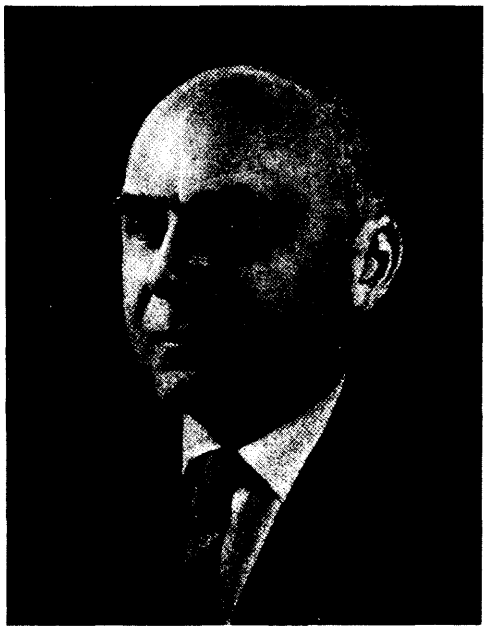
RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

May 1966



ALEKSANDR NIKOLAEVICH TERENIN

Deeply respected Aleksandr Nikolaevich!

The Editorial Board of the journal "Uspekhi Khimii" congratulates you heartily on your seventieth birthday. Your outstanding investigations in the field of physical chemistry have entered into the gold reserves of chemical science. The Editorial Board of "Uspekhi Khimii" is grateful to you for constant active assistance, and wishes you, dear Aleksandr Nikolaevich, good health and many years of life and creative work.

Editorial Board of "Uspekhi Khimii"

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THE CHEMISTRY OF THE BERYLLIDES

G. V. Samsonov

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INTRODUCTION

Compounds of beryllium with other metals are of great scientific and practical interest, since many of them have high melting points, relatively low specific gravity, high hardness, and also specific nuclear characteristics, which are united in a series of beryllides with specified properties.

Several equilibrium diagrams of beryllium–metal systems have now been investigated, the crystal structures of many beryllide phases have been studied, some of their physical, chemical, and technological properties have been studied, and definite ideas are beginning to accumulate about their crystal chemistry, electronic structure, and chemical bonding, which makes it possible to sum up all these investigations and to survey the information about compounds of beryllium with metals which is scattered in the literature.

I. BERYLLIDES OF GROUP I METALS

A. BERYLLIDES OF THE ALKALI METALS

The reaction of beryllium with the alkali metals has been little investigated[1]. Beryllium is stable up to 600°† in molten lithium, sodium, and potassium, but starts to dissolve at higher temperatures, owing to oxidation by the oxygen present in these metals[2]. According to the data given in a review[1], with the alkali metals (other than lithium) the size factor is so unfavourable that the probability of alloys being formed with beryllium, and also the possibility of their being miscible in the liquid state, are very small. Nevertheless, there have been reports[1,3] of the existence of potassium beryllide Be_2K, having $MgCu_2$-type cubic structure and of its being apparently quite a stable compound. There is no information about alloys of beryllium with sodium, rubidium, or caesium[4-6].

B. BERYLLIDES OF THE METALS OF THE COPPER SUBGROUP

Beryllium–copper system. Alloys of beryllium and copper have been studied in detail in connection with their great practical value (the beryllium bronzes). The equilibrium diagram of the Be–Cu system, first described in detail by Hansen[7] in the region from 0 to 35% Be, was subsequently repeatedly investigated and refined[8-14], the results being surveyed in reviews[1,15,16]. Fig. 1 shows the diagram of this system after Vol[15]. There are three beryllide phases: CuBe in the region of the β phase, $CuBe_2$, and $CuBe_3$ in the region of the δ phase; the existence of the phase Cu_2Be reported by Oesterheld[17] has not been confirmed by subsequent investigations[1].

The diagram shown in Fig. 1 has been confirmed completely by studies of diffusion in the Be–Cu system[18]. It was shown that the greatest diffusion coefficients and the least activation energy correspond to phases γ and δ, that is, to the approximate region of the compound CuBe.

† Temperatures are in °C throughout this article, except when °K is specifically mentioned (Ed. of Translation).

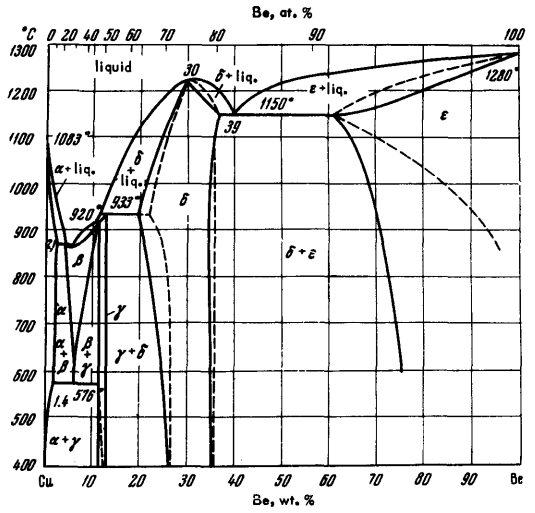


Fig. 1. Equilibrium diagram of the beryllium–copper system.

The physical and chemical properties of the copper beryllides (except for hardness) have hardly been studied (Table 1). The hardness of the quenched alloys whose compositions almost precisely correspond to beryllides[10], is relatively high and rises from CuBe to $CuBe_2$, then falls again slightly for $CuBe_3$. All the beryllides have a homogeneity region, the breadths of which have still not been found with sufficient accuracy. The properties (electrical resistivity, Hall constant, carrier current mobility) of copper–1.75 wt.% beryllium alloy, which is a mixture of the α and γ phases, have been studied in detail[19]. The resistivity of such alloys is ~ 7 $\mu\Omega$ cm.

It is difficult to prepare copper beryllides by melting the components together, owing to the great loss of beryllium at high temperatures; the best results are secured by making use of previously prepared copper–beryllium hardeners. The simplest method of making the beryllides is by powder metallurgy: by sintering copper and beryllium powders; according to Raub and Plate[20] the reaction between the compressed powders has begun even at 678°.

The beryllium–silver system has been studied[17,21,22]; Winkler[22] obtained the most reliable results, from which the diagram in Fig. 2 is constructed. There are two beryllides in the system: $AgBe_2$[23] and $AgBe_{12}$[24]. Both these phases are cubic, but $AgBe_2$ has a rather wider homogeneity region. Powder metallurgy is the most convenient method for obtaining silver beryllides, especially hot pressing of mixtures of the powders.

Beryllium–gold alloys were investigated by Winkler[22] and Chatterjee[25,26]; Fig. 3 shows the equilibrium diagram of the Au–Be system according to Winkler[22] and Fig. 4 the accurate phase diagram‡ of this system[26]. The following beryllide phases have been found in the system and identified by X-ray diffraction[1,26]: Au_3Be (β), Au_2Be (γ), AuBe (δ), $AuBe_3$ (ϵ), and $AuBe_5$ (η), and also, with great probability, phase $AuBe_{12}$, which is stabilised on replacing some of the Au atoms by W atoms[24]. At the same time the existence of the beryllide Au_4Be_3, stated by

‡ α is a solid solution of Be in Au, θ a solid solution of Au in Be.

TABLE 1. Properties of the beryllides of metals of the copper subgroup.

