bands, the ratio of $N_{5/2}:N_{3/2}$ can be determined.

Below are given the data calculated according to the given formula of the $N_{5/2}:N_{3/2}$ ratio, and with our experimental values

<u>Substance</u>	<u>Nb=Cb</u>	<u>CbN</u>	<u>CbC</u>	<u>CbB₂</u>
$N_{5/2}:N_{3/2}$	2.08	2.10	2.08	1.90

([Note]: For the filled levels, $N_{5/2}:N_{3/2} = 6:4$, and the quoted correlation ratio is transformed into the Burger & Dorgel rule .)

Conclusions

1. The L-series of Cb was investigated in compounds CbN, CbC, and CbB₂.
2. It was found that while the intensity and the shape of lines $L\alpha_{1,2}$, $L\beta_1$, $L\beta_4$, $L\beta_3$ and so on, changes a little, the intensity and the shape of bands $L\gamma_2$ and $L\gamma_1$ undergo a sharp change.
3. Bands $L\beta_2$ and $L\gamma_1$ of Cb in the compounds are only parts of the corresponding bands of pure Cb.
4. The conducted measurements are not accurate enough for reliable quantitative conclusions; however, undoubtedly in case of Cb, the departure of the d-states in compound CbB₂ is larger than in CbN and CbC.

Questions and answers

Q: What conclusions do you make as to the bond types in carbides, nitrides and borides?

Ya.E.Genkin: In order to make any conclusions, both compounds (components) of the system must be thoroughly investigated. In our case, we examined only the Cb in the compounds. The second component and all its properties must be also examined. Any kind of conclusion can be made only then.

Q.: How do you explain the splitting of the $L\beta_2$ band of Cb nitride and carbide? Why does this band differ from the band in diborides?

Ya.E.Genkin: One cannot say that the $L\beta_2$ band is split, because line $L\beta_2$ does not seem to be a strictly dispersed line, guarding the state of the internal filled levels. It seems to be a complicated complex of transitions -- at M_4, N_5 and O_1 . Therefore, we can not say that it is two separate lines. Splitting can happen if some information is available on the character or energy of this or another line.

Here, however, we have a band. Therefore, we are forced to speak of it as a whole. At successfully selecting the criteria of the combination of the $L\beta_4$ lines, we endeavoured with all effort to make it such that the $L\beta_4$ lines should coincide. Then, it was found that the edge of band $L\beta_2$ coincides with the recession of pure Cb

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line. Therefore, we say that as a whole the energy of this band generally did not change. It seems to us that we should not say that the energies of the lines are different (as allegedly the splitting of the lines seems to be). And if the energy remained one and the same, then the probability of a transition is here also constant. Only the number of transitions in the given state has changed. It is interesting that no kind of edge, i.e., electron of an arbitrary energy, slips, but separate parts of the band are slipping. This is a proof that the whole $L\beta_4$ band has zones N_4, N_5, O_1 with overlapping. We can say that these transitions are already not in columbium.

In the limits of this band, the O_1 transitions are little expressed. We are not able in every case to distinguish them. Therefore all discussion about their transitions is approximative; we cannot judge the splitting with precision.

There is still this question:-- in case of compounds, can the decrease in the relative intensity of the $L\beta_2$ band (by comparison with pure O_b) be explained only by the decrease in the number of the free states?

It seems to us that particularly since the energy does not change, the probability of transitions does not change either. But the fact that a part of the line is eliminated, proves especially that they are absent.

Discussion on the Report of M. I. Korsunskiy and Ya. E. Genkin

A. Z. Mez'shikov (Institute of Metals Physics, AN SSSR):

From our point of view, the following interesting results were reached by the discussed work:

1. For all investigated compounds and pure Cb, in the scale of energies the position of the $L\beta_2$ band remains unchanged.

2. In diboride, carbide and nitride of Cb, the relative intensity of the $L\beta_2$ band is less than in pure Cb.

The first experimental result permitted the authors to announce for all compounds the hypothesis on the constancy of probability of transition from the d and s symmetry levels to the p symmetry level. Then, according to the formula $I(E) \sim P(\cdot) \cdot n(E)$, the reduction of the intensity of the $L\beta_2$ band can be explained only by the decrease in the density of the occupied states, i.e., by less number of transitions, which gave the right to the authors to calculate the number of electrons at the levels according to the relative intensity of the $L\beta_2$ band.

However, in our opinion, this kind of calculation does not determine the veritable position of things. The point of matter is that CbC and CbN have a crystal structure of the NaCl type, and we should have here d^2sp^3 -hybridization of the wave functions. But the possibility of hybridized spd-states can lead to a change in the probability of transition from the states which condition the existence of the $L\beta_2$ -band.

Therefore, here the calculations of the electron number at the states according to the methodology elaborated by the authors, is open to doubt. Of course, the significance of the factor of diminution of the electron number at the d and g symmetry levels is by no means belittled, the less so because the existence of an ionic covalent type of bonding can be here surmised.

**X-ABSORPTION SPECTRA OF CHROMIUM IN BORIDES, CARBIDES, NITRIDES AND
SOME OTHER COMPOUNDS**

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shikov;
Institute of Metals Physics,
AN SSSR**

The solid compounds of refractory metals generally, and the intrusion phases in particular find a wide practical application in engineering since they are characterized by an interesting collection of physical and chemical properties: -- high temperature of melting, great hardness, brittleness and good electric conductivity. The originality of the crystal structures, the complexity of the electronic structure, and the character of the interatomic bonding forces make these compounds one of the interesting objects of research.

In spite of a large number of publications, whose review is well presented in the monographs [1, 2], the problem about the character of interatomic interaction in the intrusion phases continues to remain obscure. Later, attempts have been made at solving this problem by the method of roentgen spectroscopy [3 - 5], one of the most direct methods of studying the electron structure of solid bodies.

In the present work, we give the results of study of the nature of interaction between the atoms of a metal of the transition group and the metalloids of the first series of Mendeleev's Table (B, C, N, O).

The continuous change of bond type from the metallic (in beryllides) through the covalent (in carbide) to the ionic (in oxides) was presented in the publications [6, 7], and further developed in detail by G. V. Samsonov [8].

As object of research, from among the metals of the transition group, chromium was taken in its borides, carbides, nitrides and oxides (CrB , CrB_2 , Cr_3C_2 , Cr_7C_3 , Cr_2N , CrN , Cr_2O_3) and the chemically pure substances of CrCl_3 , and $\text{Cr}_2(\text{SO}_4)_3$.

The borides and carbides were obtained in the Institute of Metal Ceramics and Special Alloys of the AN USSR. The nitrides were obtained by diffusion saturation of Cr in ammonia jet by the methodology of [9]. Cr_2O_3 was obtained by oxidation of electrolytic Cr at 1000°C in free air.

The roentgen K-edge of Cr absorption was investigated on a spectrograph with focussing according to Johann in the first order of reflection from plane (1340) of a quartz crystal. As line of comparison, the $K_{\alpha 1}$ line of Fe and the $K_{\alpha 2}$ line of Mn were used. The linear dispersion was 2.5 XE/mm. The tube worked at 12-13 kV, 45-50 mA. The survey's length was 35-40 hours.

The Cr absorption spectra seemed to be of the greatest contrast at 5-6 mg/cm^2 absorber density. Not less than three spectra

were made for each substance.

For all phases investigated by us, we measured the magnetic susceptibility. The measurement was carried out (by P.G. Radomanov) on magnetic balances with a field of 8600 oersteds and at 17°C. Seasalt was used as standard.

The figure (unnumbered) represents the basic K-edge of Cr absorption in the examined compounds and metallic Cr. Along the abscissa, the

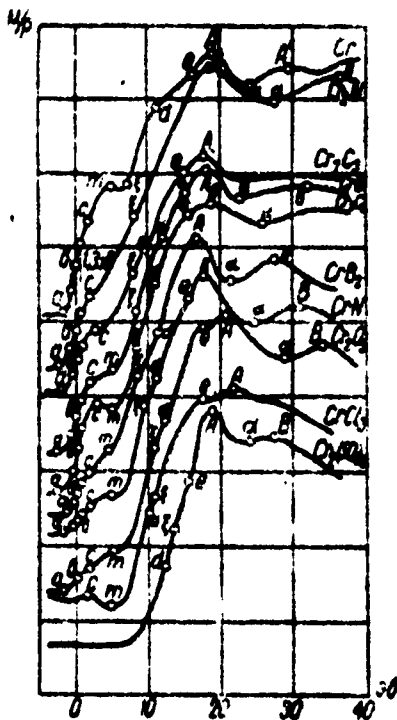


Fig. (No legend; on abscissa: electron volts)

energy(power) is laid out in eV-s, by counting from a chosen zero, and along the ordinate the magnitudes are proportional to the absorption coefficient.

According to Beeman and Friedman [10], the first region of the K-absorption spectrum of transition metals with open 3d-shells (in particular, for Cr $3d^5 4s^1$) is conditioned by transitions of l-s-electrons (one-s) into the unoccupied part of the generalised 3d-4s band with admixture of the 4p-state.

The top curve on the figure illustrates the change of absorption coefficient in the region of the main K-edge of the electrolytic Cr. It can be seen that the first region of absorption does not have an arc-tangent-shaped form, but it possesses a certain kink at Point C. By analogy with the curves of K-excitation, obtained by the isochromatic method of the characteristic spectrum [11], this kink can be also explained by transitions of Cr into the 3d-state.

And now, the first initial region of absorption in pure Cr is conditioned by transitions of K-electrons into the 3d and 4s bands, and it exactly reflects the transitions into those states which undergo changes in relation to the type of the chemical bond. But since the absorption coefficient itself depends upon the density of unoccupied states and on the probability of transition at these states, i.e., $I(E) \sim P(E)n(E)$, these two factors will influence the intensity of the initial absorption.

The experimental curves presented on the figures are arranged

[2

in such an order that along the edges the curves are arranged for substances of different bond types, i.e., Cr with metal bond, $\text{Cr}_2(\text{SO}_4)_3$ with ionic bond. From the examination of these curves it follows that in pure Cr the initial absorption by intensity is roughly one half of the whole absorption discontinuity, while in $\text{Cr}_2(\text{SO}_4)_3$ it is entirely not; moreover, the energy position of the A maximum remains unchanged.

Consequently, in the given compound of trivalent Cr, the quasi-atomic 3d-4s levels are considerably free. However, due to the weak interaction between the neighboring Cr ions in $\text{Cr}_2(\text{SO}_4)_3$ crystal, the overlaps of 3d and 4s bands with the 4p band are either entirely absent, or very small. Hence, the probability of transition of a K-electron into the 3d-4s-state is markedly reduced, which is manifested in the disappearance of the initial region of absorption in the pertinent spectrum. The given example shows how large the effect of transition probability is upon the intensity of the initial absorption.

On the transitions in the following three compounds (CrCl_3 , Cr_2O_3 , CrN) I remark that in these compounds the fine structure of the basic K-edge of Cr absorption gets richer. The initial absorption, appearing in CrCl_3 , gets larger in intensity in oxide, and still larger in nitride. The crystal structure of the given compounds of the group has an octahedral atomic coordination. According to Kimball (12), a d^2sp^3 hybridization of wave functions should here appear. It is thought that due to such a hybridization of d-functions

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with p-functions, the probability of K-electron transition into the 3d-4s-state is larger.

An interesting peculiarity of the K-absorption spectra of Cr in the given compounds of the group -- shown the first time in this work, as we think -- is the presence of fine structure in the initial region of absorption (in the figure, the kinks in the initial region of absorption are suitably designated by Points g and m).

As to the character of absorption spectrum, the diboride (CrB_2) is close to these compounds. It has a somewhat different atomic coordination (the Cr atom is within a hexagonal prism on whose apex the B atoms are arranged).

Results of the magnetic susceptibility measurement, given in the following Table, indicate that in the order of the compounds $\text{Cr}_2(\text{SO}_4)_3$, CrCl_3 , Cr_2O_3 , CrN , CrB_2 , its value diminishes from 28.0×10^{-5} to 9.0×10^{-6} cgs, which proves the diminution in the number of uncompensated electron spins in the 3d-shell of the Cr atoms.

The presence of a regular change in intensity of the initial absorption as well as the data on the magnetic susceptibility measurement make us believe that in this series of compounds, together with the ionic type of bonding, there is a rising covalent component of interatomic interaction.

In comparison with the first, the second group of compounds (Cr_3C_2 , CrB , Cr_7C_3 , Cr_2N) has a larger initial region of the K-absorption spectrum, equal roughly to 25-30 percent. of the whole absorp-

tion discontinuity, and a magnetic susceptibility (See Table) in the order of $(5 \text{ to } 6) \times 10^{-6}$ oesm, which is substantially less than the magnetic susceptibility of the preceding series of compounds. The examination of the crystal structure in the given compounds finds the presence of more or less distorted prismatic atomic coordination for which according to publication [12] there should be a $d^4 sp$ or $d^6 p$ hybridization of wave functions present.

TABLE.

1 Вещество	2 $\chi \cdot 10^{-6}$ ед. CGSM	3 Электронная конфигура- ция	4 Вещество	5 $\chi \cdot 10^{-6}$ ед. CGSM	6 Электронная конфигура- ция
$Cr_2(SO_4)_3$	28,0	—	Cr_2C_2	6,4	$d^4 sp$ или $d^6 p$
$CrCl_3$	21,8	$d^3 sp^3$	CrB	6,7	$d^4 sp$ или $d^6 p$
Cr_2O_3	19,2	$d^3 sp^3$	Cr_2C_3	3,8	$d^4 sp$ или $d^6 p$
CrN	18,0	$d^3 sp^3$	Cr_2N	5,8	$d^4 sp$ или $d^6 p$
CrB_2	9,0	—	Cr	3,4	—

(Column headings: 1...substance; 2...unit in the cgs system; 3...electron configuration; 4... "or").

If only the presence of a covalent type of bonding is assumed, then the given compounds should be diamagnetic or slightly magnetic, and the initial region of the K-absorption spectra of Cr in these compounds should either entirely vanish, or it should be small in magnitude. In our case, neither one nor the other happens. Hence, the nature of the bonding forces seems to be complex in these compounds.

and, from our point of view, it rather agrees with the idea of the resonant covalent bond developed by Pauling [13].

With a general examination of the K-absorption spectra of Cr in pure Cr and its compounds of boride, carbide, nitride, oxide, chloride, the invariability of the position of Point b in the energy scale should be noted, independently from the type of compound. The kinks of the absorption coefficient curve, corresponding to Points d and e, whose nature we do not study, as well as the A maximum are subject to changes both in the energy scale and in the intensity scale.

Point ζ (zeta) $\} = \left(\frac{A - a}{2} \right) \mu \xi$ --- the middle of the absorption discontinuity -- is regularly shifted to the short-wave side by the extent of increase of the ionic component of bonding force in the compounds.

Conclusion

1. The nature of the interaction of Cr atoms with the metalloid atoms of the first line of Mendeleev's Table (Cl, C, N, O, and B) continuously changes from ionic covalent to covalent metallic.

2. The obtained experimental results indicate that the different compounds inside one diagram of state cannot pertain to single type of bonding forces, because in this case the concentration of metalloid can play an essential role. This is particularly characteristic for the compounds CrN and Cr₂N, CrB₂ and CrB.

3. A hypothesis on the metallic state of the metalloid atom (as this is correct in case of the Pd-H system) cannot be extended

to all classes of the Haggian phase of intrusion. The typical intrusion phase of CrN is close to Cr_2O_3 by nature of the interatomic interaction, and in this oxide the bonding forces have ionic covalent character.

4. In the metalloïd compounds, the character of bonding forces is complex. Of course, the ordinary classification into ionic, covalent and metallic type of bonding is not in agreement with reality.

The authors express their deep gratitude to G. V. Samsonov for the permitted samples and his great interest in the work.