Beryllide	Be, wt. %	Structure	Type	Lattice parameters, Å		c/a	Density, g cm^{-3}	M.p., °C	Vickers hardness, kgf mm^{-2}
				a	c				
CuBe	12.4	cub.	FeSi	2.703 [23]	—	—	5.0 [15]	~ 920 [15]	311 [10]
$CuBe_2$	22.2	cub.	$MgCu_2$	5.952 [23,27]	—	—	5.277	~1140 [15]	517 [10]
$CuBe_3$	29.9	cub.	—	5.887 [23,27]	—	—	4.6 [15]	~1220 [15]	435 [10]
$AgBe_2$	14.3	cub.	$MgCu_2$	6.300 [23]	—	—	6.69 [22]	~1180 [22]	—
$AgBe_{12}$	50.2	tetr.	—	7.284 [1]	4.246	0.583	3.19 [1]	—	—
Au_3Be	1.51	tetr.	—	—	—	—	—	595 [22]	—
Au_2Be	2.25	tetr.	—	6.136 [26]	5.222	0.9	—	~645 [22]	—
AuBe	4.38	cub.*	FeSi	4.668 [28]	—	—	13.55 [28]	~730 [22]	—
$AuBe_3$	12.1	cub.**	—	—	—	—	—	—	—
$AuBe_5$	18.7	cub.	$MgCu_2$***	6.097 [25,29]	—	—	7.10 [25,29]	~1150 [22]	—
$AuBe_{12}$	35.7	tetr.	—	7.243 [30]	4.252	0.587	4.55 [30]		

* According to Chatterjee and Mines [26], AuBe has a tetragonal lattice with $c/a = 1.01$.
** Diamond-type [26].
*** According to Chatterjee and Mines [26], $AuBe_5$ has a ZnS-type f.c.c. lattice with $a = 6.098$ Å.

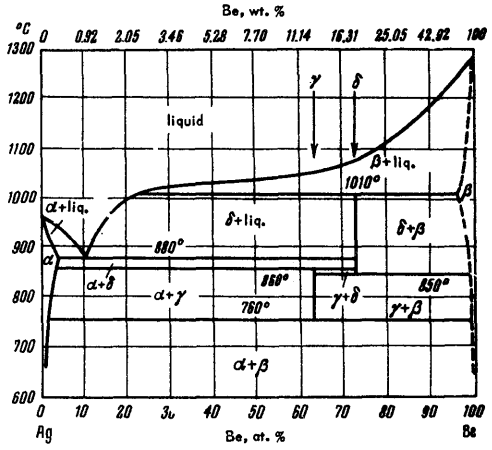


Fig. 2. Equilibrium diagram of the silver–beryllium system.

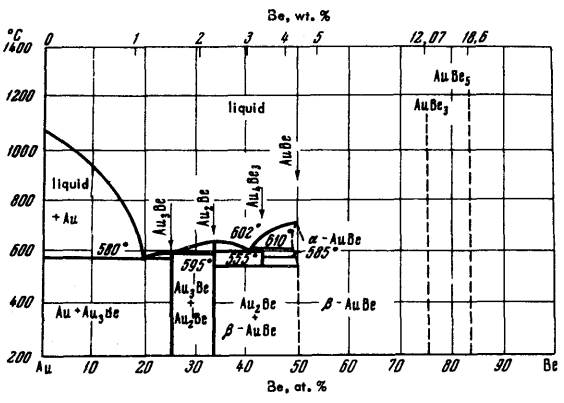


Fig. 3. Equilibrium diagram of the gold–beryllium system.

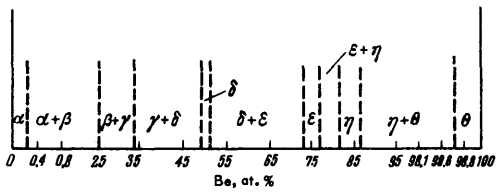


Fig. 4. Phase diagram of the gold–beryllium system.

Winkler, was not confirmed. The physical properties of the gold beryllides have not been studied much; it is known only that they exhibit great brittleness. Gold beryllides are usually prepared by powder metallurgical methods, particularly by hot pressing in a vacuum [31].

II. BERYLLIDES OF GROUP II METALS

A. BERYLLIDES OF MAGNESIUM AND THE ALKALINE EARTH METALS

Many attempts to alloy beryllium with magnesium [32,33] have failed, owing to the volatility of magnesium, and success was achieved [34,35] only by melting the metals in hydrogen under a pressure of ~ 100 atm. Later Baker and Williams [36] obtained $MgBe_{13}$, still the only compound of this system; it decomposes into the elements in a vacuum at 950°, and the authors showed that the eutectic between this compound and magnesium melts at a temperature very close to the melting point of magnesium [1,37]. Beryllium–magnesium alloys can be obtained by the methods of powder metallurgy [38] — either by impregnating a pressed blank of beryllium powder at 750° under argon, or by diffusion of magnesium from magnesium foil around a compact pressed from beryllium powder at 4.8 tf cm^2; the diffusion is also carried out at 750°.

Beryllium–calcium alloys have been obtained [32] heating solid beryllium with molten calcium; a beryllium–calcium compound $CaBe_{13}$ was observed. This compound

has been obtained[39] by the reduction of beryllium oxide with calcium and shown to be extremely stable.

Both the beryllides $MgBe_{13}$ and $CaBe_{13}$ are f.c.c., with parameters 10.166 and 10.312 Å respectively[36]. They are isomorphous with $NaZn_{13}$.[40]

There is no information about beryllides of strontium, barium, and radium.

B. BERYLLIDES OF METALS OF THE ZINC SUBGROUP

Beryllium–zinc alloys have not been obtained, owing to the high volatility of zinc, even in argon under pressure[11]. According to old information[41], beryllium does not dissolve in mercury and does not form an amalgam with it. It has been stated[42] that an amalgam was obtained at the mercury cathode on electrolysis of $BeCl_2$–NaCl mixtures; the possibility of the existence of the compound $BeHg_2$ is suggested in this work. It was established[43] that the solubility of beryllium in mercury rises from 1.10×10^{-6}% at 100° to 4.5×10^{-5}% at 800°. According to data given in a review[9], mercury had no action on a beryllium container in 330 h at 315°. There is no information about the interaction of beryllium and cadmium[44].

III. BERYLLIDES OF THE TRANSITION METALS

A. BERYLLIDES OF METALS OF SUBGROUP IIIa (THE RARE-EARTH ELEMENTS

In addition to lanthanum and the lanthanides, the rare-earth elements also include scandium and yttrium, which are close to the lanthanides as regards position in the Periodic System and physicochemical and geochemical features, although it is more correct to relate them to the *d* transition metals of the third and fourth periods.

Scandium beryllides. By sintering mixtures of fine scandium and beryllium (with 0.47% oxygen) powders at 1250° and then grinding the sinters and resintering, alloys of the Be–Sc system were obtained[45] in which from 0.5 at.% Sc onwards X-ray diffraction shows a phase with a structure of $NaZn_{13}$ type, isomorphous with the phases of analogous composition of yttrium and the lanthanides on the one hand, and of zirconium on the other. The melting point of $ScBe_{13}$ is above 1300°. Further investigation of the Be–Sc system[46,47] showed the presence of two more compounds; $ScBe_5$ and Sc_2Be_{17}, analogous to the corresponding beryllides of zirconium and hafnium.

Yttrium beryllides. In the Be–Y system, the diagram of which has been constructed by Lundin[48] (Fig. 5), there is one compound YBe_{13} with m.p. ~ 1920° and of $NaZn_{13}$-type structure[46,49]. Previously, the melting point of YBe_{13} had been taken as 1600° ± 300°.[50] The hardness of this compound is 870 kgf mm^{-2} (on the Knoop microhardness scale)[50,51], or 1240 kgf mm^{-2} from measurements[49] with a PMT-3 microhardness tester (100 g load). The compound is resistant to oxidation up to 1300°.[51]

Beryllides of the lanthanides. All the lanthanides form compounds MBe_{13} with beryllium[49,52,53]. Gladyshevskii and coworkers[53] obtained the beryllides MBe_{13} for all the lanthanides except Pm and Gd by melting

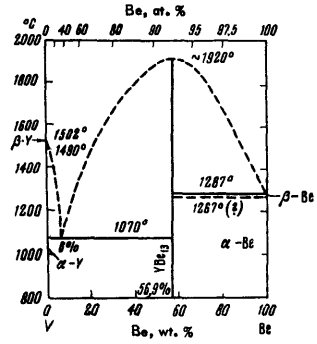


Fig. 5. Equilibrium diagram of the beryllium–yttrium system.