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Discussion on the report of S.A. Nemnonov and A.Z. Men'shikov
E.A. Zhurakovskii (Odessa Pedagogical Institute):

The question about the nature of forces of chemical interac-
tion between atoms of a metal and metalloids in the carbides, ni-
trides and other intrusion phases of transition elements presents
great practical interest, and for many years it has attracted the
attention of investigators. Nevertheless, until now it still has
not been sufficiently explained. For the foundation of present as-
sumptions, magnetic, electric, and crystallo-chemical data are used.
However, until recent times, information on the roentgen spectra of
the atoms in these compounds was not available which, in differ-
ence from the data of all other methods, could give the most direct
information about the energy state of atoms in these compounds. The

first investigations by emission spectra in this area were made recently by E.E.Weinstein and coworkers.

The solution of this problem is also the purpose of the present work in which the fine structure of the roentgen K-absorption spectra of Ti is investigated in the alloys of the Ti-C system where the metalloid content changes from 24 to 9 percent. by weight.

All investigated alloys were prepared by the methodology described in the literature, and (except the 9-percent.alloys) they pertain to the same field to which the carbide of face-centered cubic lattice belongs.

The research was conducted on a spectrograph specially constructed for this purpose,whose construction was suggested by I.B. Stary,and described earlier.

The plane of a quartz crystal prism was used as analyser. The method of recording the spectra was photographic. The optimum density of the absorber was experimentally selected. It was equal to 5 mg/cm³. At higher densities of the absorber, the fine structure of the K-edge of absorption was less clearly observed at the experiment.

For comparison,parallel with the carbides, the fine structure of the K-absorption edge of Ti and its dioxide(rutyl) was investigated. Attention was called to the fact that the energy,corresponding to the maximum of the long-wave absorption band of Ti, remained unchanged in both compounds of this metal. This is in good

agreement with the phenomenon found in the preceding researches, and it does not agree with the hypothesis that at the formation of the carbides of transition elements a "metallization" of the bond occurs, which would be manifested by a partial filling of the 3d-energy levels of the transition metal atoms. More detailed experimental investigations will be continued in the very near future.

V.S. Meshper (Institute of Metal Ceramics and Special Alloys, AN USSR):

Something should be said in connection with the communication on roentgen spectral research of the metalloid phases. As a direct method of studying the character and strength of bonds in metals and in compounds, these researches are of great interest. Yet, their detailed examination remains still a failure until now. The data of individual researches occasionally disagree with each other, and they are being arbitrarily treated by one school or the other.

Therefore, it seems to me that according to the results of researches of a number of physical characteristics of these substances, such a structural model could be now roughly presented for these compounds on whose basis the separate spectral data could be dealt with.

While talking of electron transitions to this or to that side, they cannot be examined only from the point of view of the zonal theory, but the individual peculiarities of the structure of atom components of the compounds must be studied. Undoubtedly, the greatest effect upon the physical properties of metalloid compounds is

exercised by the degree of filling of the 3d-shell of the transition metal atoms and the ionization potential (or electro-negativity) of the metalloid atoms. These factors determine the density of the occupied states both in the valency zone and in the conductivity zone, and hence they show a substantial effect upon the position and intensity of the spectral lines of metals in compounds, particularly in case of the L-series.

The type of crystal structure and the number of bonds should be also studied.

From the results of the work reported by M.I. Korsunskii and A.Z. Genkin, it can be seen that the greatest number of electrons leaving the metal are in boride (CbB_2), and a less number in nitride and carbide, which corresponds to a larger number of B bonds in the boride lattice ($5Me - B$ and $3B - b$) than the number of C and N is in the carbide and nitride ($CMe - X$). In nitrides, the metal loses more electrons, in correspondence with the greater electro-negativity of N, than in case of carbide which has a smaller electronegativity of C.

The researches of the initial absorption region in ionic and metalloid compounds are of considerable interest. But, at the end, one cannot agree with the conclusions drawn in this work as to the transition from the purely ionic $Me - X$ bond in chloride and sulphate to the covalent bond in borides, carbides and nitrides.

Researches of the temperature relation of electric conductivity of the latter phase, presented in our report, indicate the metal-

lic nature of conductivity of the transition metal carbides and borides i.e., the presence of free carriers of electric current in them, subordinated to the Fermi-Dirac statistics.

Thus, it is apparently correct to consider the changes in the region of initial absorption in the compounds investigated by S.A. Nemnov and A.Z. Mer'shikov as result of subsequent gradual transference of the density maximum of the electron shell in the Me - X bond from metalloid to metal in the sequence of sulphate(chloride) - oxide - nitride - carbide - boride, which is also pointed out in our report.

In our opinion, such a model also fits the results of the work of Vaynshteyn and Vasil'yev according to the examination of the K-emission spectra of Ti compounds. The growth of the metallicity of compounds also happens to be in this direction.

M.D. Glinchuk (Institute of Metal Ceramics and Special Alloys, AN USSR):

Investigation of the behavior of admixture in solid solutions is of considerable interest. I wish to touch on the problem of the effect of the admixture's concentration upon the energy spectra of the base metal.

In works of foreign authors and in recent works of the Soviet scientists Gurov and Borovski, it was shown that change in the admixture's concentration effects the shift of the Fermi state of the base metal. For each base metal, a certain definite concentration exists below which the dislocation of the Fermi level can be disregarded.

At concentrations above this definite one, due to interaction of the admixtures, the shift of the Fermi level considerably increases. Thus, if the basic solution is copper, then with the admixture's concentration of an excessive single charge of about 50 at. percent., the Fermi level shift is roughly about 0.5 eV (according to the data of Friedel, Advancements of Physics, 1954)

We were interested in the solid solutions on iron base. In transition metals (i.e., with larger effective masses) the excess charge of admixture is quickly shielded.

Therefore, the solved elements mutually interact only when the concentration of admixture is sufficiently large. For iron, the concentrations must be more than 60 at. percent. With smaller concentrations, the Fermi level can be considered practically unchanged.

Redistribution of the excess electrons among the open 3d and 4s shells of iron occurs on account of electron scattering at thermal vibrations of the crystal lattice of the base metal. As the researches of a number of authors show, the electron fraction of those which slip out into the d- and s-bands, should be proportionate with their relative level densities in the vicinity of the Fermi surface.

Since the density of d-states is larger than the density of the s-state, the larger part of the excess electrons must go for the building of the d-band of the base metal.

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M.I. Korsunskii (Kharkov Polytechnical Institute):

I would like to make a few comments.

In their report, S.A. Neamonov and A.Z. Men'shikov emphasized the great possibilities of roentgen spectral analysis. With this method it should be in agreement that it gives good basis for the judgment of the electron behavior in the various states. From these data then, conclusions are drawn on the electric conductivity of the substance and on its other properties.

However, as I.I. Frantsevich correctly remarked, the chemical compound must be investigated in a complex manner, i.e., the spectral method must be combined with other methods of research.

What is then trustworthy in the discussed report and what causes doubt?

The data entered in Table are particularly informative. They can undergo some changes in this way or another. These data, as the spectral curves themselves also, were obtained in a hurry; their methodology of processing was also developed literally in a few days.

Therefore, these data should be considered as approximative.

I wish to call attention to those additional possibilities which this method reveals. It seems to me that firstly in the roentgen spectral practice there is a possibility to determine the number of electrons which leave for bonding.

Particularly interesting are, undoubtedly, the results of study-

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ing the effect of concentration changes in the range of the area of homogenousness of the metalloid phases of the type of nitride, carbide, boride and other compounds.

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COMPARATIVE BRITTLINESS OF HEAT-RESISTANT COMPOUNDS

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Articles from refractory compounds of the type of carbides, borides, nitrides and silicides, more and more widely used in contemporary engineering, should possess sufficient stability against a thermal shock. The realization of this property in material which has high strength of atomic bonding, low capacity of relaxation of internal stresses, and which are brittle by their nature, is extremely difficult, and is not always feasible.

The attempt at preparing and investigating the details for the basis of the refractory compounds indicates that, regardless of their apparent identical brittleness and resistivity to the action of normal tensile forces, they react in different way to thermal shock, which proves their considerable difference in regard to brittleness and relaxation capacity.

However, since these materials possess identical macroscopic

brittleness, as mentioned above, for appropriate selection of those among the refractory compounds which could serve as basis for the preparation of super-refractory materials resistant to heat shock, it seems to be necessary to resort to microscopic research for the study of their comparative properties at small scale.

Therefore, we have undertaken a comparative microscopic investigation of the mechanism of destruction and brittleness in relation to the potential capacity of resisting the action of thermal shock. In these researches we used 1) the method of constructing statistical curves of microbrittleness by the cracking ability of the impressions caused by the microdurometer's indenter at different loads, and 2) the method of electron microfractography.

Regardless of the extraordinary importance of the estimation of comparative brittleness of refractory compounds, until now a sufficiently clear, simple and reliable method has not been available for such an estimation:

Various methods have been proposed for the comparison of the brittle properties of refractory compounds: -- by compressibility of powders [1], by the number of hits upon the sample which cause destruction [2], by the work spent on deformation of material at obtaining an impression by the durometer [3], and others.

Let us stop a while for the detailed description of the latter method. By this method, a relationship is built between the number of impressions which have cracks and the magnitude of the load,

and that P_k load is determined by which 50 percent of the impressions will crack. At the determination of hardness N , the diamond prism of the indenter does some work spent on plastic deformation of the material. This work is computed for force P_k . By knowing P_k , the hardness N , and the apical angle of the pyramid, the work S_k , called by the author [2] "viscosity", can be calculated. For Eicker's pyramid the formula is:

$$S_k = 2 \times 10^{-4} \sqrt{\frac{P_k^3}{H}} \quad [\text{gon}].$$

From our point of view, the greatest prospect has the so-called microbrittleness method which, as it is known, consists of the construction of curves which are related to the number of impressions that crack under the indenter of the microdurometer from the load put upon the indenter, or -- after reaching the load at which all impressions have cracks, -- the number of cracks in one impression with a certain load magnitude [4,5]. Moreover, obviously at a given load, the more brittle materials will have a larger number of impressions with cracks (or correspondingly, fewer uncracked impressions). Thus, by the comparison of the curves of microbrittleness, we can also judge the relative brittleness of the investigated materials.

We constructed such curves for a number of refractory compounds and silicon which enters into some fire-resistant compositions: -- they are given in Fig.1. On the micro-sections prepared by diamond powder, the measurements were made on a PMT-3 apparatus for

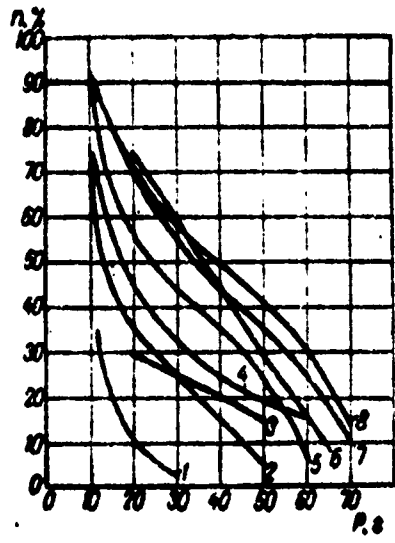


Fig.1. Curves of microbrittleness for several refractory compounds and silicon: 1...silicon; 2 ... OsB_2 ; 3...TiN; 4...SiC; 5...ZrO; 6...TiC; 7... CrB_2 ; 8... Cr_3C_2 .
(Abcissa: Pressure ,in grams)

the determination of micro-hardness. Data obtained from 50-70 measurements enter into one point of the curve. The reproducibility of the data, obtained in the two halves of one and the same sample, is $\pm 5\%$ which apparently can be considered as the accuracy of the method itself, and can characterize the satisfactory degree of its objectiveness.

At the scrutiny of the microbrittleness curves, first of all the fact is noted that several curves intersect each other, for ins-

tance for Cr₂O₃ and TiO₂, for ZrC and SiC.

This brings a certain disorientation into the problem of determination of comparative brittleness, since in case of small loads, e.g., ZrC proves to be less brittle than β -SiC, but with larger loads the opposite happens.

The question arises, what should then characterize the comparative brittleness of materials:-- mutual situation (i.e., the run of the curves); the start of the curves, i.e., the load at which the impressions start to crack; or their end, i.e., when all impressions have cracks?

From Fig. 1 it is evident that the maximum load at which cracks are still not formed around the impression differs very little for the different materials so that apparently this magnitude cannot be considered characteristic.

As to the mutual situation of the curves, obviously we should take here in account the behavior of the separate grains of tested material. Under actual conditions of a polycrystal sample, a grain which is subjected to the action of the indenter will be under conditions of a disproportionate allround compression, particularly when we take in account that the refractory compounds are destroyed in the area of elastic deformations [6]. Evidently, therefore, the field of stress where the tested grain is located will depend upon different factors, e.g., on granularity, presence of internal stresses and

so on. In agreement with this, the grains of the material tested for micro-brittleness will behave in different ways, since they will be in different force fields. This will also cause that for the different materials the curves of microbrittleness go different ways, especially that they intersect. To be able to compare the different curves with each other, we must know how their course is influenced by the field of stress in the sample.

For the estimation of this influence, we calculated the relative derivative

$$\alpha = \frac{P}{n} \cdot \frac{dn}{dP}$$

along each curve, and constructed the relation of this magnitude to the load. In this formula, P ... is the load at which the number of non-cracking impressions is n (percent.). The derivative is calculated at the point which is characterized by the given values of P and n . The obtained relations are shown in Fig. 2.

From Fig. 2 it is evident that the majority of the examined materials are characterized roughly by an identical α derivative within the range of 20-40 grams of load. At larger loads, the curves $\alpha = f(P)$ begin to differ markedly. In our view this proves that, as to brittleness, materials can be compared by the run of the curves $n = f(P)$ only within the limits indicated by us, and at roughly identical values of α . Moreover, the samples must be evidently of identical granulation. The most reliable results should be obtained

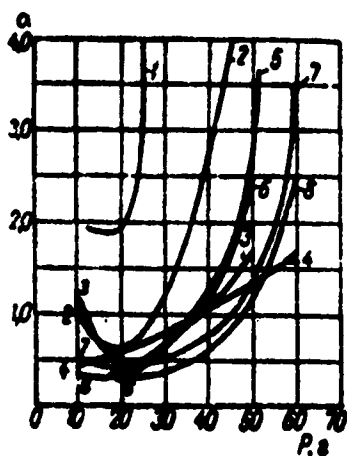


Fig. 2. Relation of relative derivative α to load for a few refractory compounds and silicon: 1...Si; 2...CbB₂; 3...TiN; 4...SiC; 5...ZrC; 6...TiC; 7...CrB₂; 8...Cr₃C₂.
(On abscissa: \bar{P} , in grams).

at the comparison of the microbrittleness curves in case of a load that corresponds to the minimum value of α , i.e., in the given case with a load of $\bar{P} = 20$ g.

The analysis of the curves $\alpha = f(\bar{P})$ indicates that with larger loads the effect of the stress field sharply increases, and it is different for different materials. Therefore, obviously, the comparative brittleness cannot be characterized by comparison of the curves by loads at which all impressions have cracks, since these

magnitudes depend not only on the physical nature of the tested sample but also on the stress field in which each measured grain happens to be.