TABLE 2. Properties of the beryllides of the rare-earth metals.

Beryllide	Be, wt. %	Structure	Lattice parameters, Å		Density, g cm^{-3}	M.p., °C
			a	*c*		
$ScBe_5$	50.1	$CaCu_5$-type hex.	4.55[46,47]	3.50[44,45]	—	—
Sc_2Be_{17}	58.0	Th_2Ni_{17}-type hex.*	7.61[46]	7.50[44]	—	—
$ScBe_{13}$	72.4	$NaZn_{13}$-type cub.	10.10[47]	—	—	>1300
YBe_{13}	56.8	ditto	10.239[45,48—50]	—	2.57[47—50]	1920[48,50] 1600[51]
$LaBe_{13}$	45.8	»	10.43[57] 10.44[58] 10.457[47] 10.450[55]	—	2.79[57]	1720[57,59,60]
$CeBe_{13}$	45.6	»	10.375[40] 10.378[47,55]	—	2.81[57]	1720—1925[57]
$PrBe_{13}$	45.4	»	10.374[57] 10.367[55]	—	3.06[53]	—
$NdBe_{13}$	44.9	»	10.390[53] 10.356[55]	—	—	—
$PmBe_{13}$	44.8	»	10.33[55]	—	—	—
$SmBe_{13}$	43.9	»	10.325[53] 10.28[55]	—	—	—
$EuBe_{13}$	43.4	»	10.300[53] 10.288[55]	—	—	—
$GdBe_{13}$	42.9	»	10.27[55]	—	—	—
$TbBe_{13}$	42.3	»	10.254[53] 10.251[55]	—	—	—
$DyBe_{13}$	41.9	»	10.239[53] 10.240[55]	—	—	—
$HoBe_{13}$	41.6	»	10.225[53] 10.220[55]	—	—	—
$ErBe_{13}$	41.2	»	10.210[53,54] 10.20[54] 10.215[55]	—	—	—
$TuBe_{13}$	40.9	»	10.199[53] 10.192[55]	—	—	—
$YbBe_{13}$	40.6	»	10.182[53] 10.19[56,60]	—	—	—
$LuBe_{13}$	40.3	»	10.173[53] 10.177[55]	—	—	—

* Or Th_2Zn_{17}-type; and then the parameter is *c* = 11.25 Å (the two types are difficult to distinguish by X-rays).

distilled beryllium (99.8% purity) with metals of 95–99% purity in crucibles of BeO (or of Al_2O_3 lined with BeO) under argon in a Tammann furnace. An erbium beryllide of the same composition was obtained earlier[54]. Beryllides of a series of lanthanides were obtained[55] by reduction of the oxides with beryllium in a vacuum at 1300°:

$$M_2O_3 + 29Be = 2MBe_{13} + 3BeO.$$

Yttrium and lanthanum beryllides have been obtained[56] by sintering the metal powders with an excess of beryllium in tantalum crucibles at 1180° for 2 h in a vacuum of not below 5×10^{-6} mmHg followed by removal of the excess of beryllium by vacuum distillation at 1050° for 5 h.

In the same work the behaviour of YBe_{13} and $LaBe_{13}$ in a vacuum at temperatures up to 1550°K was investigated; it was found that the two compounds are appreciably dissociated above 1050° and equations were derived for the temperature dependence of the vapour pressure of beryllium over the beryllides during their thermal dissociation:

$$\text{for } YBe_{13}\text{: } \log P_{mm} = -\frac{16\,420}{T} + 8.30 \quad (1040\text{–}1290^\circ),$$

$$\text{for } LaBe_{13}\text{: } \log P_{mm} = -\frac{16\,600}{T} + 8.73 \quad (1080\text{–}1270^\circ).$$

Table 2 gives some information about the properties of beryllides of the rare-earth metals.

B. BERYLLIDES OF METALS OF SUBGROUP IVa

Titanium beryllides. Misch[23] obtained the compound $TiBe_2$ and showed that this beryllide crystallises in the $MgCu_2$ type. A systematic investigation of Be–Ti alloys was made by Erlich[62] on specimens obtained by sintering mixtures of titanium and beryllium powders, the sintering temperatures being: 1600° for alloys of empirical formula $TiBe_{0.4}$, 1300° for $TiBe_{0.5}$, and up to 1500° for $TiBe_{1.0}$ and alloys richer in beryllium. Erlich thinks that the composition $TiBe_{0.5}$ corresponds approximately to the eutectic of the system. X-Ray investigation of the alloys with empirical formulae from $TiBe_{0.1}$ to $TiBe_{10}$ showed that the solubility of beryllium in titanium is less than corresponds to the composition $TiBe_{0.1}$; the compounds have according to Erlich's results, the compositions TiBe, $TiBe_2$, $TiBe_4$, and $TiBe_{10}$, of which the first and the two last compounds have not been identified by X-ray diffraction. The compound TiBe evidently has a wide homogeneity region, since even the composition $TiBe_{0.75}$ gives an X-ray diagram identical with that of the alloy TiBe. The $TiBe_2$ phase has, according to Misch's data[23], a structure of $MgCu_2$ type with a parameter $a = 6.42_7$ Å, and this compound also has a certain region of homogeneity, since the determination of the lattice parameter of this phase in an alloy of conventional composition $TiBe_3$ gave a rather higher value, 6.45_6 Å. Later, $TiBe_{12}$[63] and Ti_2Be_{17}[58] were obtained directly from the elements; they are both hexagonal — the first of $ThMn_{12}$ type (sub-type $TiBe_{12}$ with 48 atoms in the unit cell) and the second of U_2Zn_{17} type. Later these phases were the subject of repeated investigations, which have been reviewed[64], and it is now accepted that $TiBe_{12}$ is not hexagonal but has a tetragonal structure of $ThMn_{12}$ type (analogous to the structures of VBe_{12} and $CrBe_{12}$), and that the Ti_2Be_{17} phase, which had been thought to be rhombohedral[65] or trigonal[66] is really hexagonal[64], with lattice parameters somewhat different from those found by Paine and Carrabine[58]. The $TiBe_{12}$ structure, as shown by Gillam and Rooksby[64] readily changes into the related Ti_2Be_{17} structure on loss of some of the beryllium atoms. The part of the diagram from Ti to $TiBe_2$ was studied[67] again in detail and the compounds TiBe and $TiBe_2$ were identified by X-ray diffraction; the general form of this part of the diagram was also confirmed. Hence the existence of at least four titanium beryllides, TiBe, $TiBe_2$, Ti_2Be_{17}, and $TiBe_{12}$, can now be considered established. Two of these are discounted in the hypothetical equilibrium diagram of the system constructed by the McQuillans[68] (Fig. 6), which now needs considerable modification.

Erlich[62] obtained titanium beryllides by sintering titanium and beryllium powders and also by arc melting in argon with a non-consumable tungsten electrode. According to Raub and Plate[20] the reaction between titanium and beryllium in powder mixtures starts at 800°. It is reported[69] that $TiBe_2$ is readily formed on heating briquettes, pressed from beryllium and titanium powders, in argon at 1200° for 1 h. $TiBe_2$ is also made by vacuum hot pressing[70] under a pressure of up to 100 kgf cm^{-2} in graphite dies coated with Al_2O_3.

Specimens of $TiBe_{12}$ with density 94%, obtained by vacuum hot pressing have high resistance to oxidation at 1260° for 100 h.[70] The high oxidation resistance of $TiBe_2$ and $TiBe_{12}$ has also been mentioned in a review[59].

Table 3 gives some information about the properties of titanium beryllides.