Attention is called to the fact that magnitude α is comparatively large for pure Si, and sharply increases with the growth of the load. Starting from the above made assumptions, as a result of this, it can be expected that for samples of silicon of different grain sizes the micro-brittleness curves will be different. Experience confirms this assumption. On Fig.3, microbrittleness curves are shown for

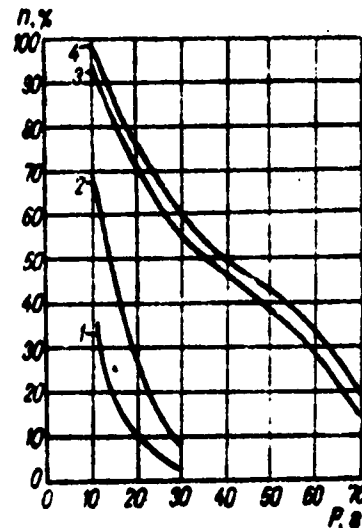


Fig.3. Curves of microbrittleness for coarse-grained and fine-grained samples of silicon and chromium carbide: 1...silicon, sample No.1; 2...Si, sample No.2; 3... Cr_3C_2 sample No.1; 4... Cr_3C_3 sample No.2. (On abscissa: P, in grams)

coarse-grained and fine-grained silicon. The fine-grained samples seem to be less brittle than the coarse-grained. This can be ex-

plained so that in the fine-grained sample the tested grain is under conditions of a more all-round disproportionate stress than in the coarse-grained sample, which causes the endurance of greater loads without destruction. Generally speaking, similar conclusions can be also drawn on the basis of the Orowan-Griffith theory.

For sake of comparison, Fig. 3 also shows the microbrittleness curves for samples of Cr_3O_2 of different grain size. The samples differ from each other by granularity in the same way as the Si samples. In correspondence with the considerably smaller magnitude of α for Cr_3O_2 in contrast with Si, the difference in the micro-brittleness curves for Cr_3O_2 is also much less. If at $P = 20$ g, the value of microbrittleness for Cr_3O_2 differs only by 7 percent., then at the same load it is $2\frac{1}{2}$ times larger for Si. This difference in the curves increases with the load, together with the increase of the value of α , as shown in Table 1.

TABLE 1.

Si			Cr_3O_2		
P, g	α	$\frac{n_1}{n_{11}}$	P, g	α	$\frac{n_1}{n_{11}}$
12	1,9	1,72	10	0,3	1,02
20	1,9	2,50	20	0,3	1,07
25	3,0	3,00	40	0,6	1,11
—	—	—	60	2,2	1,22

(NOTE: P is given in grams)

Parallel with the method of construction of microbrittleness curves for qualitative comparison, we have widely used the method of electron microfractography.

The method of electron fractography, developed by K. Zapf, i.e., the study of the structure of ruptures, lately finds larger and larger application for the investigation of the character of destruction of metals and alloys, e.g., of steel, in connection with composition, structural peculiarities, ageing, and so on, as well as for the solution of other problems of metallurgy. Deficiencies, limitations inherent in an optical microscope, -- the comparatively small magnification, the low resolving power and chiefly the small depth of sharpness -- were the motive that, in the majority of cases of steel, fractographic investigation is made with the aid of an electron microscope.

We applied the electro-micro-fractographic investigation of refractory compounds of the type of carbides, borides, nitrides and silicides in order to clarify their mechanism of destruction in connection with the study of their comparative brittleness.

Applied to fractures of refractory compounds, we worked out a special methodology of sample preparation [5] which consists of two steps. The first is the formation of an impression by pressing the tested fracture surface into acetone-softened celluloid. After drying of the impression and its separation from the surface of

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the sample, on the contact side a second impression was dusted on with titanium or silicon protoxide (second step). The separation of the second impression was accomplished by the dissolution of the first in acetone.

According to this methodology, structures of brittle fractures were examined for a series of multi-crystal refractory compounds for which data were obtained on microbrittleness. All samples were obtained by hot pressing of the powders of limited (maximum) compositions. The samples under testing were destroyed by bending impact destruction.

The study of the structure of fractures discovered substantial differences in the fine structure of fractures of the different classes of compounds. We give below microphotographs of the fracture structures which are most characteristic for this or that type of compound. They were chosen from among 50 - 100 pictures observed in the electron microscope, and they show the statistical character of the electron microscopic observations.

A number of compounds, e.g., columbium boride CbB_2 (Fig. 4), silicon and columbium silicide, are destroyed along a clearly formed surface of cleavage or separation, which can be related to the low resistance of detachment along this surface under the action of normal stresses. Considering that, as a rule, under conditions of heat shock, by the effect of thermal tensile stresses the material is destroyed, owing to normal stresses, the low resistivity of these materials



Fig. 4. Structure of fracture of cerium boride CeB_2 ($\times 600$)



Fig. 5. Density of cleavage in ZrC ($\times 5000$)



Fig. 6. Structure of fracture of TiN ($\times 600$)



Fig. 7. Structure of fracture of TiC ($\times 600$)



Fig. 8. Structure of structure of chromium sesquioxide Cr_3O_4
($\times 5000$)



Fig. 9. Structure of structure of iron sesquioxide Fe_2O_3 ($\times 5000$)

against detachment along a certain crystallographic surface should be related to their negative characteristics.

In the other large group of refractory compounds, in the structure of the fracture, parallel with the surfaces of cleavage and separation, signs of destruction appear along secondary surfaces of cleavage with characteristic terrace-like structure of the fracture, reflecting the blocky structure of the crystals. In the majority of cases, in these fractures the cleavage surfaces coincide with the crystallographic surfaces of the primary cleavage, as it is seen, e.g., in zirconium carbide ZrC (Fig. 5), where the surface of cleavage seems to be a surface of type (100) . On Fig. 6, the terrace-shaped fracture of silicon carbide is presented, and on Fig. 7 that of titanium carbide.

We find the majority of carbides in this group of compounds.

Finally, in still another group of compounds, e.g., Cr_3C_2 and B_4C , new elements appear in the structure of the fractures which can be apparently related to plastic deformation in micro-volume.

From this point of view, Fig. 8 is characteristic where the structure of the fracture of Cr_3C_2 is given. Here, two systems of bent displacement surfaces can be distinguished, including three neighboring grains. In one of the grains, two plane-slippage surfaces intersect, due to which the grain seems to be smashed at a large number of blocks somewhat disoriented with regard to each other.

Still more direct signs of somewhat increased plasticity are

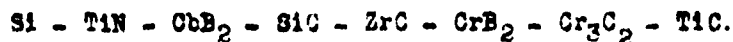
the traces of dislocations (apparently, growth dislocations) whose outcrops at the boundary line appear to be in the shape of punctate chains in the structure of the fracture of boron carbide B_4C (Fig. 9) and chromium carbide Cr_3C_2 . In these materials, higher resistivity to thermal shock as well as a known capacity of deformation at higher temperatures can be foreseen when even in these materials of very great strength of interatomic bond the dislocation acquires the ability to shift.

Conclusions

The qualitative (construction of microbrittleness curves) and the quantitative (microfractographic) investigations of brittleness of refractory metalloid compounds make possible to draw a few preliminary conclusions.

1. The statistical curves of microbrittleness distinctly illustrate the difference in the microbrittleness of the different compounds.

Considering the most appropriate comparison of micro-plasticity indices at a load of 20g, the following series of the examined compounds can be recorded according to decreasing brittleness:



2. The obtained series is basically reproduced at taking the plasticity of "viscosity", determined by Palmquist [3], as a criterion. In Table 3, we give the data obtained for some compounds by Palmquist's method and by the method of constructing curves of microbrittleness.

TABLE 2.

1 Phase	2 H, kg/mm	3 P, %	4 S. 10 ⁴ , g/cm	5 n, % (20 g)
Cr ₂ C ₃	1300	40	14,00	71
CrB ₂	1785	34	9,12	68
TiC	3000	37	8,26	73
ZrC	2925	25	4,58	57
SiC	3000	18	2,80	45
NbB ₂	2595	12	1,64	35

(Column headings: 1...phase; 2...H, kg/mm; 3...P, %;
4...S. 10⁴ g/cm; 5 ...n, % (20g).

As it can be seen from the Table, the qualitative coincidence of the results obtained by both methods (with exclusion of TiC) is rather fair.

3. Investigation of the different refractory compounds of the titanium basis (carbide, boride, nitride, and silicide) shows that the increase in brittleness runs in the order of TiSi₂ - TiC - TiB₂ - TiN (Fig. 10). This conclusion is somewhat contradictory to the data of Sameonov and Meshner [1] who obtained an increase in brittleness from titanium nitride through boride to carbide. It seems to us that such difference is explained by an imperfection of the method of determination of the brittle properties by the compressibility of these powders that were used by the authors [1].

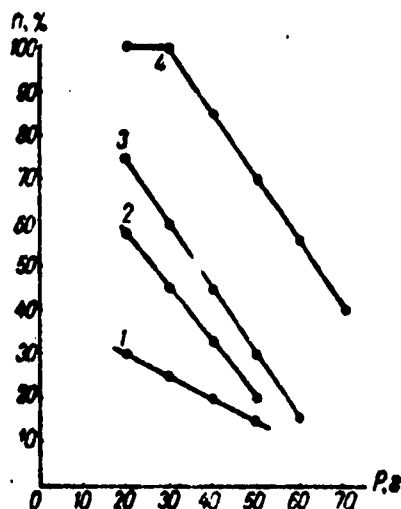


Fig.10. Curves of microbrittleness for refractory titanium compounds: 1...TiN; 2...TiB₂; 3...TiC; 4...TiSi₂.

The theoretical explanation of this change in brittleness from one compound to the other [1], based upon the calculation of only the force of interatomic bond does not seem to be sufficiently strict in our presentation either, since -- parallel with the bonding forces-- it is absolutely necessary to calculate the type of bond and the different relaxation capacities. Without regard to the fact that the value of the average square dislocation for TiC is less (0.067) than for the boride (0.073), according to our data TiC is more plastic, which is also qualitatively confirmed by fractographic researches. This is apparently explained by the greater metallicity of the bonding and by the greater relaxation capacity

of the carbide than of the boride. Further examinations should show how correct such a viewpoint is.

4. Quantitative data on the comparatively large degree of microbrittleness of TiO_2 , chromium carbide, and qualitative data correlated with them and obtained by means of fractography, confirm the very good hot-compressibility and relative high resistivity to thermal shocks.

5. The correlative qualitative and quantitative data also coincide for other examined materials:-- silicon, columbium boride, titanium nitride, and so on.

In conclusion, the authors express thanks to G.V. Samsonov for the samples presented for the investigation.

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Questions and answers

Q.: What is the comparative brittleness of silicon nitride, particularly in reference to silicon carbide and other compounds?

A.N.Pilyankevich: We did not study silicon nitride.

Q.: What was the purity of the initial materials -- of boride, nitride, and so on?

A.N.Pilyankevich: They were rather pure samples, prepared from pure original materials by direct synthesis.

Q.: What was the purity of the examined silicon?

A.N.Pilyankevich: Technical silicon was examined.

Q.: What is the reproducibility of the data on microbrittleness?

A.N.Pilyankevich: We made such experiments, particularly for the chromium carbide samples obtained from a particular party. The reproducibility of the results is 5 to 10 percent, at the construction of microbrittleness curves.

CODIFFUSION OF TWO ELEMENTS INTO HARD METAL

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Uralak State University

In the present article the codiffusion of two elements into a third is examined in systems of the type of $\left. \begin{array}{l} \text{hard metal -- mixture} \\ \text{of two chemically active gases} \end{array} \right\}$. For brevity, these systems are designated further on as



where Me...is metal(hard)

X' ...the first element(gas)

X''....the second element(gas).

The theoretical value of such investigations includes the obtaining of experimental data for the explanation of the physical mechanism of the reaction diffusion in general, practically conditioned by the need of studying the technological processes related to the action of gases upon the third phase, especially the processes of gas corrosion and chemical thermal processing of alloys.

For the study of the structural configuration in the reaction

diffusion layers and of the kinetics of the growth of diffusion layers in the triple systems of the above shown type, they must be classified.

The classification can be based upon a few factors which may affect the process of reaction diffusion.

Diagrams of the state of systems formed by compounds existing in binary systems of the Me-X type

The first case is a pseudobinary diagram of the state of compounds with inorganic solubility which are formed in the Me-X' and Me - X'' binary systems. In this case, the formation of a diffusion layer is observed which consists of a single phase with a concentration gradient that for both components decreases by the layer depth. This case is schematically presented on Fig.1 (a...for reaction diffusion; b...for formation of triple solid solutions).

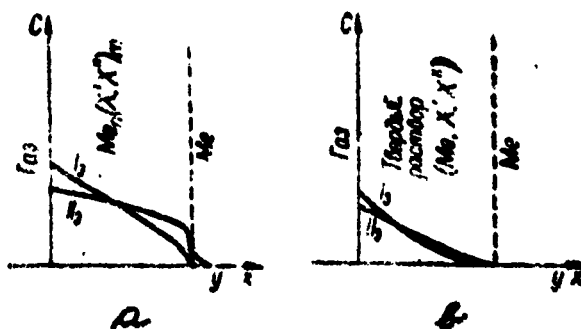


Fig.1
(Words on figure: Ordinate...gas; on "b" diagram: Solid solution)

The second case is a pseudobinary diagram of a state of X' and X'' with organic solubility in compounds formed in the $Me - X'$ and $Me - X''$ binary systems. Here the diffusion picture already has another type (Fig.2).

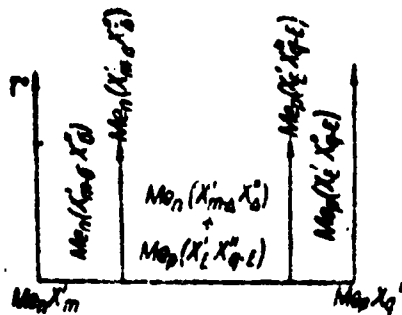


Fig.2.

The surface layer will consist of a phase which contains more of the element that has smaller diffusion mobility. At a certain depth, the layer of the other phase can also exist which has increased concentration of the element of greater diffusion mobility. This case is schematically presented on Fig.2 (a...for reaction diffusion; b... for formation of triple solid solution).

As a result of different diffusion mobilities of the elements in the reaction layers, the depth of penetration of one element will be greater than that of the other in both of the above cases.

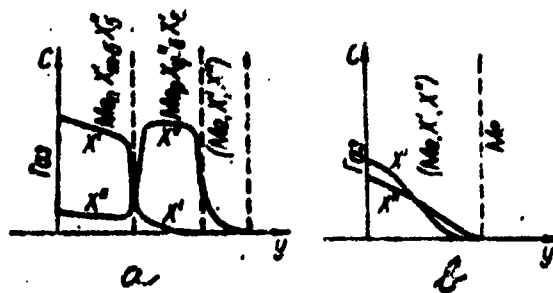


Fig.3. (No legend)
(Oa ordinate: Gas)

The third case is the absence of solubility of X' and X'' in the binary compounds of the pseudo-binary system $Me_n X'_m - Me_p X''_q$.

In this case, divergence in the chemical relationship of elements X' and X'' to the metal (e.g., the chemical relationship of element X' is larger to the metal) will play the main role in the formation of the structure of diffusion layer. Here, it is supposed that under the considered conditions (at definite temperatures and pressure of the gas) both components $Me_n X'_m$ and $Me_p X''_q$ are thermodynamically stable.

On the surface of metal, a layer starts to form which consists of phases existing in the $Me - X'$ binary system. [Note: If other compounds are present in this system beside $Me_n X'_m$, then each of them forms an independent layer; the layers are arranged one after another.]

in the order of the increase in metal content. Due to the absence of solubility of element X'' in it, this layer does not permit X'' to penetrate into the metal, and to form a compound in the $Me - X''$ binary system. Thus, in this case there will be no interaction of the two gaseous components with each other. If they are interacting, however, then the process can become complicated, since the metal is in an atmosphere composed from the compound $X'_a X''_b$ (which is possible, with free excess of one of these elements). The process will limit and regulate the interaction of the metal with the surplus element and with the phase newly formed from the gaseous components.

Reaction diffusion mechanism in the $Me - (X' + X'')$ system

The diffusion mechanism in the $Me - X'$ and $Me - X''$ binary systems shows influence upon the diffusion mechanism in the $Me - (X' + X'')$ system. We admit that in the $Me - X'$ binary system the metal preferably diffuses outwardly through the reaction layer, but, contrarilywise, in the $Me - X''$ binary system, element X'' plays the advantageous role in the diffusion. It penetrates into the depth of the metal on whose surface a reaction layer happens to be formed. In the triple system $Me - (X' + X'')$ the layer arrangements are formed one after another, correspondingly composed from phases of the $Me_n X'_m$ and the $Me_p X''_q$ phases (accurately speaking, $Me_n X'_{m-\delta} X''_{\delta}$ and $Me_p X'_{q-\epsilon} X''_{\epsilon}$). The character of diffusion is here qualitatively the same in each layer as also in the corresponding binary system.

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The kinetics of such processes are determined on the basis of diffusion velocity in that of the layers of $Me_n(X'_{n-1} X'_2)$ type where the diffusion is the most hampered. Moreover, kinetics depends upon the possibility of the formation of solid phases between the gaseous components on the metal surface. This can delay the speed of the penetration of diffusing atoms into the metal, or the metal on the surface prepares a scale -- a gaseous medium. This factor can also affect the structural formation, since the low-lying diffusion layers will be now under other thermodynamic conditions than without this layer (different partial pressure of the gaseous components above the phase of the type $Me_n X'_m$ and $Me_p X'_q$).

The kinetics of the processes also depend upon the phase elements (or upon one of them) which are able to accelerate or slow down the diffusion process.

The data published on the discussed problem are very few, and for the present all mentioned cases cannot be directly confirmed by experiments.

The second of the considered cases is confirmed by investigation conducted on co-diffusion of carbon and nitrogen in chromium [1]. This system is practically very interesting. It is found that N and C participate simultaneously in the process of diffusion into Cr. On the surface of Cr, phases of the chromium carbide type (Cr_3C_2 , Cr_7C_3) are formed with changed parameters, which indicates the solution of N in these phases. Under the carbide layers, the roentgen-

Micrographic and metallographic examinations found the Cr_2N phase. Consequently, the front of N diffusion is more quickly changing place than the carbon front, by penetrating deep into the metal and forming a nitride phase. In publication [1], it was shown that the overweight of samples at the codiffusion of C and N into Cr is greater than at the saturation with C alone. This is explained in the following manner. At the intrusion of N into Cr, the volume-centered Cr lattice is transformed into the hexagonal lattice of Cr_2N which in its turn, at diffusion of carbon, is transformed into the hexagonal lattice of Cr_7C_3 . The transformation of the hexagonal lattice of Cr_2N into the hexagonal lattice of Cr_7C_3 is easier than the transformation of the volume-centered chromium lattice into the lattice of Cr_{23}C_6 at the intrusion of the carbon alone into chromium.

In case of chromium oxide in the air, N will also participate in the process of the reaction diffusion of O into Cr [2]. On the surface of Cr, chromium oxide Cr_2O_3 is formed. Under this layer, the layer of the hexagonal chromium nitride Cr_2N is found. Here also, the front of N diffusion is transferred into the depth quicker than that of the oxygen. The lattice parameters of chromium oxide, which is formed at the oxidation of Cr in the air, differ from the parameters of pure Cr_2O_3 . This difference indicates that N diffusion takes place through the oxide layer into the metal, forming a nitride layer between the oxide layer and the metal.

In both examined cases, a qualitative picture can be imagined for the distribution of the diffusing elements in the diffusion zone. The change in the parameter of the phases which form the external layer is insignificant. The content of the third element, solved in this phase, is very small. But under the external layer, a nitride layer is situated in both cases. In this layer more nitrogen is contained than in the top layer. As a result, the content of the third element (in our two examples -- the nitrogen) at a certain depth of the diffusion zone is greater than its content in the direct neighborhood to the surface (See diagram in Fig. 3a).

From the published experimental data on the research of codiffusion of N and C into iron, it can be concluded that nitrogen accelerates the saturation of iron with C, and diminishes the temperature at the beginning of the interaction of C with iron [3]. It was also established that at codiffusion of C and N into iron, the diffusion front of N is transferred into the depth quicker than the diffusion front of C. At simultaneous saturation of iron with C and N, the surface layer is depleted from nitrogen [3], i.e., the N concentration is the greatest at some depth of the diffusion zone.

In our opinion, the here introduced experimental data directly confirm the second case, considered in our report at the classification of the diffusion phenomenon in triple systems of the Me-(X'+X'') type. As to the first and the third case, unfortunately, they were not specially investigated.

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Questions and answers

Q.: Has there been any kind of quantitative computation for the case of diffusion of two elements?

V.N.Konev: I have already said that the first stage of the study of diffusion in triple systems was the classification of the phenomenon. Quantitative computations will be the next step.

Q.: How will the codiffusion of nitrogen and carbon monoxide run in silicon at high temperatures?

V.N.Konev: It is difficult to answer this question, because we did not learn the nature of behavior of silicon in relation to gases, especially in relation to CO. It is not known what kind of medium CO is for silicon at high temperatures -- carburizing? or oxidizing? If it is both carburizing and oxidizing, then a triple system is created.

The diagram of the state and the relation of each element or compound in the silicon should be known. Then, this question can be answered.

Discussion on the report of I.N. Frantsevich, A.N. Pilyakevich,
and of V.I. Arkharov and B.N. Konev

V.S. Neshpor (Inst. of Metal Ceramics and Special Alloys, AN USSR):

It seems to me that attention should be paid to the nature of the forming phase. The point is that in the metal-metalloid systems a few phases are formed with different contents of metalloid atoms. Attention should be also paid to what kind of phase, upper, lower or in-between, is formed at the diffusion of this or that metalloid into the metal, and how the second component affects the formation of this phase.

In the works of G.V. Samsonov, it was shown that at the diffusion of silicon, as a rule, an upper phase, a disilicon, i.e., $MeSi_2$ is formed.

This is so explained that the difference between the configuration of silicon bonds is the smallest in the elementary state, and in this phase. It is true, we should say, that the discussed researches were made only with a single metalloid, and there was no second metalloid.

This question should be studied in a further later work.

I have a number of remarks on the report of I.B. Frantsevich and A.N. Pilyankevich about microbrittleness. Their data basically coincide, with this difference that according to the data of I.N. Fran-

tsevich and A.N.Pilyankevich the nitrides are less brittle than the carbides.

In my opinion, in general the evaluation of brittleness only by the tempo of the increase of destruction with the increase of load is not sufficiently accurate. The point is that the character of the appearing cracks itself depends upon the brittleness of the substance which is being examined.

In reality, if there is any kind of impression, then at exceeding the limit of strength when the material does not have sufficient ability to disperse the elastic stresses, concentration of stress will occur at the boundaries of the impression, and as a result there is destruction of the materials. Moreover, one, two or more cracks can be formed. Obviously, the character of destruction reflects the grade of brittleness of the substance. If we say that there are two substances from which one has greater capacity of dispersing the elastic tensions, and the other has less, then the probability of crack appearance will be less in the first case.

In our works on microbrittleness, we need some other factor of brittleness which it should take in account in detail, i.e., the degrees of brittleness were evaluated not only in relation to the number of impressions, but also to their character.

We have selected the five-degree system for the evaluation of brittleness. The average degree of destruction is:

$$Z = 0 n_0 + 1 n_1 + 2 n_2 + \dots$$

where n_1 ... is the number of impressions; the subscripts indicate the character of impressions (1...one crack on the impression; 2...two cracks, and so on). We took degree 0 for absence of cracks; degree 1... for one or two cracks; degree 2...for 2-3 cracks; degree 4...for more than three cracks, and finally degree 5 ...for complete destruction of the impression.

Such a graduation of brittleness obviously characterizes the behavior of the sample in case of brittle loading. Of course, to count only the magnitude of this degree is not enough. One has also to count the tempo of its growth with the load. It is probable that the material will be more brittle the larger is the degree of destruction, i.e., the more cracks are on the impression, and the quicker this sign increases with the load. We accepted this final factor of brittleness:

$$\alpha = Z \frac{dz}{dp}$$

where Z ...is the degree of brittleness; dz/dp ...is the tempo of increase in the degree of brittleness by the load.

In our experiments, the following order of brittleness was obtained: -- silicide, boride, nitride, carbide. Here, by comparison with the data of I.N. Frantsevich and A.N. Pilyankevich, carbide and nitride change place.

These data fully coincide with the data on brittleness which we obtained by way of estimating the packing speed of the powders of

compounds at compression.

The coincidence of the brittleness factor, determined by two completely different methodology, gives basis for the assumption that these data are the most correct. Moreover, in the carbides the directed bonds are more marked, and the rigidity of bonding is greater, the asymmetry of vibrations smaller; therefore, they should be still more brittle than the nitrides. The dispersion of stresses in the carbides is connected with greater difficulties. This corresponds to the knowledge on the bond forces and lattice rigidity.

One should agree with the remark of A.N. Pilyankevich that not only the bonding forces influence brittleness. In the dispersion of elastic and thermal stresses, in addition to the interatomic bond, the mass of atomic complex also plays a role which also determines the vibrational mobility. Both these factors are reflected in the magnitudes of the amplitudes of atomic vibrations, computed by the Debye-Valler formula. With this magnitude, namely, we also compared the brittleness indices (See V.S. Neshpor, & G.V. Samsonov, Fizika metallov i metallovedenie (Physics of metals and metallurgy), vol. 4, 1957, p. 181; G.V. Samsonov, V.S. Neshpor, L. Khrenova, Ibid., vol. 8, 1959, p. 623).

The mentioned vibration considers both the bonding forces and the mass of the complex, since the frequency of vibrations and the atom mass enter into the formula.

Finally, this question is still not completely clarified, since reliable estimates of the degree of brittleness are still unavailable.

V.N.Konev(closing remarks): A remark was made here that attention should be paid to the nature of the phases which are formed at reaction diffusion in the triple systems. We are in agreement with this. The point is that, in compounds of a binary system of a metal with one element, one type of bond can predominate, and in compounds of a binary system of the same metal with another element another type of bond can predominate. At codiffusion of these elements into the metal, the indicated reason can play a substantial role both in phase formation and in the kinetics of the process of diffusion layer formation. How this is then reflecting upon the structural formation and kinetics, it is difficult to say now. We need experimental data on the study of reaction diffusion in systems of the type of {Metal-Chemically active gases}. For instance, it was pointed out here that at the diffusion in the Me-Si system G.V.Samsonov observed the formation of only a single phase of higher molybdaenum silicide, $MoSi_2$. It should be remarked that there are also other data (Kiffer, Nachtigal, and Fitser) on the phases formed at the reaction diffusion in this binary system. The mentioned authors also observed the formation of a second molybdaenum silicide, Mo_3Si_2 , arranged between the disilicide and the metal in form of a very thin layer. It seems to us that the phase detected in the diffusion zone depends upon which stage of process the formed phases are in (has the diffusion process stabilized? or are there still initial phases of formation?), and upon the methods which we use for the detection of the formed phases (an intermediate layer can form

between the two others in the shape of a very thin film).

In a short communication, all factors cannot be elucidated which could have an influence upon the process of reaction diffusion (in complex systems).

The remark of V.S. Neshpor is correct as to the kind of phases that can be formed at diffusion: -- lower, or upper in reference to the metalloid.

The point is that we have to consider here the totality of factors which influence the process of phase formation. For the establishment of the general law of reaction diffusion in triple systems of the type of {Hard metal -- Two chemically active gases} we have to have a sufficient number of experimental data on the study of diffusion in concrete systems of the indicated type.

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STRUCTURE AND PROPERTIES OF RARE-EARTH METAL BORIDES

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AN USSR &
Moscow State University

[Note: The following persons participated in this work: B.M. Tsarev, Moscow Engineering Physical Institute; G.A.Kudintseva, V.S.Nashpor, and Yu.B.Paderno, Institute of Metal Ceramics and Special Alloys, AN USSR M.M.Umanskly, A.A.Stepanova, Moscow State University.]

Borides of the rare earth metals, of scandium, yttrium, lanthanum, and of the lanthanides, lately found application in the electronics [1,2] where their high thermal emission characteristics are utilized: -- low work function at thermal emission, stability at low pressures, stability in regard to ionic bombardment, ability to work at high field intensities. Due to the complete absence of poisoning by the cathodes of borides of rare-earth metals in air, they can be used in sectional systems of electronic devices.

The use of cathodes from lanthanum boride in the synchrophasotron with high field intensities (up to 10^5 V/cm) and with a working temperature of 1650° permits the tapping of current densities up to

70 A/cm^2 . With the selection of a current of 40 A/cm^2 , the service life of such a cathode consists of about 250 hours, but with the making of a few special technical measures, this life can be increased even to 700-750 hours.

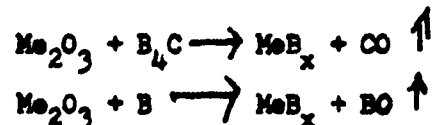
The boride cathodes work well as magnetron type amplifiers with a current density of 5 A/cm^2 at a field voltage of 2000 V/cm and with a working temperature of 1500° [3].

The lanthanum boride cathode at the cyclotron of the Institute of Physics of the AN USSR has been working for many dozens of hours. The tantalum cathode at the same cyclotron worked 12 hours.

The auto-electronic emission of the rare-earth metal borides, and particularly of lanthanum hexaboride [4], with a cold point, under the effect of external electric field, permits the obtaining of a current of about 1 A, which at an about 5-6-micron diameter, corresponds to a current density of emission exceeding 10^6 A/cm^2 . [5]

In connection with these advantageous and specific properties of boride cathodes, the Institute of Metallic -Ceramics and Special Alloys of the AN USSR, the Chair of Physics of Solids at the Moscow State University, and the Scientific Research Institute of Radio Engineering and Electronics started a wide research on the conditions of obtaining the properties and the structure of rare-earth metal borides.

For the preparation of rare-earth metal borides the interaction reactions of metal oxides with boron carbides, or with boron in vacuum were used:



A number of new phases were detected here, among them the diboride of scandium [6], yttrium [6], lanthanum and cerium [8], praseodymium, neodymium, samarium [9], europium [10], gadolinium [6], terbium and dysprosium [11,12], holmium [11,12], erbium [12], ytterbium and lutetium [11,12]. Moreover, a number of new phases were detected, among them the diboride of scandium [6,13], the tetraborides of gadolinium, dysprosium, holmium, erbium and lutetium [6,11,12,14].

Structures and Crystallo-Chemical Peculiarities of Rare-Earth Metal Borides

Presently, the rare-earth metal borides of compositions MeB_2 , MeB_4 and MeB_6 are known. Among them the best known are the structure and properties of the MeB_6 hexaborides. The first hexaborides were described by Stackelberg and Neumann in 1932 [15] for lanthanum, cerium, praseodymium, neodymium, and erbium.

The borides of composition MeB_6 have cubic lattice of the type of caesium chloride, with a centered octahedron from six boron atoms (Fig.1). It is crystallo-chemically correct when we interpret their structure in the shape of an octahedron frame formed by B atoms in whose hollows the metal atoms are placed (Fig.2). The common shape of the structure of the compounds, and to first approximation the size of the cell are basically determined by the frame of the B

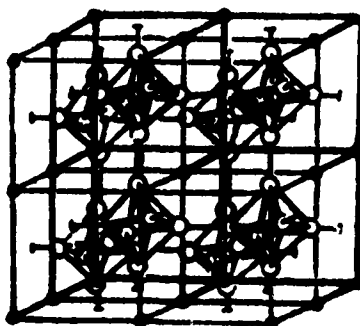


Fig.1. Structure of hexaboride; ● ...metal; ○...boron.