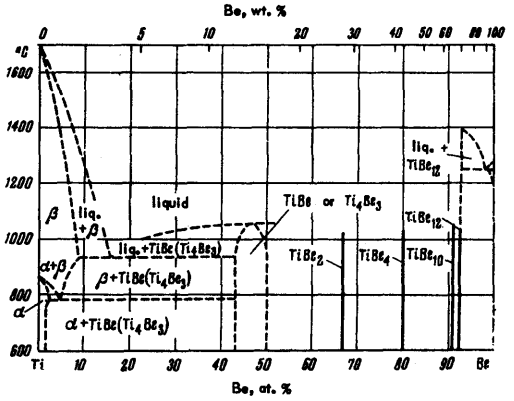


Fig. 6. Equilibrium diagram of the beryllium–titanium system.

TABLE 3. Properties of titanium beryllides.

Property	Beryllide			
	TiBe	$TiBe_2$	Ti_2Be_{17}	$TiBe_{12}$
Be content, wt. %	15.8	27.3	61.5	69.4
Structure	hex.	cub.	hex.	tetr.
Structural type	—	$MgCu_2$	U_2Zn_{17}	$ThMn_{12}$
Lattice parameters, Å				
a	3.20[64]	6.42[23,62,67]	7.35[64]*	7.36[64,66]**
c	3.69[64]	—	7.26	4.195
c/a	1.15	—	0.984	0.571
Density (X-ray), g cm^{-3}	—	—	—	2.26[70]
Melting point, °C	—	1800—1900	—	1427[70]
Gain in weight on oxidation at 1260° for 100 h, mg cm^{-2}	—	—	—	3.0[70]
Bend strength, kgf mm^{-2}				
1260°	—	—	—	7.8[59]
1370°	—	—	—	2.5
1510°	—	—	—	1.9
Limit of proportionality, kgf mm^{-2} (1260°)	—	—	—	1.4[59]
Superconductivity transition temperature, °K	—	<1.02[73]	—	—
Emissivity (at 800–1800°, λ = 650 μm)	—	0.73[73]	—	—

* See also Refs. 58, 65, 66, and 71.

** See also Refs. 63 and 65.

Zirconium beryllides. The first systematic investigation of beryllium–zirconium alloys was made by Hausner and Kalish[74] on specimens made by powder metallurgy. Lustman and Kerze[75] constructed the Be–Zr equilibrium diagram from the data of Hausner and Kalish[74], McGurty and coworkers[76], and others, but it was investigated again[77], from the results of which work Fig. 7 has been constructed. According to these results, the system contains the compounds $ZrBe_2$, $ZrBe_6$, and $ZrBe_9$, which are formed by peritectic reactions at 1235°, 1475°, and 1555° respectively, and $ZrBe_{13}$, which melts congruently at 1645°. Whereas the compositions of the beryllides $ZrBe_2$ [76–78] and $ZrBe_{13}$ [40,47] are accepted as the result of all the studies, the compositions of the beryllides with intermediate beryllium concentrations are at variance. Thus whereas some workers[76,77] take the composition of a beryllide as $ZrBe_6$ (evidently the most reliable), another[79] gives the composition as $ZrBe_5$. The beryllide of composition $ZrBe_9$, according to some[76,77] obviously corresponds to the most reliable composition Zr_2Be_{17}. Evidently, the composition $ZrBe_{16}$ given in one paper[76] is erroneous, and it obviously is the highest beryllide $ZrBe_{13}$ with beryllium impurity.

The zirconium beryllides Zr_2Be_{17} and $ZrBe_{13}$ — one of the most refractory of the transition metal beryllides (Table 4) — exhibit relatively high hardness; Fig. 8 shows the temperature dependence of the hardness of $ZrBe_{13}$.[59] There are marked differences in the hardness for $ZrBe_{13}$ obtained by different authors: 1650 kgf mm^{-2} according to Lewis[59], 790 kgf mm^{-2} according to Chubb and Dickerson[50], and 1130 kgf mm^{-2} according to Getz[79].

At high temperatures (~ 1400–1500°), Zr_2Be_{17} and $ZrBe_{13}$ show considerable resistance to oxidation[79,80], but over a certain temperature range they react rapidly with moisture, which leads to their rapid oxidation and disintegration into powder[81]. According to this work[81], hot-pressed $ZrBe_{13}$ showed this effect in the range 593–927°, but it is not observed below 538° nor above 982° in tests lasting 100 h. In this connection there have been several detailed investigations of the oxidation of $ZrBe_{13}$ in the medium-temperature range; they are cited in Getz' review[79]. In particular, it has been shown that the oxidation proceeds mainly inside the grain, although the oxidation products are partly liberated at the grain boundaries;

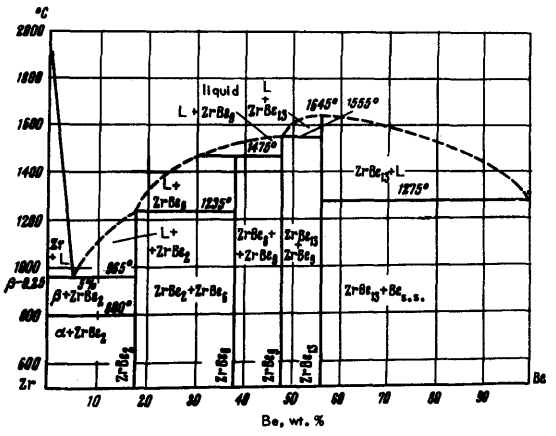


Fig. 7. Equilibrium diagram of the beryllium–zirconium system.

TABLE 4. Properties of zirconium beryllides.

Property	Beryllide			
	$ZrBe_2$	«$ZrBe_6$»	Zr_2Be_{17}	$ZrBe_{13}$
1	2	3	4	5
Be content, wt. %	16.5	33.0	45.6	56.3
Structure	hex.	hex.	rhombohedral	f.c.c.
Structural type	AlB_2	$CaZn_5$	U_2Zn_{17}	$NaZn_{13}$
Lattice parameters, Å				
a	3.82[78]	4.564[83]	7.548[83]*	10.067[40]
c	3.25	3.485	10.997	—
c/a	0.85	0.764	1.457	—
Density, g cm^{-3}	—	—	3.08[79]	2.72[51,79]
Melting point, °C	1200[76]	1530[76]	1980[79]	1927[79]
Vickers hardness at 20°, 2.5 kg load, kgf mm^{-2}	—	—	1750[75,84]	2000[51]
	—	—	1130[79]	1000[79]
	—	—	—	1650[59]
Knoop hardness (50 g load), kgf mm^{-2}	—	—	—	790[50,51]
Gain in weight in oxidation at 1260° for 100 h, mg cm^{-2}	—	—	—	7.8[70]
Depth of oxidation after 100 h, mm				
1371°	—	—	0.0127[79,80]	0.0127[79,80]
1482°	—	—	0.0305[79,80]	0.0330[79,80]
Bend strength, kgf mm^{-2}				
20°	—	—	17.5[76]	17.5[79]
982°	—	—	16.1[79]	12.6[79]
1260°	12.1[79]**	—	27.7[59]	19.8[59]
			28.0[79]	28.0[79]
1371°	5.2[79]***	—	19.0[59]	19.8[59]
			28.0[79]	26.0[79]
1510°	—	—	17.2[59]	12.6[59]
			24.6[79]	17.5[79]
Young's modulus, kgf mm^{-2}				
20°	—	—	~33 500[79]	~33 000[79]
871°	—	—	~28 000[79]	~28 000[79]
1260°	—	—	18 300[59]	14 100–28 100[59]
1371°	—	—	10 500–21 100[59,79]	14 000[79,59]
1510°	—	—	7000[59]	7000[59]
Elongation in bending, %				
20°	—	—	0.1[79]	0.05[79]
871°	—	—	0.1[79]	0.07[79]
1371°	—	—	0.3[79]	0.25[79]
1510°	—	—	1.1[79]	0.6[79]
Limit of proportionality, kgf mm^{-2}				
1260°	—	—	16.4[59]	1.4[59]
1370°	—	—	7.1[59]	3.3[59]
1510°	—	—	2.6[51]	—
Ultimate compressive stress, kgf mm^{-2}				
20°	—	—	—	133[79]
871°	—	—	—	105[79]
1371°	—	—	—	49[79]
Impact strength, kgf cm^{-2}				
20°	—	—	—	< 1.15[59]
				0.115[57]
1095°	—	—	—	13.8[85]
Resistance to thermal shock				
1260°	—	—	—	better than for MgO at 100°[59]
Heat capacity per unit mass, cal g^{-1} deg^{-1}				
538°	—	—	—	0.38[79]
1482°	—	—	—	0.47[79]
Thermal conductivity, cal s^{-1} cm^{-1} deg^{-1}				
760°	—	—	—	0.067[57,59]
1370°	—	—	—	0.085[57,59]
1385°	—	—	—	0.082[59,84]
1482°	—	—	—	0.0869[79]
Coefficient of thermal expansion (× 10^6), deg^{-1}	—	—	8.39[79]	9.86[79]
Electrical resistivity, μΩ cm				
27°	—	—	—	16.4[79]
649°	—	—	—	76.9[79]
1260°	—	—	—	100.4[79]
Vapour pressure (× 10^3), mmHg				
1260°	—	—	1.4[82]	—
1371°	—	—	11.3[82]	—

* For a pseudocubic cell a = 5.69 Å.

** For $ZrBe_9$.

*** For "Zr_2Be_{13}".

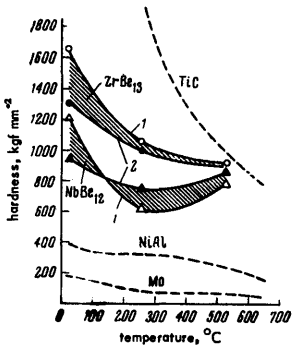


Fig. 8. Temperature dependence of hardness for some beryllides and other heat-resistant materials. Load: 1) 26 g; 2) 100 g.

TABLE 5. Properties of hafnium beryllides.

Property	Beryllide			
	$HfBe_2$	$HfBe_5$	Hf_2Be_{17}	$HfBe_{13}$
Be content, wt. %	9.18	20.2	29.9	39.7
Structure	hex.	hex.	cub.	
Structural type	AlB_2	$CaZn_5$	U_2Zn_{17}	$NaZn_{13}$
Lattice parameters, Å				
a	3.788 [86]	4.534 [86]	7.499 [86]	10.010 [86]
c	3.168	3.471	21.905	—
c/a	0.836	0.765	2.921	—
Microhardness (100 g load), kgf mm^{-2}	980 [86,87]	1340 [86,87]	1085 [86,87]	1200 [86,87]
Knoop microhardness, kgf mm^{-2}	77 [87] *	87 [87] **	98 [87] ***	—
Melting point, °C	1273 [87] *	1270 [87] **	1486 [87] ***	—

* For the alloy with 10.0 wt. % Be.
** For the alloy with 20.0 wt. % Be.
*** For the alloy with 33.0 wt. % Be.

the stresses created by the formation of the oxides can bring about the destruction of the beryllides. That this takes place in the medium-temperature region is compared with the fact that at 984–1093° $ZrBe_{13}$ partly loses beryllium, being converted into Zr_2Br_{17} (a layer of which is situated between the $ZrBe_{13}$ and the oxide layer)[81], which has a thermal expansion coefficient quite different from that of $ZrBe_{13}$. The addition of 0.35–0.45 wt. % Al to $ZrBe_{13}$ brings about a sharp rise in its oxidation resistance in the middle-temperature region, both in dry and in moist (dew point 14°) air, at the cost of some deterioration in high-temperature strength, and a marked increase in room-temperature strength. It was shown in this work that aluminium is very slightly soluble in $ZrBe_{13}$ and much more soluble in Zr_2Be_{17}, with which is evidently also connected the beneficial effect of the additions of aluminium on the oxidation resistance of the beryllide $ZrBe_{13}$ in the middle-temperature region. The rate of oxidation of zirconium beryllides obeys a logarithmic law[59,81], which agrees with the protective nature of the oxide film.

According to Bookhand and others[82] the vapour pressure above Zr_2Be_{17} at 1200–1400° is relatively low, $\sim 10^{-3}$ mmHg.

Zirconium beryllides can be made by powder metallurgy methods, either by sintering previously compacted mixtures of beryllium and zirconium powders[74] in argon (the reaction between zirconium and beryllium is reported[20] to start at 685°) or by hot pressing[76] at 1600–1800°.

Beryllium–zirconium alloys have been made[77] by fusing the components in an argon arc furnace; a similar method has been described[51] for $ZrBe_{13}$.

The same work[51] describes various methods for making articles from $ZrBe_{13}$ and some other beryllides ($NbBe_{12}$, $MoBe_2$) — in particular, by vacuum (~ 0.1 mmHg) hot pressing of mixtures of powders (200 mesh), the temperature being raised to 1500° over a period of 2–3 h, and then held at 1550–1600° for 1–2 h (all the regimes are quoted for cylindrical articles with a diameter and height of ~ 50 mm). Good results are also obtained by using casting (induction heating) and extrusion at $\sim 1620°$.

Hafnium beryllides. The beryllium–hafnium system is quite similar to the beryllium–zirconium system; the existence of four compounds in it has also been established[58,65,86-88]: $HfBe_2$, $HfBe_5$, Hf_2Be_{17}, and $HfBe_{13}$. The beryllide $HfBe_2$ has a hexagonal lattice of the AlB_2 type; $HfBe_5$ also has a hexagonal lattice, of the $CaZn_5$ type; the Hf_2Be_{17} phase is reported[65] to have two modifications: α-Hf_2Be_{17}, rhombohedral (a = 7.494, c = 10.93 Å), and β-Hf_2Be_{17}, hexagonal (a = 7.44, c = 7.38 Å), but others state[86,87] that there is only a hexagonal type of Nb_2Be_{17} identical in type with U_2Zn_{17} or Th_2Zn_{17}. Finally, $HfBe_{13}$ has a cubic structure of $NaZn_{13}$ type[87]. This work[87] drew attention to the fact that the lattice parameters of the hafnium beryllides are less than those of the corresponding zirconium phases; this is connected with the atomic radius of hafnium (1.59 Å) being less than that of zirconium (1.60 Å). The main information on the properties of the hafnium beryllides is given in Table 5.

According to these data[87] as the proportion of beryllium in the compounds with hafnium is increased, the distance between its atoms diminishes ($HfBe_2$ 2.179, $HfBe_5$ 2.17, Hf_2Be_{17} 2.14, $HfBe_{13}$ 2.07 Å) but the distance between the hafnium atoms increases, which indicates an increase in the covalency of the bond between the beryllium atoms.

Hafnium beryllides can be obtained either by melting the components together under argon in a high-frequency (beryllium-rich) or arc (hafnium-rich) furnace[86,87] or by powder metallurgy methods, especially by hot pressing of mixtures of the powders[88] followed by annealing.

C. BERYLLIDES OF METALS OF SUBGROUP Va

Vanadium beryllides. Misch[23] found the existence of the beryllide VBe_2 with a hexagonal lattice of $MgZn_2$ type and parameters a = 4.385, c = 7.130 kX, c/a = 1.639, with four molecules in the unit cell. Further investigations of the compounds in this system[89-91] confirmed the existence of VBe_2 and its structure, and also showed the compound VBe_{12} with a tetragonal lattice of $ThMn_{12}$ type.