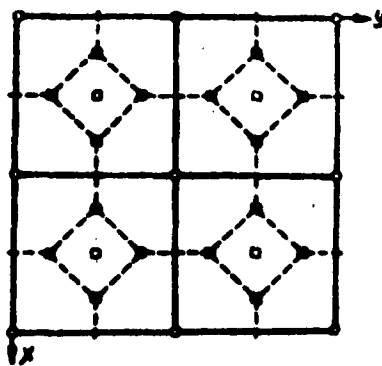


Fig.2. Projection of the structure of MeB_6 upon the 001 plane; ○...metal; □...boron; ■ boron.

atoms. The metal shows a comparatively lesser effect, although the peculiarities of the cell dimension, and frequently also the properties are related to the metal atoms. This is explained so that the hollows between the B octahedrons are rather large so that the metal atoms could be distributed in them without strong deformation, and in some cases even with supply of free distance.

The rare-earth metal hexaborides can be divided into two subgroups [16] the pertinence to which is determined by the valency of the metal atom. An analogous thought is announced in work [17] where curves of effective atomic radii of rare-earth metals were compared after Klemm and Bommer [18] with the lattice periods of the hexaborides of these metals, and correspondence was found between the course of the curves. While for the majority of rare-earth metals the course of curves is characterized by a drop as the order number of metal is growing, for europium and ytterbium an anomalous course is present, i.e., a sharp rise in both curves. For atomic radii this is related to a double-plus effective valency of europium and ytterbium from whose external shell the exit of a single electron for replenishing the defect in the internal shell causes an enlargement in the size of these atoms.

The close run of the mentioned curves indicates that the effective valency of metals in the hexaborides is near the valency in the strictly metal crystals and, moreover, it emphasizes the metallic character of bonding in the hexaborides. On Fig. 3, both curves are illus-

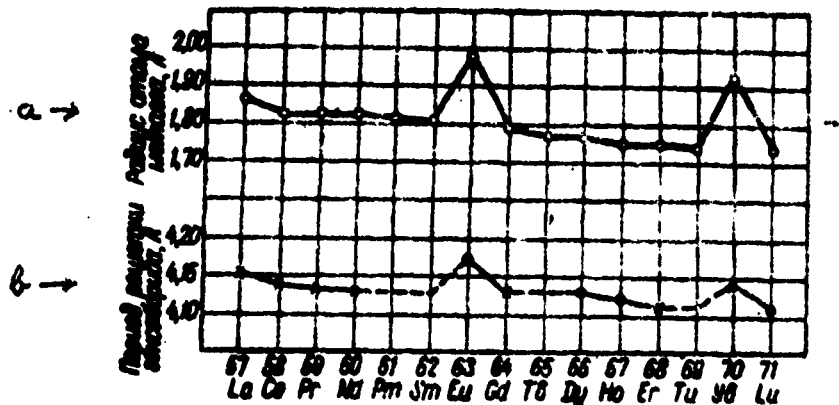


Fig.3. Relation of atomic radii of rare-earth metals /8/ and lattice periods of their hexaborides to the order number: o...our data; x...data of other authors. (On ordinate: a...radius of metal atom, Å; b...lattice period of hexaboride, Å).

trated with computation of the data obtained by us for lattice periods of the hexaborides of europium, holmium, dysprosium and lutetium.

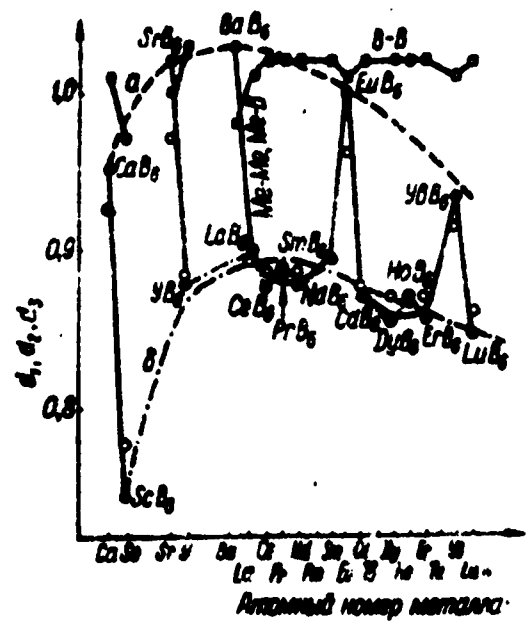
In its turn, with consideration of its above indicated interpretation, the character of the course of lattice period curves permits to chose the latter values from the existing values of lattice periods GdB_6 $a=4.112 - 4.110 \text{ \AA}$ [11,19], and $a=4.13 - 4.14 \text{ \AA}$ [6,20] as well as to interpolate the approximate values of lattice periods of the still unknown hexaborides of promethium ($a \approx 4.128 \text{ \AA}$), terbium

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r ($a \approx 4.12 \text{ \AA}$) and thullium ($a \approx 4.11 \text{ \AA}$).

We tried to establish the criteria of metal hexaborides formation as follows [21]. In the MeB_6 borides the greatest number of mutual bondings is formed between the B atoms (five), directed by the vertex of the octahedron. The construction of these bondings cannot be realized only by single electrons of the B which has the maximum valency, equal to three. Additionally, the attraction of about two electrons from the metal atoms is also required, which is confirmed by quantum mechanical computations [22,23]. Due to this, the possibility of hexaborides formation should be related to definite magnitudes of the first and second potentials of metal ionization characterizing the degree of linkage of two outer electrons. By comparing the factual material on the presence of hexaborides in metals with the ionization potentials of the latter, we conclude that the metals can form hexaborides in the case if the magnitude of their first ionization potential does not exceed 6.6-6.8 eV, and that of the second --- 11.5 to 12 eV. All rare-earth metals satisfy this condition, also such bivalent metals as Ca, Sr, and Ba which, as well known, also form metalloid hexaborides.

On the basis of the data known from the literature and obtained by us on the values of lattice periods of hexaborides, the lengths of the Me-Me, Me-B and B-B bonds were computed. The value of the parameter of the B atom was accepted equal to 0.207, in analogy to the structure of CaB_6 . The obtained lengths of bonds are given in Table 1. The ratio of the bond length to the sum of atomic radii (ρ) can serve as



$$\bullet - a_1 = \frac{2r_{me}}{Me-Me}; \quad \circ - a_2 = \frac{r_{me} + r_B}{Me-B};$$

$$\square - a_3 = \frac{2r_B}{B-B}$$

Fig.4. Relationship of values of the lines of bond lengths in hexaborides to the order of number of lanthanides. (On abscissa: Atomic number of metal)

relative characteristic of the bond's strength.

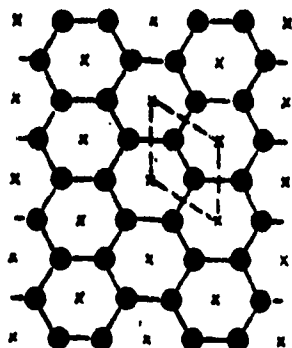
From the examination of the relationship of these ratios for Me-Me, Me-B, and B-B bonds to the atomic number of the metallic compo-

ments of the compounds, it follows that in each period the Me-Me and Me-B linkages are diminished at the transition from bivalent into trivalent metals (Fig.4). In the lanthanides group, this ratio for the Me-Me linkages gradually decreases with the increase of the metal's atomic number. However, two sharp peaks are for the hexaborides of europium and ytterbium in which metal ions apparently are present in the bivalent state, similarly to the ions of Ca, Sr and Ba.

The ratio $2 r_B / (B-B)$ will change relatively little with the change of the atomic number of the metallic components in hexaborides, but in hexaborides of the lanthanides group it almost remains constant, somewhat decreasing in hexaborides of europium and ytterbium, which is related to the comparatively large atomic radii of the latter.

This shows the great rigidity of the linkages of B atoms with each other, and it explains the stability of the MeB_6 lattice.

Borides of MeB_2 composition, found for scandium and yttrium [6,13,24], typical for the transition metals with closed d-electron state, have a structure represented by successive alternation of hexagonal layers of metal atoms, arranged in the nodes (points) of the closely packed hexagonal lattice with a small ratio of c/a , and layers of B atoms forming hexagonal two-dimensional cells (Fig.5). The spatial structure of the MeB_2 type can be represented as if built from trihedral prisms. The B atom is surrounded by three B atoms, and six metal atoms. The B atoms are in the centers of the prisms, the metal atoms at the vertices. The metal atom is in the center of hexahedral prisms



x Атом металла
● Атом бора

Fig.5. Structure of diboride (MeB_2).
(On figure: x...metal atom;
●...boron atom)

and is surrounded by 12 B atoms. The lattice period of diborides is given in Table 2.

Borides of the MeB_4 composition --- According to the data in the literature, the tetraborides of uranium, thorium, cerium [17], and yttrium [24] are crystallized in the MeB_4 structural type. The same structural type was found by us for the tetraboride of gadolinium, holmium, dysprosium, and lutetium [11,12,14].

In Table 2, the values of the g and g periods (constants) of te-

TABLE 1. Lengths of bonds in hexaboride lattices

Phase	Me—Me, Å	$a_1 = \frac{2 r_{Me}}{Me-Me}$	Me—B, Å	$a_2 = \frac{r_{Me} + r_B}{Me-B}$	B—B, Å	$a_3 = \frac{2 r_B}{B-B}$
CaB ₆	4,15	0,952	3,06	0,925	1,72	1,01
SrB ₆	4,20	1,020	3,09	0,970	1,74	1,00
BaB ₆	4,29	1,030	3,16	0,980	1,78	0,98
ScB ₆	4,35	0,746	3,20	0,775	1,80	0,97
YB ₆	4,08	0,877	3,01	0,885	1,69	1,03
LaB ₆	4,15	0,900	3,06	0,853	1,72	1,01
CeB ₆	4,14	0,877	3,05	0,885	1,71	1,02
PrB ₆	4,13	0,885	3,04	0,885	1,71	1,02
NdB ₆	4,13	0,877	3,04	0,885	1,71	1,02
SmB ₆	4,13	0,896	3,04	0,893	1,71	1,02
EuB ₆	4,16	1,000	3,07	0,961	1,72	1,01
GdB ₆	4,14	0,870	3,04	0,877	1,71	1,02
DyB ₆	4,13	0,855	3,04	0,870	1,71	1,02
HoB ₆	4,12	0,870	3,04	0,870	1,71	1,02
ErB ₆	4,10	0,855	3,03	0,870	1,70	1,02
YbB ₆	4,14	0,934	3,05	0,916	1,72	1,01
LuB ₆	4,11	0,846	3,03	0,861	1,70	1,02

(Note: 1...Phase)

taborides are quoted according to the different data.

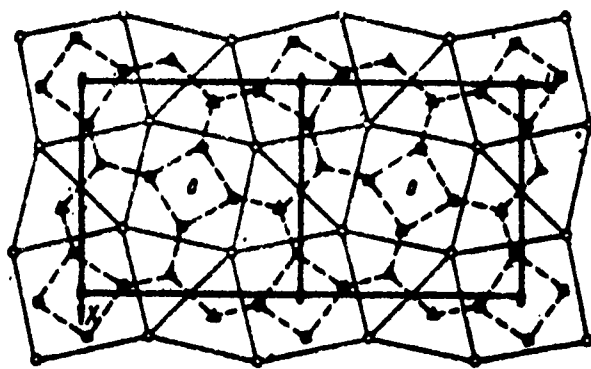
The structure of tetraborides can be represented as a combination of structure MeB₂ and MeB₆ where MeB₄ formula itself is obtained as an arithmetic average $MeB_4 = \frac{1}{2} (MeB_2 + MeB_6)$. In the MeB₄ structure there are both trihedral prisms of the MeB₂ type and tetrahedral ones

TABLE 2. Lattice periods of the di- and tetra-borides of lanthanides.

① Боридная фаза	a	c	c/a	Литературный источник ②
ScB ₂	3,140	3,810	1,118	[14]
YB ₂	3,78	4,40	1,163	[24]
YB ₄	7,01	4,00	0,573	[17]
CeB ₄	7,205	4,090	0,568	[25]
PrB ₄	7,200	4,11	0,570	[17]
SmB ₄	7,12	4,07	0,572	[17]
GdB ₄	7,13	3,86	0,541	[6]
GdB ₄	7,079	4,030	0,569	[14]
DyB ₄	7,23	4,09	0,564	[11, 12]
HoB ₄	7,15	4,09	0,572	[11, 12]
HoB ₄	7,050	3,992	0,568	[14]
LuB ₄	7,18	4,04	0,562	[11, 12]
LuB ₄	6,983	3,930	0,567	[14]

(Note: 1...boride phase; 2...source in literature).

similar somewhat to distorted MeB₆ cubes (Fig.6). In the centers of the trihedral prisms the individual B atoms are distributed, but in the channels leading through the tetrahedral prisms there are octahedrons of B atoms. The octahedrons do not have common vertices. The B atoms from the square cross sections of the octahedrons and the B atoms in the trihedral prisms form flat cells of 4-member and 7-member rings. Thus, the structural ground of MeB₄ appears to be a combination of MeB₂ and MeB₆.



• — 4M; 0 — 4B_I; ▲ — 4B_{II}; ■ — 8B_{III}.

Fig.6. Structure of tetraborides.

Physical properties of rare-earth metal borides

Thermionic emission.- The parameters of thermionic emission of almost all rare-earth metal hexaborides have been now investigated. On Fig.7, the relation of work function of rare-earth metal hexaborides is shown to the order number of the metallic components according to the data of [25] and supplementary data acquired by us, together with B.Tsarev and G.A.Kudintseva.

For the explanation of this relationship, the work [27] made use of the theory of atomic structure of rare-earth elements elaborated by M.A.El'yashevich [28] and of the representation of the electronic

structure of hexaborides (12,22,23,29 - 31).

The essential content of this explanation is the following.

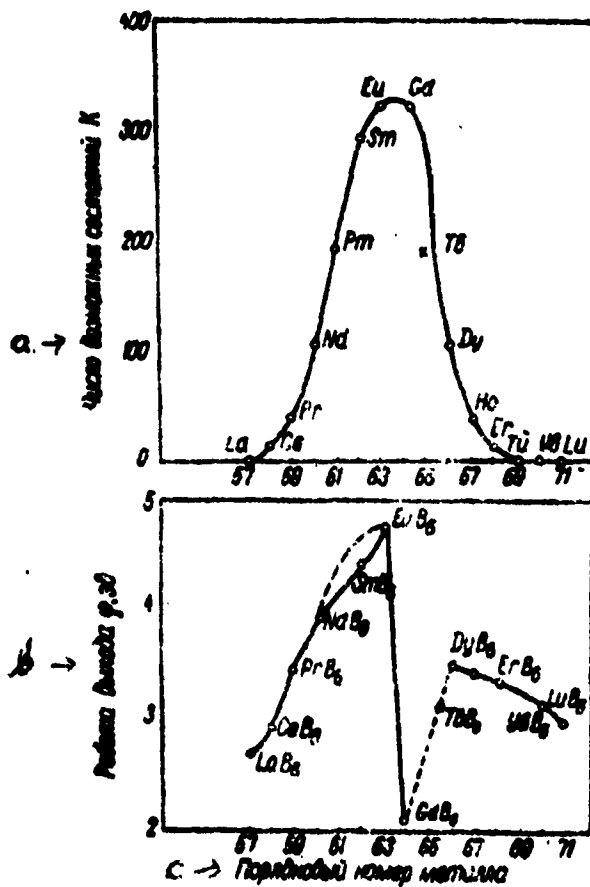


Fig.7. Relation of work function of rare-earth metal hexaborides and of the number of possible states to the order number of the metallic components.

(a...number of possible K states; b...work function, $\varphi=3b$; c...order number of metal).