The icosahedral configuration of the beryllium atoms in this structure and also the decrease in the distance between the beryllium atoms on going from VBe_2 (2.25 kX) to VBe_{12} (2.19 kX) shows a considerable proportion of covalency in the bond between the beryllium atoms.

The existence of VBe_{12} was further confirmed by Batchelder and Raeuchle[92], who gave values of the lattice parameters for single crystals which were different from those quoted[89-91].

Vanadium beryllides are obtained by melting the components together in quartz containers in a resistance furnace under argon (Table 6).

Niobium beryllides. In the Be–Nb system the existence of a compound $NbBe_{12}$ with a face-centred tetragonal lattice was established[86,87,92] and then rhombohedral Nb_2Be_{17} was observed[93]. In addition there have been reports of the existence of $NbBe_2$,[91,94] Nb_3Be_2,[95] $NbBe_5$,[91,96] of which $NbBe_2$ and $NbBe_5$ were accepted in the construction of a tentative variant[96] of the Be–Nb equilibrium diagram (Fig. 9). This diagram, which has been described in detail[96,97] was confirmed by additional investigation[98] and it was shown that the solid solubility of niobium in beryllium is very small (considerably less than 0.7 wt.% Nb), eutectic crystallisation of α-Be + $NbBe_{12}$ from the melt takes place at 2.5 wt.% Nb, and the eutectic temperature is close to the melting point of pure beryllium. Furthermore, it is stated that the phase $NbBe_{12}$ may not be formed as a compound with an open maximum melting point but by a peritectic reaction between the melt and compound Nb_2Be_{17}, which obviously throws doubt on the part of the diagram in Fig. 9 between the phases Nb_2Be_{17} and $NbBe_{12}$; this part requires further, more detailed investigation.

In a thermal diffusion study of the beryllium–niobium system[96] the temperature dependence of the diffusion coefficients was determined approximately for "$NbBe_8$" (Nb_2Be_{17}) and $NbBe_{12}$:

$$D_{\text{«NbBe}_8\text{»}} = 5.7\times10^{-9}\exp(-14\,740/RT),$$

$$D_{NbBe_{12}} = 7.66\times10^{-4}\exp(-32\,000/RT)$$

TABLE 6. Properties of vanadium beryllides.

Property	Beryllide	
	VBe_2	VBe_{12}
Be content, wt. %	26.2	68.2
Structure	tetr.	tetr.
Structural type	$MgZn_2$	$ThMn_{12}$
Lattice parameters, Å		
a	4.394[88]	7.278[92]*
c	7.144	4.212
c/a	1.639	0.579
Density, g cm^{-3}	—	2.37[92]

* According to other results[88–91], a = = 7.266 Å, c = 4.195 Å, c/a = 0.577.

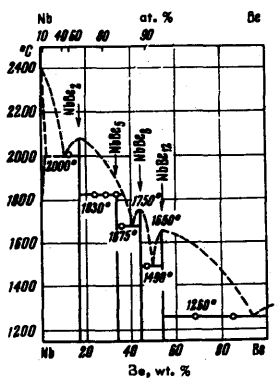


Fig. 9. Equilibrium diagram of the beryllium–niobium system.

A review of the data on the oxidation resistance of beryllium–niobium alloys has been given in a monograph[97]; that of the niobium beryllides proper has been investigated[59,79]. The moderate oxidation resistance of the beryllide $NbBe_2$ and its alloys with niobium was demonstrated[97]; the beryllides $NbBe_5$ and especially Nb_2Be_{17} and $NbBe_{12}$ are stable to oxidation, but the effect of a diminution in this stability in the middle temperature region noted for the higher beryllides of zirconium also occurs with the niobium beryllides, but is not so sharply expressed[79].

The niobium beryllides have relatively high hardness, which increases with the beryllium concentration[96–98]; Fig. 8 shows the temperature dependence of the hardness of $NbBe_{12}$ (data taken from Lewis[59]), the hardness minimum at 290° is still unexplained. The strength of the

TABLE 7. Properties of niobium beryllides.

Property	Beryllide			
	$NbBe_2$	$NbBe_5$	Nb_2Be_{17}	$NbBe_{12}$
Be content, wt. %	16.2	32.7	45.3	54.0
Structure	hex.	hex.	rhombohedral	tetr.
Structural type	—	—	Th_2Zn_{17}	$ThMn_{12}$
Lattice parameters, Å				
a	4.465[96]	—	5.599[93]	7.376[92]
c	7.302	—	α = 82.84°	4.258
c/a	0.628	—	—	0.577
Density, g cm^{-3}	—	—	3.28[93]	2.88[92]
Melting point, °C	2080[97]	~1900[97]	1750[97]*	1650[97]
			1704[79]	1700[59,79]
Heat of formation, kcal mole^{-1}	14.6±1.9[97]	46.4±3.8[97]	20.5±2[97]*	29.8±9.6[97]
Heat capacity per unit mass, cal g^{-1} deg^{-1}				
538°	—	—	—	0.39[75]
1482°	—	—	—	0.44[79]
Thermal conductivity, cal cm^{-1} s^{-1} deg^{-1}				
760°	—	—	0.0778[79]	0.0723[79]
1482°	—	—	0.0819[79]	0.0785[79]
Coefficient of thermal expansion (× 10^6) (27–1510°), deg^{-1}	—	—	8.83[79]	9.36[79]
Electrical resistivity, $\mu\Omega$ cm				
27°	—	—	—	55.6[79]
649°	—	—	—	166.7[79]
1260°	—	—	—	~200[79]
Microhardness, kgf mm^{-2}	—	—	1400[96]	1200[96]
			1430[98]	1900[98]
			1000[97]	1200[59]
Knoop hardness (50 g), kgf mm^{-2}	—	—	—	1100[81]
Vickers hardness	—	—	1060[98]	~480[98]
	—	—	1000[79]	500[79]
Young's modulus, kgf mm^{-2}				
20°	—	—	30100[79]	33 000[79]
871°	—	—	~28000[79]	28 000[79]
1260°	—	—	15500[59]	21 100[59]
1370°	—	—	~17500[79]	17 500[79]
			9800[59]	14 800[59]
1510°	—	—	—	14 100[59]
Bend strength, kgf mm^{-2}				
20°	—	—	21.7[79]	13.4[79]
982°	—	—	24.5[79]	10.5[79]
1260°	—	—	49.1[79]	31.5[79]
			27.4[59]	26.3[59]
1370°	—	—	44.2[79]	31.5[79]
			26.4[59]	25.4[59]
1510°	—	—	25.2[79]	13.4[79]
			11.5[59]	14.3[59]
Elongation in bending, %				
20°	—	—	0.1[79]	0.1[79]
871°	—	—	0.15[79]	0.1[79]
1370°	—	—	2.0[79]	1.0[79]
1510°	—	—	~7[79]	2.2[79]
Limit of proportionality, kgf mm^{-2}				
1260°	—	—	6.6[59]	—
1370°	—	—	2.5[59]	—
Ultimate compressive stress, kg mm^{-2}				
20°	—	—	—	140[79]
871°	—	—	—	91[79]
1370°	—	—	—	56[79]
Impact strength, kgf cm^{-2}				
20°	—	—	—	<1.15[59]
				0.115[83]
1260°	—	—	—	27.6[85]
Depth of oxidation after 100 h, mm				
1370°	—	—	0.01525[79]	0.0229[79]
1482°	—	—	0.0483[79]	0.0508[79]
Gain in weight in oxidation at 1260° for 100 h, mg cm^{-2}	—	—	2.6[70]	1.7[70]

* For "$NbBe_8$".

niobium beryllides is of the same order as that of the beryllides of other transition metals but at high temperatures the strength is somewhat higher than that of other beryllides. The heats of formation of all the beryllides shown in Fig. 9 and the temperature dependence of the diffusion coefficients for Be in Nb with formation of beryllide phases have been determined[96]. Table 7 summarises the properties of the niobium beryllides.

The niobium beryllides can be made by the methods of powder metallurgy[59,91]. Cherkashin and coworkers[91] sintered mixtures of the powders at 1000° in a protective medium (molten sodium chloride) for 5–24 h, followed by long (10 days) annealing at 400°. However, it is more customary to obtain them by melting the components together, for example, under argon in a high-frequency furnace[98].

TABLE 8. Properties of the highest tantalum beryllides.

Property	Beryllide	
	Ta_2Be_{17}	$TaBe_{12}$
Be content, wt. %	29.7	37.6
Structure	rhombohedral	tetr.
Structural type	Th_2Zn_{17}	$ThMn_{12}$
Lattice parameters, Å		
a	7.388 [58,65]	7.334 [97,100]
c	10.74	4.267
c/a	1.458	0.582
Density, g cm^{-3}	5.05 [79]	4.18 [93]
Melting point, °C	1988 [79]	1850 [59,79]
	1980 [59]	
Microhardness, kgf mm^{-2}	1120 [58,79]	—
Vickers hardness, H_v (load 2.5 kg)	1120 [79]	729 [79]
Young's modulus, kgf mm^{-2}		
20°	35000 [79]	18 900 [79]
871°	~28000 [79]	23 200 [79]
1260°	12000 [59]	16 900 [59]
1370°	~14000 [79]	23 800 [79]
	9100 [59]	9800 [59]
1510°	7000 [59]	7000 [59]
Bend strength, kgf mm^{-2}		
20°	21.0 [79]	21.7 [79]
982°	28.1 [79]	—
1260°	54.7	37.2 [79]
1370°	39.3 [79]	30.2 [79]
	—	25.3—37.4 [59] *
1480°	—	4.5 **
1510°	24.6 [79]	18.2 [79]
		18.6 [59]
Elongation in bending, %		
20°	0.1 [79]	0.1 [79]
871°	0.2 [79]	0.1 [79]
1371°	2.6 [79]	1.1 [79]
1510°	~5 [79]	2.6 [79]
Limit of proportionality, kgf mm^{-2}		
1370°	—	2.5—13.0 [59]
1510°	—	2.5 [59]
Ultimate compressive stress, kgf mm^{-2}		
20°	—	~105 [79]
871°	—	133 [79]
Depth of oxidation after 100 h, mm		
1371°	0.0076 [79]	0.0127 [79]
1482°	0.0229 [79]	0.0229 [79]
1649°	0.0763 [82] ***	—
704°	0.00025 [82]	—
871°	0.00125 [82]	—
Gain in weight during oxidation at 1260° for 100 h, mg cm^{-2}	—	18.0 [70]
Vapour pressure (× 10^3), mmHg		
1260°	1.7 [82]	—
1366°	5.6 [82]	—
1371°	5.2 [82]	—
Heat capacity per unit mass, cal g^{-1} deg^{-1}		
538°	0.22 [79]	0.27 [79]
1482°	0.26 [79]	0.30 [79]
Thermal conductivity, cal s^{-1} cm^{-1} deg^{-1}		
760°	0.0715 [78]	0.0732 [79]
1482°	0.0781 [79]	0.0897 [79]
Coefficient of thermal expansion (27–1510°) (× 10^6), deg^{-1}	8.72 [79]	8.42 [79]
Electrical resistivity, μΩ cm		
27°	—	43.5 [79]
649°	—	111.2 [79]
1260°	—	133.4 [79]

* For grain size 12 μm.
** For grain size 45 μm.
*** 10 h.

Tantalum beryllides. The investigation of alloys of beryllium and tantalum was started by Kaufmann and coworkers[11], and later Gladyshevskii and Kripyakevich[100] found the compound $TaBe_{12}$ with a tetragonal structure of $ThMn_{12}$ type (a = 7.322, c = 4.247 kX); simultaneously the same compound was established in another study[92]. Later, the compounds Ta_2Be, $TaBe_2$, Ta_3Be_2, $TaBe_3$, and Ta_2Be_{17} were reported[58,65,179]. The properties of the higher beryllides Ta_2Be_{17} and $TaBe_{12}$ have been studied best — they are refractory compounds with m.p. 1900–2000°, resistant to oxidation; unlike the zirconium and niobium beryllides, the tantalum beryllides are not subject to catastrophic oxidation in the middle-temperature region[79]. At high temperatures Ta_2Be_{17} has a vapour pressure of the same order as metallic beryllium[82]. Information about the properties of the lower tantalum beryllides is limited to what is known about their crystal structure[65]. $TaBe_2$ is cubic with lattice parameter a = 6.51 Å, Ta_3Be_2 is tetragonal with a = 6.5, c = 3.32 Å, $TaBe_3$ is rhombohedral with a = 4.53, c = 20.95 Å. The melting point of $TaBe_{12}$ is 1845° and its density 9.79 g cm^{-3}.[57] Table 8 gives the properties of the higher tantalum beryllides. The Be–Ta equilibrium diagram has not been studied.

Tantalum beryllides are obtained predominantly by powder metallurgy methods[59,100].

D. BERYLLIDES OF METALS OF SUBGROUP VIa

Chromium Beryllides. The diagram of the Be–Cr system was constructed by Edwards and Johnstone[101] up to 30 wt. % Be and shows the existence of a beryllide of composition $CrBe_2$ (Fig. 10), which had been found even earlier and identified by X-ray diffraction[23,102]. $CrBe_2$ is a phase of variable composition, homogeneous (according to Cherkashin and coworkers[91]) in a region extending at least from 70.9 to 77.5 at. % Be. A second compound has been established[90–92]: $CrBe_{12}$, which exists in a narrow concentration region at beryllium concentrations close to 92 at. %.[91] This compound is denoted by the symbol X in Fig. 10. Table 9 gives information about the properties of the chromium beryllides.

Chromium beryllides have been made by melting the components in pure argon[91,101]; they can also be obtained successfully by powder metallurgy[59].

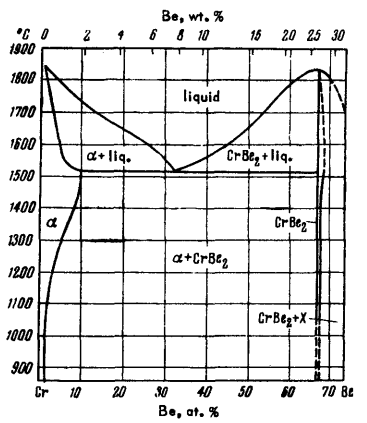


Fig. 10. Equilibrium diagram of the beryllium–chromium system.

TABLE 9. Properties of chromium beryllides.

Property	Beryllide	
	$CrBe_2$	$CrBe_{12}$
Be content, wt. %	25.8	68.1
Structure	hex.	tetr.
Structural type	$MgZn_2$	$ThMn_{12}$
Lattice parameters, Å		
a	4.259 [101]	7.234 [89–91]
c	6.975	4.176
c/a	1.638	0.577
Density, g cm^{-3}	4.34 [89]	2.44 [89]–2.51 [91]
Melting point, °C	1845 [101]	—
	1840 [89]	
Emissivity (λ = 650 nm, 800–1800°)	0.76 [73]	—
Microhardness, kgf mm^{-2}	1288 [89]	—
Gain in weight on oxidation at 1260° for 100 h, mg cm^{-2}	2.4 [70]	—

Molybdenum beryllides. Only the molybdenum-rich part of the Be–Mo diagram (up to 7 wt. % Be) has been constructed [1]. The existence of two compounds in the system has been rather reliably established: $MoBe_2$ [23,103] and $MoBe_{12}$ [89,91,100,104]; in one work [103] the latter was given the composition $MoBe_{13}$, but this was later corrected by Raeuchle and Batchelder [104] and also by Gladyshevskii and Kripyakevich [100], who confirmed the composition $MoBe_{12}$. Furthermore, there is proof [58] of the compound Mo_3Be with a cubic structure of type O_h^3 with a = 4.89 Å and also a compound richer in beryllium $MoBe_{20}$ with structure $O_h^7(T_h^7)$ and a = 11.64 Å. A later investigation [105] confirmed the existence of this phase, but its composition was described by the formula $MoBe_{22}$ (instead of $MoBe_{20}$) with a structure of $ZrZn_{22}$ type, parameter a = 11.634 Å. The compounds Mo_3Be and $MoBe_{22}$ have hardly been studied, therefore Table 10 gives the properties for $MoBe_2$ and $MoBe_{12}$ alone.