The bonding between the metal and boron atoms in the hexaborides is realized by electron cooperatives formed by electrons of the normal or excited d-shell and partly of electrons pertaining to the s-shells of the metal, and not used in the linkage with boron. In the hexaborides two systems of energy bands have to be considered -- a narrow, weakly excited 4f-band, and a comparatively wide hybrid 5d-6s band.

It is known that at the normal state the majority of the atoms in rare-earth elements do not have 5d-electrons, but on account of the vicinity of energies of the 4f and 5d states, the latter ones apparently penetrate into the hexaboride crystals, due to f-d transitions. In particular, for the doubly ionized atoms of rare-earth elements, $4f \rightarrow 4f^{n-1}.5d$ transitions take place [28].

The probability of f-d transitions and consequently also the degree of free conductivity electrons in the hybrid sd-band are determined by the degree of filling of the 4f-band and by the number of possible states of the f-electrons in these bands.

Since the 4-f-shell of rare-earth elements is comparatively weakly excited at the formation of chemical bond [32], the maximum multiplicity of Hund(?) [33] can be applied to it, according to which the larger is the stability of the shell and the degree of linkage of its filling electrons, the higher is the number of the possible terms. On Fig.7, the number of the possible terms is given for the 4f-electrons in relation to the atomic number of the metals.

The maximum multiplicity and, consequently, the greatest degree

of electron linkage and the smallest possibility of f-d transitions fits europium and gadolinium according to these data; each of them has seven electrons in the 4f-shell in the normal state.

Obviously, with the increase of linkage degree of the f-electrons and with the difficulty of the f-d transitions, the work function of the electrons ought to grow, which is qualitatively also shown by the comparison of the relation of work function and the number of possible terms to the atomic number. A sharp drop appears for gadolinium which has one 5d-electron that seems to be essentially free, similarly to the unique electron of alkaline metals. In the last rare-earth element, the lutetium, the appearance of one 5d-electron outside the closed 14-electron 4f-shell does not provoke a sharp drop in the work function at the transition from ytterbium hexaboride to lutetium hexaboride. This is due to the powerful shielding of the sd-orbits of the 4f-shell which is very much saturated with electrons in the dysprosium-lutetium series. Essentially, after its atomic structure, lutetium should be considered not a rare-earth metal but a d-transition metal, the first in the order of lutetium - platinum.

The values of work function of scandium and yttrium (correspondingly 2.96 and 2.22 eV) are subject to the laws established in work [34] for the borides of transition metals.

Thus, the hexaborides of yttrium, lanthanum, gadolinium, and lutetium which have the smallest work function have the best prospect for application in electronics.

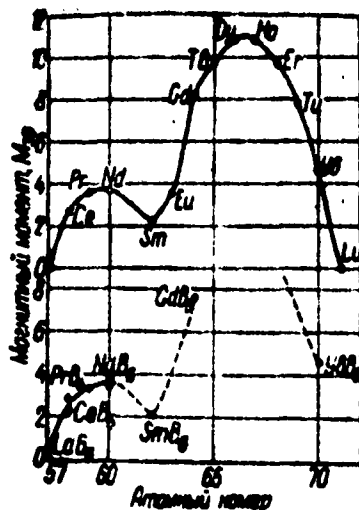


Fig.8. Magnetic moments of the lanthanoids and of their hexaborides. (On ordinate: Magnetic momentum, $M_{3\phi}$; on abscissa: Atomic number)

Magnetic properties.- On Fig.8, according to the data of the works [32,36,37] we gave the relations of the magnetic moments of lanthanoids and of their hexaborides to the atomic number. Both curves practically coincide. This fact points to a very weak participation of the deeply situated, strongly shielded 4f-states in the organization of bondings between the metal atoms and the complex atoms of B_6 in the hexaborides.

Electric and thermoelectric properties.- Information on the electric resistance of borides of lanthanides is very little at present. At room temperature, the specific resistance is 17 microhm cm for LaB_6 ; 60.6 microhm cm for CoB_6 [8], and 260 microhm cm for SmB_6 [9].

Thus, the resistance of hexaborides increases with the growth of the filling of the 4f-state, i.e., with the growth of their stability, according to the rule of Khurd(?)

In connection with this, it can be expected that the resistance of europium hexaboride will be the greatest and that of the hexaborides of gadolinium, ytterbium and lutetium the smallest. The character of the resistance measurement with the temperature for the hexaborides, as it was shown on the example of lanthanum hexaboride [38], is typical for the metals.

The investigation of the thermoelectric properties of hexaborides [38] indicates that the practical absence of vacancy states in the hexaborides causes a low value of thermoelectromotive force in metal vapors.

Other physical properties.- As for the borides of the transition metals, the lanthanide hexaborides are distinguished by melting at high temperatures, hardness, moderate thermal expansion coefficient, and high thermodynamic strength.

The most fully investigated are the thermal expansion coefficients of those hexaborides which with a sufficiently good expression reveal a bond with the atomic radii of the metallic components, by being increased with the decrease of the latter. [19].

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Questions and answers

Q.: In which form are the hexaborides used -- in the form of tapes, wires, or round pellets?

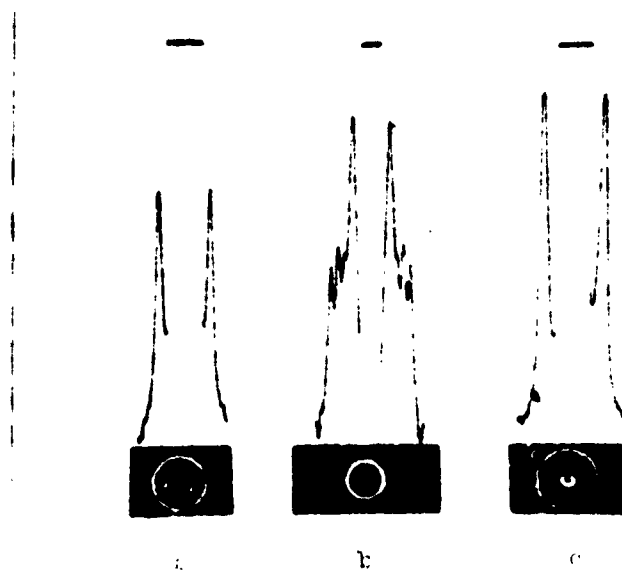
G.V. Samsonov: Hexaborides for cathodes are used in the shape either of powder which, with the aid of a nitro binder, is smeared upon the tantalum cathode, and then the cathode is processed by suitable manner, or in the shape of hot-pressed specimens. At hot-pressing, cylinders are made, then these small cylinders are processed into forms required for the cathode. This processing is done by electric erosion or plate-mechanical method as well as by ultrasound.

Can wires, pellets and tapes be made from hexaborides? -- this is difficult to answer at present, but the preparation of such sections would be extremely useful and necessary. The tapes or wires of hexaboride could play an important role in electronic devices. Such a question, therefore, would best be put to the researchers of powder rolling.

PRECISION DETERMINATION OF THE LATTICE PERIODS OF BORON CARBIDES OF
B_{2.75} TO B_{6.75} COMPOSITION BY MEANS OF ROENTGENOGRAMS
OBTAINED WITHIN THE RANGE OF LARGE ANGLES OF
SCATTERING ($\Theta \rightarrow 90^\circ$)

V.I. Kudryavtsev and G.V. Sofronov
(All-Union Scientific Research Institute
of Abrasives and Polishing)

Last year in the All-Union Scientific Research Institute of Abrasives and Polishing much attention was paid to the problem of increasing the accuracy of the roentgen method of research, particularly at the precision determination of the crystal lattice constants of different substances, and firstly of the abrasive materials-- the silicon carbide, corundum, boron carbide. As a result of the conducted experiments, first in the national practice of roentgenography, the problem of fixation of the roentgen reflection maxima in the range of large scattering angles has been solved in an exceptionally simple manner. At present, in the ordinary Debye camera (ϕ 57.3 mm), roentgenogram can be obtained with setting the reflection at $\Theta = 88.5^\circ$, and with the Sachs camera, at $\Theta = 89.5^\circ$.



a- SiC-II; b- P₃O₅; c- α-A₂O₅.

Fig.1. Roentgenogram taken by the large-angles method with a camera having a needle collimator.

The intensity of the roentgen lines in the range of large scattering angles is rather large, and the shape of line is satisfactory which alone permits the determination of the Θ value with very great accuracy (Fig.1,2).

The absolute values of the lattice constants are calculated directly by the angle Θ , without the use of any analytical or graphical method of extrapolation, with an accuracy in the order of ± 0.001 percent. of the measured magnitude.

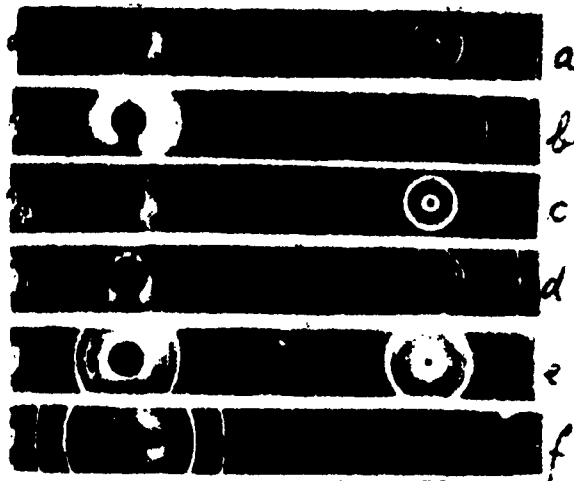


Fig.2. Roentgenogram taken by the large-angles method with a camera having a needle collimator.

a...pyrite, alpha-radiation of cobalt; b...fluorite, alpha-radiation of nickel; c...zirconium boride, alpha radiation of copper; d...tantalum boride, alpha radiation of copper; e... alpha-radiation of quartz, alpha radiation of cobalt; f... sodium fluoride, alpha radiation of copper.

In our investigations needle collimators were used for the camera of the Debye type (Fig.3a) and a flat cassette of new design with needle collimator for the reverse film (Fig.3b).

The preliminary roentgen analysis of the technical samples of boron carbide of unstable composition showed that the values of its lattice periods are changed from sample to sample. In some cases, on the roentgenograms obtained by the large-angles method, we observed a



Fig.3a.Roentgen Debye camera with needle collimator.

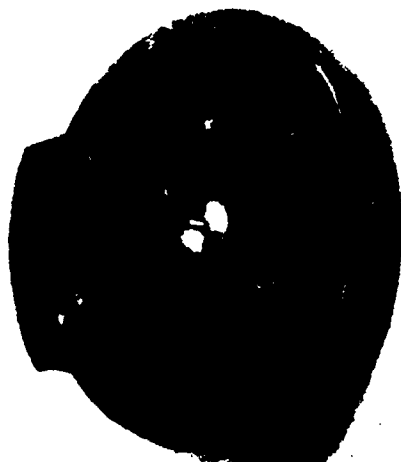


Fig.3b.Flat cassette with needle collimator for reverse film.

Very large shift of the lines, reaching 5° (from 82 to 87°). This shift of the lines also resulted in a longer study of the lattice constants a and b of boron carbide. As standard, we used two boron carbide samples of the following chemical composition:

for $B_{4.45}C$: 78.68% B_{bond}; 17.60% C_{bond}; 0.20% C_{free}; 0.75% B₂O₃;
 for $B_{6.75}C$: 82.86% B_{bond}; 13.62% C_{bond}; 0.33% B₂O₃.

These samples were subjected to multiple roentgen examinations in copper, cobalt, nickel and chromium radiation.

In the flat-cassette camera, the distance between sample and film was standardized by silver, photographed in nickel rays ($hkl = 422$) ($\theta = 83^\circ 43'$). (Fig. 4). Lattice constant a for silver, according to [2] was equal to 4.07724 kX.

The photography in the cylindrical camera with asymmetric charge of film made it possible to determine the effective radius of the camera for each roentgenogram with great precision.

The obtained roentgenograms were photometered on a recording MPH-4 microphotometer. The microphotograms were measured on an IZA-2 comparator. The accuracy of the Debye ring camera was ± 0.05 mm.

The precision determination of the lattice periods of boron carbide was made by roentgenograms obtained in the range of large-angle scattering. For instance, at the photograph of boron carbide ($B_{4.45}C$) in copper rays, the reflections on the roentgenograms was fixed at

$\theta_{\max} = 85^\circ 57'$, and in chromium rays at $\theta_{\max} = 84^\circ 54'$.

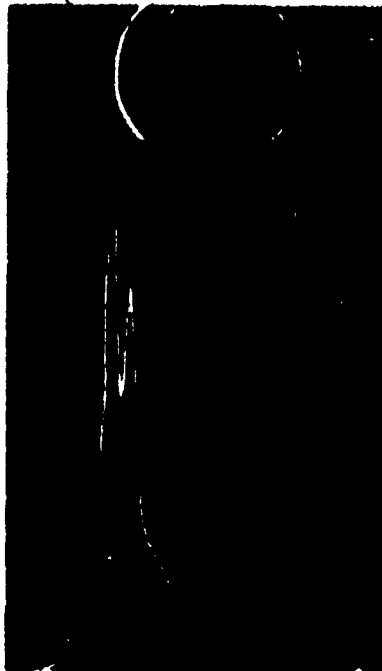


Fig.4. Roentgenogram of silver obtained at reverse reflection in nickel rays.

The hkl indices of the reflection plane have the following values:

344 for copper α_1 radiation,
328 for cobalt " "
419 for nickel " "
226 for chromium " "

At roentgenograms taken in cobalt rays (Fig.5) and copper rays, the hexagonal crystal was composed of a system of two equations of quadratic form. The solution of the two-equation system gave the following



Fig.5. Roentgenogram of boron carbide $B_{4.45}C$ and $B_{6.75}C$ taken in cobalt rays with asymmetric film placement in a camera having needle collimator.

values of magnitude a and c for the examined samples of boron carbide:

	a, kX	c, kX	c/a
$B_{4.45}C$	5.5897	12.0500	2.156
$B_{6.75}C$	5.6300	12.1940	2.166

The shift of lines on the roentgenograms in the range of large-angle scattering, reaching 5° , seems to be the result of distortions of the crystal lattice which arise in the boron carbide as a result of the formation of a hard solid solution of boron of very high concentration.

In Table 1 we give the values of the lattice periods of boron carbide obtained by various authors.

We think that our results are very accurate and reliable since the values of lattice periods were determined by roentgenograms obtained

TABLE 1. Values of lattice constants a and c of boron carbide

1 Авторы	а. кх	с. кх	c/a	hkl	θ	$B_m C$	Излучение
А.Ален [3], 1953 г. Жданов Г. С., Меерсон Г. А., Журавлев Н. Н., Самсонов Г. В., [4], 1954 г.	5,5867	12,0456	2,151	306	37°30'	B_4C	Cu
Кудрявцев Е. И., Софронюв Г. В., 1957 г.	5,5867	12,0955	2,165	603	76°00' 87°30'	,	Cu
	5,5867	12,0500	2,156	344	87°00'	$B_{4,45}C$	{ Cu Co

(Column headings: 1...authors; 2...radiation. --

Names of authors under 1: Allen [3], 1953; Zhdanov, G.S., Meer-
son V.A., Zhuravlev N.N., Samsonov F.B. [4], 1954; Kudryavtsev
E.I., Sofronov G.V., 1957).

in the large -angle range of scattering.

For the standard boron carbide, i.e., the carbide with the small-
est value of a and c constants, with the proposed hkl indices and wave-
length values of the K_α -radiation of copper, cobalt, nickel and chromium
we calculated the possible magnitudes of Θ reflections (Table 2).

The experimentally observed values for boron carbide, taken in
cobalt rays, are also given.

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TABLE 3. Values of the θ angles

(Column headings : 1... hkl of reflection plane; 2...computed value, $K\alpha_1$ -radiation of copper; 3...computed value, $K\alpha_1$ -radiation of cobalt; 4...experimental value, $K\alpha_1$ radiation of cobalt; 5...calculated value, $K\alpha_1$ radiation of chromium.)

1 hkl	2 Расчетное значение, $K\alpha_1$ -излучение меди	3 Расчетное значение, $K\alpha_1$ -излучение кобальта	4 Экспериментальное значение, $K\alpha_1$ -излучение кобальта	5 Расчетное значение, $K\alpha_1$ -излучение хрома
011	9° 51'	11° 27,5'	11° 18'	14° 44'
003	11° 02'	12° 50,5'	12° 32,5'	16° 31,5'
102	11° 45'	13° 41'	13° 36'	17° 39'
110	15° 58'	18° 37,5'	18° 31'	24° 07,5'
014	17° 29,5'	20° 25,5'	20° 20'	26° 32'
201	18° 54'	22° 08'	22° 00'	28° 47'
113	19° 34,5'	22° 52'	22° 47,5'	29° 52'
022	20° 01'	23° 25'	—	30° 34,5'
105	20° 52,5'	24° 26,5'	24° 39'	31° 58,5'
006	22° 30'	26° 23,5'	—	34° 40,5'
204	24° 02,5'	28° 14'	28° 04'	37° 16'
121	25° 09'	29° 34'	29° 24,5'	39° 10'
212	26° 02,5'	30° 39,5'	—	40° 44,5'
025	26° 45'	31° 31'	31° 24'	41° 59,5'
116	28° 07,5'	33° 11'	—	44° 28'
017	28° 17,5'	33° 23,5'	33° 16'	44° 47'
300	28° 27'	33° 35'	—	45° 04,5'
124	29° 26,5'	34° 48,5'	34° 43'	46° 56'
303	30° 53,5'	36° 35,5'	36° 34'	49° 44'
215	31° 50'	37° 46,5'	37° 41,5'	51° 38'
108	32° 18,5'	38° 22'	38° 17,5'	52° 36'
207	33° 13,5'	39° 31'	—	54° 32'
270	33° 22,5'	39° 42'	39° 36,5'	54° 50,5'
009	35° 02,5'	41° 49'	—	56° 34,5'
311	35° 10,5'	41° 59,5'	41° 54'	58° 54'
223	35° 37,0'	42° 33,5'	42° 27,5'	59° 57,5'
132	35° 55'	42° 55'	42° 50,5'	60° 40,5'
028	36° 57'	44° 16'	44° 10'	63° 18'
306	37° 40'	45° 12,5'	45° 12'	65° 16'
127	37° 49'	45° 24'	—	65° 41'
314	38° 49'	46° 42,5'	—	68° 41,5'
119	38° 32,5'	47° 40'	47° 42'	71° 07'
041	38° 40'	47° 50,5'	—	71° 35,5'

(Table 2, cont.)

1 №№	Расчетное значение, K_{α_1} -излучение меди	Расчетное значение, K_{α_1} -излучение кобальта	Экспериментальное значение, K_{α_1} -излучение кобальта	5 Расчетное значение, K_{α_1} -излучение хрома
402	40° 02'	48° 20'	—	72° 58'
135	40° 57'	49° 33,5'	—	76° 56'
01,10	41° 06'	49° 46'	49° 31,5'	77° 42,5'
218	41° 22'	50° 08,5'	50° 05,5'	79° 15,5'
226	42° 04,5'	51° 05,5'	51° 01'	84° 54'
044	43° 12'	52° 38,5'	52° 32'	—
231	44° 02'	53° 49,5'	—	—
322	44° 44'	54° 49'	54° 45'	—
405	45° 17,5'	55° 37,5'	—	—
20,10	45° 27'	55° 50,5'	55° 47'	—
10,11	46° 00,5'	56° 40'	—	—
410	46° 11,5'	57° 40,5'	—	—
234	47° 32'	58° 56,5'	58° 57,0'	—
309	48° 15'	60° 02'	60° 03'	—
413	48° 48'	60° 54'	—	—
325	49° 39'	62° 15'	—	—
12,10	49° 48'	62° 30'	62° 25'	—
00,12	49° 57'	62° 44,5'	—	—
138	50° 05'	62° 57,5'	—	—
02,11	50° 22,5'	63° 26'	—	—
047	50° 56'	64° 22,5'	—	—
229	52° 35'	67° 15,5'	—	—
501	52° 48'	67° 40'	—	—
052	53° 32'	69° 02,5'	—	—
11,12	54° 20,5'	70° 39'	—	—
408	54° 34'	71° 07'	71° 05'	—
21,11	54° 52,5'	71° 47'	—	—
416	55° 18,5'	72° 42,5'	—	—
237	55° 27,5'	73° 02,5'	73° 01,5'	—
330	55° 36'	73° 22'	73° 22,5'	—
504	56° 30,5'	75° 34'	—	—
421	57° 25,5'	78° 07'	78° 07'	—
01,13	57° 36,5'	78° 40'	78° 40'	—
333	57° 53,5'	79° 36,5'	79° 36'	—
242	58° 12'	80° 44'	80° 43'	—
055	58° 50'	83° 31,5'	83° 31'	—
31,10	59° 00'	84° 30'	84° 36'	—
328	59° 18,5'	87° 00,5'	87° 03'	—
424	61° 25'	—	—	—
151	62° 25,5'	—	—	—
20,13	62° 37,5'	—	—	—
512	63° 17,5'	—	—	—
245	64° 00'	—	—	—
04,10	64° 11'	—	—	—
30,12	64° 22,5'	—	—	—
13,11	64° 54,5'	—	—	—
336	65° 27'	—	—	—
507	65° 38'	—	—	—

(Table 2, Cont.)

1 <i>hkl</i>	2 Расчетное значение, K_{α_1} -излучение меди	3 Расчетное значение, K_{α_1} -излучение кобальта	4 Экспериментальное значение, K_{α_1} -излучение кобальта	5 Расчетное значение, K_{α_1} -излучение хрома
154	66° 57,5'	—	—	—
419	67° 57,5'	—	—	—
12,13	68° 23'	—	—	—
518	70° 02'	—	—	—
23,10	70° 16,5'	—	—	—
22,12	70° 30'	—	—	—
058	70° 42,5'	—	—	—
40,11	71° 10,5'	—	—	—
02,14	71° 25'	—	—	—
600	72° 19,5'	—	—	—
00,15	73° 07'	—	—	—
341	75° 28'	—	—	—
603	76° 21,5'	—	—	—
432	76° 59'	—	—	—
248	79° 27'	—	—	—
32,11	80° 17'	—	—	—
21,14	80° 44,5'	—	—	—
157	82° 06'	—	—	—
520	82° 36'	—	—	—
11,15	84° 38'	—	—	—
344	87° 29,5'	—	—	—

(NOTE. The 419 plane in the K_{α_1} -radiation of nickel gives a reflection under an angle of $\theta = 85^{\circ}87'$).

From the calculated data of Table 2 these practical conclusions are drawn.

1. At the precision determination of the interplanary distances of the lattice of boron carbide, roentgenograms must be used obtained on one of the indicated anode plates. The maximum reflection angles which can be reached here are the following:

	<u><i>hkl</i></u>	<u>Theta</u>
copper anode	344	87°30'
cobalt anode	328	87°00'

	<u>hkl</u>	<u>Theta</u>
nickel anode	419	85° 87'
chromium anode	226	84° 54'

2. For the precision determination of the lattice constants of boron carbide, copper and cobalt plates must be used. By two obtained roentgenograms, a system of two equations of quadratic form of the hexagonal crystal is composed. The solution of this system gives the value of constants a and c with an accuracy of $\pm 0.001\%$ of the measured magnitude.

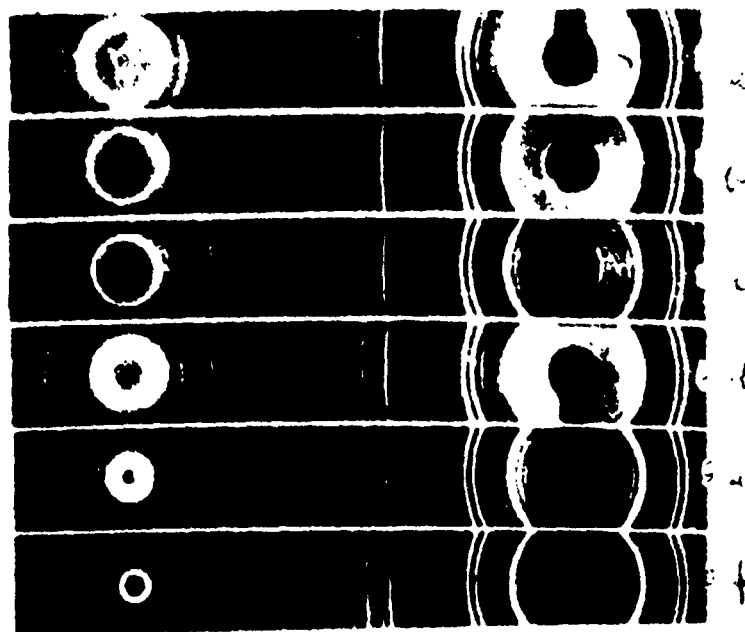
In some cases, the reflection 055 and 328 in cobalt rays can be used. The corresponding reflection angles will be $83^{\circ}31'$ and $87^{\circ}00'$.

The calculated values of reflection angles θ for the normal boron carbide with the proposed hkl indices and parameters $a = 5.56967$ kX, and $c = 12.050$ kX are given in Table 2 (spatial group $D_{3d}^5 - R_{3m}^-$, condition of existence of reflections in the hexagonal aspect $h - k \pm l = 3n$)

After the extreme values of the lattice periods of boron carbides of composition $B_{2.75}C$ and $B_{6.75}C$ have been determined, firstly, with the method of large angles, the precision determination of the a and c constants of boron carbide can be made at all intervals of the compounds from $B_{2.75}$ to $B_{6.75}$. Secondly, the limits of the solubility of B and C in boron carbide can be accurately determined. Thirdly, it can be tried to give a structural diagram of the formation of a continuous series of boron carbides of different chemical

compositions from $B_{13}C_5$ to $B_{15}C_2$ from the elementary boron carbide $B_{12}C_3$.

For this we carried out roentgen analysis of boron carbide samples whose chemical composition is presented in Table 3 (see next page).



a	$\theta = 37^{\circ}00'$, B/C=2.76--4.63;	α	$\theta = 37^{\circ}15'$, B/C=5.20;
b	$\theta = 36^{\circ}33'$, B/C=4.60;	β	$\theta = 32^{\circ}47'$, B/C=5.30
c	$\theta = 34^{\circ}11'$, B/C=5.0;	γ	$\theta = 31^{\circ}48'$, B/C=6.75.

Fig. 6. Roentgenogram of boron carbide of different chemical composition, taken with cylindrical camera ϕ 68.5 mm, with needle collimator, in filtered Co rays, with asymmetric film charge.

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(Addition to Fig. 6, see previous page: Last plane of reflection 328 (m_{max})).

The precision determination of the lattice periods of boron carbide, as well as the exact determination of the limits of boron and carbon solubility in boron carbide was made by the large-angles method [1]. All samples were taken twice:-- in cobalt rays with the use of reflection from $hkl = 328$, and in chromium rays with use of reflection from $hkl = 228$.

For each sample, the values of a and c of the boron carbide lattice were determined. The results are entered in Table 3, and the roentgenograms are in Fig. 6. (See preceding page).

The obtained results permit to draw the following conclusions.

1. In case of the minimum values of boron carbide, these values of lattice periods a and c are at the rate of $B_{\text{bond}}/C_{\text{bond}} = 2.76$ to 4.63, and the maximum values at the rate of $B_{\text{bond}}/C_{\text{bond}} = 4.75 - 6.75$.

2. The values of periods a and c in the $B_{2.75^{\circ}} - B_{4.63^{\circ}}$ interval are practically constant.

At ($a = 5.5883 - 5.5908 \text{ kX}$; $\Delta a = 0.0023 \text{ kX}$; $c = 12.044 - 12.058 \text{ kX}$; $\Delta c = 0.011 \text{ kX}$).

Periods a and c in interval $B_{4.75^{\circ}} - B_{6.75^{\circ}}$ suffer marked changes. For instance (Fig. 7):

TABLE 3. (First half). Characteristics of the Boron Carbide samples

$B_{2.75}C$ to $B_{6.75}C$

(Note: a...Chemical composition %; 1... B_{bound} ; 2... O_{bound} ; 3... O_{free} ; 4... Si_{bound} ; 5... Si_{bound}).

a. Химический состав, %								
B_{chem} (1)	C_{chem} (2)	C_{comb} (3)	B_2O_3	Al_2O_3	Fe_2O_3	Si_{comb} (4)	Si_{chem} (5)	I %
69,10	27,78	0	0,36	—	—	—	—	97,25
75,00	24,96	0	—	—	—	—	—	99,96
87,28	22,00	9,25	0,92	—	—	—	—	99,45
61,82	19,56	11,45	2,14	—	—	—	—	97,97
66,27	19,73	7,05	2,63	—	—	—	—	95,68
72,59	20,15	1,80	1,72	1,11	0,46	0,64	—	96,67
69,34	18,33	2,20	4,15	—	—	—	—	94,06
73,72	19,34	2,16	—	—	—	—	—	95,22
70,29	18,27	3,20	5,40	—	—	—	—	97,16
72,39	18,70	2,15	3,39	0,86	1,22	0,25	—	98,97
78,68	19,60	0,20	0,75	—	—	—	—	99,23
71,57	17,48	0,38	7,42	—	—	—	—	96,53
63,77	15,27	1,56	10,86	0,47	1,15	0,21	—	93,25
73,81	17,12	0,21	2,02	—	—	—	—	93,15
77,16	17,49	1,80	0,78	—	—	—	—	97,23
74,04	16,20	0,87	4,23	—	—	—	—	96,34
76,60	16,52	—	1,90	—	—	—	—	95,02
77,02	16,53	0,42	0,55	—	—	0,13	1,27	95,92
7,32	16,21	0,25	—	—	—	—	—	93,78
62,86	13,62	0,50	—	—	—	—	—	96,88

Table 3. (Second half) Characteristics of boron carbide samples

B_{2.75} to B_{6.75}

B/C	a, μ X	c, μ X	c/a	θ_{Co-328}
2.75	5,5894	12,047	2,155	87°08'
3.33	5,5893	12,055	2,157	87°00'
3.39	5,5905	12,044	2,154	87°06'
3.67	5,5897	12,045	2,155	87°05'
3.72	—	—	—	87°00'
3.99	—	—	—	87°00'
4.20	—	—	—	—
4.23	5,5891	12,049	2,156	87°08'
4.27	5,5902	12,046	2,155	87°04'
4.29	—	—	—	87°00'
4.45	5,5897	12,050	2,156	87°00'
4.54	—	—	—	87°00'
4.63	5,5894	12,048	2,155	87°
4.78	—	—	—	86°30'
4.89	—	—	—	—
5.07	5,608	12,148	2,166	83°32'
5.13	—	—	—	—
5.17	—	—	—	83°15'
5.29	5,616	12,166	2,166	82°47'
6.75	5,630	12,194	2,166	81°49'

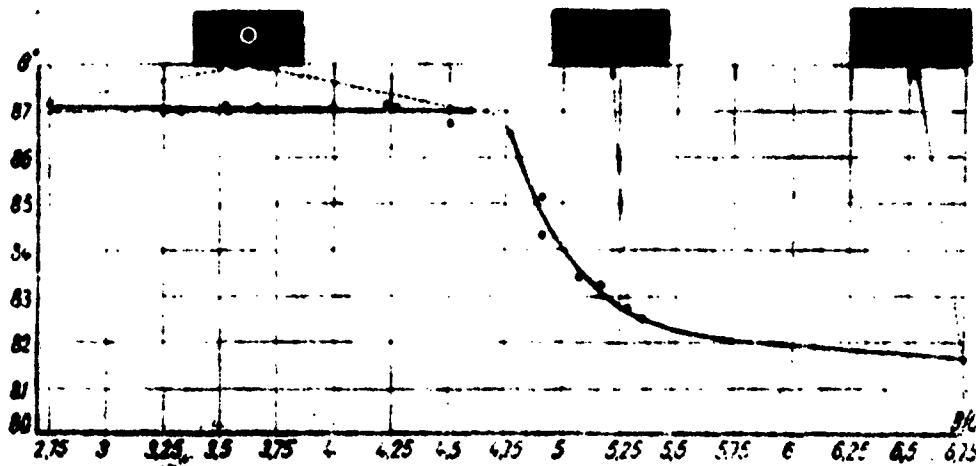


Fig. 7. Relation of reflection angle θ to the proportion of boron and carbon in boron carbide, taken by the large-angle method in cobalt rays; field of reflection $hkl = 328$.

We have the values

for $B_{5.07}C$	$a = 5.606 \text{ kX}$	$c = 12.148 \text{ kX}$
for $B_{5.29}C$	$a = 5.616 \text{ kX}$	$c = 12.166 \text{ kX}$
for $B_{5.75}C$	$a = 5.630 \text{ kX}$	$c = 12.194 \text{ kX}$

3. The boron carbides of the $B_{5.75}C$ -- $B_{4.53}C$ interval appear as a continuous series of solid intrusion solutions of carbon or B into the $B_{12}C_3$ lattice according to the following formula:



where $B_{12}C_3$... is the elementary boron carbide. The lattice of the $B_{12}C_3$ boron carbide is distinguished from the lattices of other compositions so that all hollows,--holes--existing in it are vacancies, i. e., not occupied by either a B or a C atom.

According to Glaser and Moskowitz [5], the maximum number of C atoms, freely arranged in the vacancies of the icosahedric lattice of $B_{12}C_3$ equals two, and this time $B_{12}C_3$ transits into $B_{12}C_5$. According to Clark and Hoard [6], two B atoms are freely arranged, and $B_{12}C_3$ transits into $B_{14}C_3$.

Thus, boron carbide of the composition $B_{12}C_5$ ($B_{2.4}C$) has a lattice saturated with C atoms to the maximum, and $B_{14}C_3$ ($B_{4.67}C$) is saturated with B atoms to the maximum. We consider these compositions of boron carbide critical.

4. The intrusion of additional B atoms into the lattice of the critical composition $B_{14}C_3$ may occur only by way of their replacing the central C atoms in the linear chain $C = C = C$. In case of complete replacement, $B_{12+2+2}C_3 = B_{15}C_3$ is formed with a linear chain $C - B - C$. In the $B_{14}C_3 - B_{15}C_3$ interval a continuous series of solid replacement solutions is formed.

The lattice periods of boron carbide are here markedly changed: -- the larger the boron concentration is in the solid solution, the larger the value of a and b is, and the smaller the angle theta is (Fig. 7).

In case of boron carbide with a solid intrusion solution into the whole interval of $B_{2.75}C - B_{4.63}C$, the ratio of c/a equals 2.156, and in case of boron carbide with solid replacement solution of $B_{4.63} - B_{6.75}$, this ratio is increased, and it is 2.156.

According to Zhdanov, Zhuravlev, Meerson, and Samsonov [4], the formation of a continuous series of solid replacement solutions starts earlier, i.e., with $B_{12}C_3$, and in case of a full substitution, a boron carbide of the composition $B_{13}C_2$ is formed.

Results of the investigations

1. Industrial samples of boron carbide of variable composition from $B_{2.75}C$ to $B_{6.75}C$ were investigated roentgenographically, i.e., by the large angles method.
2. Precision determinations were conducted of the values of lattice periods of boron carbide in the $B_{2.75}C - B_{6.75}C$ interval.
3. A range of continuous solid intrusion solutions of B or C was established in $B_{12}C_3$ without change in the lattice periods in the $B_{12}C_5 - B_{12}C_3 - B_{14}C_3$ intervals (See Fig. 7).
4. A range of continuous series of solid replacement solutions of the central C atoms in the linear chain $C - C - C$ was established in $B_{14}C_3$ boron.
5. It was shown that in case of full substitution, boron carbide of composition $B_{15}C_2$ is formed. The value of boron carbide periods in the $B_{14}C_3 - B_{15}C_2$ interval does not remain constant, but it depends upon the B concentration in the solid solution of boron

carbide. The larger the B concentration is, the larger the parameters g and g are, and the smaller is the reflection angle Theta.

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Questions and answers

Q.: Does constant g change in the $B_{12}C_5 - B_{14}O_3$ interval?

V.I. Kudryavtsev: The magnitude of constant g in this interval remains without change.

Q.: What is the diameter of the needles used in the camera of needle collimator?

V.I. Kudryavtsev: For work with the Debye camera, we used a needle whose external diameter is 2 mm, and the internal diameter of the aperture is 0.4 - 0.6 mm. Needles can be also used with smaller diameter of internal aperture, but in this case the quality of the roentgenograms deteriorates.

Q.: What was the photoexposure time?

V.I. Kudryavtsev: The exposure depends upon many factors ---

on the examined material, the wave length, and so on. E.g., for boron carbide photographed in cobalt rays on "Agfa" roentgen film, the maximum exposure was 3 hours. The films were exclusively legible.

Q.: What films did you use?

V.I. Kudryavtsev: We started working with Agfa film, but later we changed to the MF-3 film type (single-side aero-photo film) which gives almost no background. It is true, the exposure time was increased, but this was compensated by the clarity of the roentgenograms.

Q.: How many samples were examined and their density measured?

V.I. Kudryavtsev: The total number of examined samples reached 200. The reliability of the results can be guaranteed. The density was determined by roentgen data from the magnitudes ρ and q .

The experimental data obtained by us, expressed in the form of a graph $\rho_{max} = f(B/C)$, made possible to precisely determine the chemical composition of boron carbide. And they allowed the following conclusions:

1. if the ratio is $B/C < 4.67$, then $\rho_{max} \approx 87^\circ$ (cobalt radiation, $hkl = 326$);

2. if $B/C > 4.67$, then $\rho_{max} < 87^\circ$.

Reverse conclusion:

1. if $\rho_{max} \approx 87^\circ$, then $B/C < 4.67$;

2. if $\rho_{max} < 87^\circ$, then $B/C > 4.67$.

Q.: Samples of technical boron carbide contain Si. Is it possible that the icosahedron vacancies are filled with Si atoms?

V.I. Kudryavtsev: In the Tashkent samples of boron carbide, as a rule, the Si content is always 5 to 7 per cent.

Discussion on the report of V.I. Kudryavtsev and G.V. Sofronov
N.N. Zhuravlev (Moscow State University):

In the report of V.I. Kudryavtsev and G.V. Sofronov interesting experimental data were obtained by changing the parameters of the elementary cell of the technical samples of boron carbide with change of the content of C bound in the carbide.

The investigation of B alloys with C was done comparatively early both in our country and beyond the borders. In addition to roentgen examinations, the properties of boron carbide were also searched by different methods. The results of the measurement of the density of boron carbide samples with different content of bound C, obtained in the work of Gleizer and others, and our results of density measurements confirm to some extent the conclusion drawn in the expounded work on the formation of solid intrusion solution.

According to the data of Gleizer and others, the maximum pykometric density in the carbon-rich boron carbide samples reaches 2.63 g/cm^3 . In the carbon-rich samples examined by us and by G.V. Samsonov, the maximum pykometric density was 2.60 g/cm^3 , whereas the roentgenographic examination of the sizes of elementary cells of carbon-rich samples showed the minimum of its size.

The roentgen density, calculated from the $\text{B}_{12}\text{O}_3(\text{B}_4\text{C})$ composition is 2.51 g/cm^3 .

The different experimental and roentgen densities permit to state that supplementary atoms intruded into the lattices of boron carbide of $B_{12}O_3$ composition, i.e., that solid intrusion solutions were formed.

It is interesting to compare the data of the latter investigations with the constitution diagrams suggested in the works of Samsonov and Meyerson, Samsonov, Zhuravlev, and Amuyel' and others.

According to the data of the work of Samsonov and Meyerson, rhombohedral boron carbide is formed according to the peritectic reaction (Fig.1). This is not in agreement with the data of the works of Kudryavtsev and Gleizer and coworkers which point to the presence of a solid solution in a considerable range of concentrations.

In the work of Samsonov, Zhuravlev and Amuyel', another possible variant of diagram was suggested for the composition of the boron-carbon system. In this case, the formation of two boron carbides of closely similar structures was suggested (work of Zhuravlev, Meyerson, Zhdanov, Samsonov). This supposition is based upon the results of roentgenographic examination of a series of boron carbide samples, rapidly cooled from high temperatures. On the roentgenograms obtained with such samples, the ends of the line splinter, i.e., as if two types of crystal, with closely related structures, were obtained, but with different sizes of elementary cells. These samples were related to a two-phase range.

Later, in connection with the appearance of the work of Gleizer and others, the earlier examined boron carbide samples, showing splintering of the line ends on the roentgenogram were subjected to a more delicate reduction. Then, in a heavy fluid the crystals of various densities were separated. For the separation, bromoform diluted with benzol was used. In the bromoform the crystals of maximum and minimum density separated from the sample. Roentgenographic examination showed that the boron carbide crystals, possessing both minimum and maximum densities separated from a single sample, have identical structure and are distinguished by the size of their elementary cells. Crystals with large density have smaller elementary cells than the crystals with less density.

In addition to these crystals, the samples contained particles with intermediate value of density in the range from small to large. On roentgenograms obtained from these particles, the line ends were eroded, which is explained by the presence of boron carbide crystals of different sizes of the elementary cells. Thus, the presence of boron carbide samples does not show a composition from two phases, but from crystals of different size of the elementary cells.

The results of the works of Gleizer and Kudryavtsev will harmonize with the constitutional diagram if it is assumed that on the diagram of constitution of the boron-carbon system, there is a maximum, and that boron carbide, while appearing in a phase of constant state, has a considerable area of solubility.

I.N.Frantsevich (Institute of Metal Ceramics and Special Alloys,
AN USSR):

Here we witnessed the exposition of the interesting methodology of precision roentgen structural examination of structures, which in my opinion raised two questions.

Obviously, the first condition of a work with fine diaphragm is a fine-grained structure of the studied objects. N.O.Paton Institute of Electric Welding, AN USSR, gave opportunity to Mochan a few years ago to build a roentgen camera in which the same needle collimator was used as collimator. With the aid of this camera, roentgenograms of monocrystals could be taken in polycrystal objects. By the method of reverse photography, Mochan oriented the X-ray beam upon microscopic monocrystals, where the beam had a cross-section in the order of hundredths of millimeter, and he actually obtained roentgenograms for monocrystals. You probably worked with a very fine - -grained preparation, since with such fine beams you nevertheless obtained a continuous ring.

Now, as to the accuracy of determination of the parameters. Significant figures to the fourth place were given here, usually corresponding to the method of standard reverse photography. In the given case, the standard was not applied. Of course, doubt arises as to the reliability of the last significant figure introduced by You. As a rule, the method of asymmetric photography guarantees up to the third place, and not to the fourth or still less to the fifth. I

reckon that in this case it is completely unnecessary to work with standard.

V.I. Kudryavtsev : A few words in reference to the comment of I.N. Frantsevich.

Our first investigations with the use of injection needles started in 1961. The experimental material what we gathered was repeatedly verified.

Due to the shortage of time, I did not say anything about the fact that at the photography of flat edges we used silver as a standard, but later, we used a more reliable standard --monocorund or thermocorund-- whose linear expansion coefficient is a few times less than for silver.

The latter comment is about boron carbide. We reckon that in the $B_{12}C_5 - B_{12}C_3 - B_{14}C_3$ interval, solid intrusion solutions of B or C atoms are formed in the boron carbide lattice without a change in the lattice constant.

In the $B_{14}C_3 - B_{15}C_2$ interval, solid solution is also formed with B replacement of the central C atoms of the C - C - C linear chain.

G.V. Samsonov (Institute of Metal Ceramics and Special Alloys, AN USSR): The data given in the report are very interesting, and they deserve attention, the more so because they mostly coincide with the data of Gleizer and coworkers and the data of Allen.

However, these data, contrary to the confirmation of V.I. Kudryavtsev, do not refute at all the assumptions about boron carbide and about the boron-carbon system earlier developed by G.A. Meerson and myself, B.F. Ormont and coworkers and myself, N.N. Zhuravlev and I.O. Annuel', and so on, but in our opinion they seem to be only their further development and supplementation (Zhurn. phys. khim., No. 8, 1958).

It is a pity that at the time of the publication of the article in the Zhurnal phys. khim., we did not know the data of V.I. Kudryavtsev, yet this changes practically nothing, since his data are close to the results of Gleizer and Allen. The "compromise" forms of diagram given on our work can serve as a start for further supplementation and more accurate study.

As it follows from this diagram, the lower boundary of homogeneous region of the well freed samples of the beta-phase almost accurately corresponds with the $B_{14}O_3$ (19.2% C) composition indicated by V.I. Kudryavtsev. As to the upper boundary, this is much lower than for $B_{12}O_5$ according to Kudryavtsev's data, although it would be already containing 31.2 percent. C, because it goes beyond the boundary of the well-established eutectics. The mechanism of the replacement of the C atoms in the C - C - C linear chain by B atoms [NOTE: original has O atoms. An error ?], as indicated by Kudryavtsev is also not new. It was worked out in the investigations of G.S. Zhdanov and coworkers, with our participation, and previously pub-

lished in a series of communications, where only another boundary of these substitutions was indicated, corresponding to the formula $B_{6.5}C$ instead of $B_{6.75}C$ as indicated by V.I.Kudryavtsev.

The continuity of transition from the $B_{6.5}C$ phase (or, according to Kudryavtsev, from the $B_{7.65}C$) to the $B_{12}C_3$ phase (or, according to Kudryavtsev, to the $B_{12}C_2$) raises doubt since at the formation of these two phases the physical processes are not identical. Phase $B_{13}C_2$ is formed by substitution of the vacancies (the holes) with C atoms, and phase $B_{12}C_3$ -- by substitution of the B atoms with C atoms.

We established this mechanism as a result of a thorough study of the physical properties of boron alloys with carbon in a wide range of carbon concentrations.

In the report, the purity of samples also raises doubt. In the majority of cases, the samples were obtained by arc fusion, which makes them strongly contaminated with silicon.

Under all circumstances, further investigations should be conducted on the properties of alloys of this important diagram, which were obtained from very pure initial components. We are now conducting such an investigation with N.F.Zhuravlev. It would be very useful if V.I.Kudryavtsev would join us. The precision method of the roentgen analysis of boron carbides which he has elaborated can find very serious application.

The first results of this work are in agreement with our pre-

vious results obtained by N.N.Zhuravlev and I.O.Amuel', with the addition of carbon to boron, the resistance of the latter sharply decreases on account of the decomposition of the bonds between the B atoms, where the boron carbide structure is formed with a large number of holes on place of the C atoms.

Such alloy samples possess a high conductivity of the hole type, and high thermoelectromotor force in metal vapors (250 - 300 microV / °C).

It should be mentioned that the expounded results are prospective in the sense of simplicity of technologically creating reproducible semiconductor properties of boron alloys with carbon, and in the sense of building upon this basis high-temperature semiconductor devices, e.g., thermocouples resistant to high temperature, which is the goal of research in our laboratory.

To sum up, still once more I wish to emphasize the importance of the scientific research of the boron-carbon system, and I wish to remark on the value of the methodology and the results of V.I.Kudryavtsev, which in themselves represent a turning point on the road of more precise ideas about this very complicated system.

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