Molybdenum beryllides can be made by melting the components in BeO crucibles under argon in a high-frequency furnace [100] and also by powder metallurgy [59]. The diffusion reaction of beryllium in molybdenum has been investigated [106] and it was shown that the phases $MoBe_2$, $MoBe_{12}$, and $MoBe_{22}$ are formed: $MoBe_2$ predominates up to 1000°, a mixture of $MoBe_2$ and $MoBe_{12}$ from 1000° to 1150°, and the phase $MoBe_{22}$ appears at higher temperatures. The layer on molybdenum consists successively of

TABLE 10. Properties of molybdenum beryllides.

Property	Beryllide	
	$MoBe_2$	$MoBe_{12}$
Be content, wt. %	17.4	53.2
Structure	hex.	tetr.
Structural type	$MgZn_2$	$ThMn_{12}$
Lattice parameters, Å		
a	4.442 [103]	7.271 [104]
c	7.356	4.234
c/a	1.658	0.585
Density, g cm^{-3}	5.92 [103]	3.02 [55]
	6.12 [89]	—
Melting point, °C	1840 [59]	~1700 [59],
Microhardness, kgf mm^{-2}	—	950 [57,58]
Young's modulus, kgf mm^{-2}		
1260°	—	10 500 [59]
1370°	—	8400 [59]
1510°	—	700 [59]
Gain in weight on oxidation at 1260° for 100 h, mg cm^{-2}	2.6	—

TABLE 11. Properties of the tungsten beryllides.

Property	Beryllide		
	WBe_2	WBe_{12}	WBe_{22}
Be content, wt. %	8.95	37.3	52.1
Structure	hex.	tetr.	cub.
Structural type	$MgZn_2$	$ThMn_{12}$	$ZrZn_{22}$
Lattice parameters, Å			
a	4.446 [23]	7.362 [92]	11.631 [58,105]
c	7.289	4.216	—
c/a	1.63	0.573	—
Density, g cm^{-3}		4,25 [92]	
Microhardness, kgf mm^{-2}	2188 [107]	1145 [107]	1080 [107] *

* For "WBe_{24}".

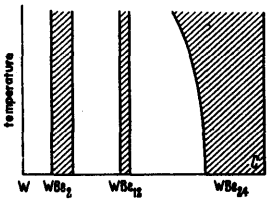


Fig. 11. Equilibrium diagram of the beryllium–tungsten system.

beryllide phases from the lowest beryllides to the highest; the diffusion proceeds preferentially through the beryllide layers.

Tungsten beryllides. In the beryllium–tungsten system, analogous to the beryllium–molybdenum system, the existence of the following beryllide phases has been established with sufficient reliability: WBe_2, [23,91,178] WBe_{12}, [91,62,100] and WBe_{22}, [58,105], the main properties of which are given in Table 11. Thermal diffusion has been investigated [107] in the Be–W system, the formation of three phases being established: WBe_2, WBe_{12}, and WBe_{24}; the last is evidently identical with the phase WBe_{22} which has been well identified by X-ray diffraction. According to the results, all three phases have homogeneity regions: the widest is the "WBe_{24}" phase, WBe_2 is narrower, and WBe_{12} is the narrowest (Fig. 11). The temperature dependence of diffusion coefficient in each phase has been determined approximately:

$$D_{WBe_2} = 1.10\times10^{-4}\exp(-3315/RT),$$
$$D_{WBe_{12}} = 2.36\exp(-66\,950/RT),$$
$$D_{<WBe_{24}>} = 1.175\times10^{-3}\exp(-33\,800/RT).$$

It is reported [20] that on heating a compacted mixture of tungsten and beryllium powders, reaction between them to form intermetallic compounds begins at 880°; in the diffusion interaction of beryllium powder with the compact metal at 1100° for 4 h, all the beryllide phases are formed [107].

E. BERYLLIDES OF METALS OF SUBGROUP VIIa

Manganese beryllides. The solubility of beryllium in manganese is low [11,108]. According to some [23,93] there is a beryllide $MnBe_2$ of variable composition of $MgZn_2$ structure type; this structure type was also described by Hume-Rothery and Raynor [109]. A second compound [89,91]

TABLE 12. Properties of manganese beryllides.

Property	Beryllide		
	$MnBe_2$	$MnBe_8$	$MnBe_{12}$
Be content, wt. %	25.4	55.9	66.8
Structure	hex.	cub.	tetr.
Structural type	$MgZn_2$	$MgCu_2$	$ThMn_{12}$
Lattice parameters, Å			
a	4.239 [93]	5.931 [91]	7.276 [93]
c	6.923	—	4.256
c/a	1.632	—	0.585
Density, g cm^{-3}	—	—	2.40 [93]

has the composition $MnBe_8$ (at 400°) with a homogeneity region which broadens with temperature (at 1100° this region extends from $MnBe_2$ to $MnBe_{12}$); this beryllide has a cubic lattice of $MnCu_2$ type. Batchelder and Raeuchle [92] found the presence of a third beryllide $MnBe_{12}$.

It has been shown [20] that the reaction between compacted manganese and beryllium powders starts at 800°; the beryllides $MnBe_2$ and $MnBe_8$ have been obtained [91] by melting the components in a quartz container under argon. Table 12 gives information on the properties of manganese beryllides.

Technetium beryllides. There is no information about technetium beryllides.

Rhenium beryllides. According to Misch [23], the beryllium–rhenium system contains the compound $ReBe_2$; a beryllium-rich phase, which has been ascribed the composition $ReBe_{20}$, has been found [58]. It is evident that the true composition of this phase is $ReBe_{22}$, analogous to the corresponding phases of molybdenum and tungsten [105], with a cubic structure of the $ZrZn_{22}$ cubic type, lattice parameter [58] a = 11.64 Å.

The composition of the phase $ReBe_{22}$ has been established [110]; this beryllide is made by heating mixtures of rhenium and beryllium powders (in stoichiometric proportions) in BeO crucibles at 1650° for ~5 min under argon at a pressure of 0.5 atm. The lattice parameter is a = = 11.561 Å. In this beryllide the beryllium atoms form a complex skeletal polyhedron.

The beryllide $ReBe_2$ has a hexagonal lattice of $MgZn_2$ type with a = 4.354, c = 7.101 Å, c/a = 1.631. [23] $ReBe_2$ is prepared by heating pressed mixtures of the powders of the components under argon at 1200° and melts at a temperature above 2000°. The emissivity of $ReBe_2$ at 800–1600° (λ = 650 nm) is 0.80. [73]

F. BERYLLIDES OF METALS OF GROUP VIII

1. Beryllides of Metals of the Iron Group

Iron beryllides. The equilibrium diagram of the beryllium–iron system, constructed from published information [111,112] is shown in Fig. 12. Three beryllides exist in the system: $FeBe_2$, [113,114] $FeBe_5$, [113,114] and $FeBe_{12}$. [92,114] The beryllide $FeBe_5$ has high hardness and is ferromagnetic [112] with a Curie point at 643°.

The phases $FeBe_2$ and $FeBe_5$ have wide homogeneity regions [114], the $FeBe_{12}$ phase according to previous data [114] has the composition $FeBe_{12}$ and a hexagonal structure, although Batchelder and Raeuchle [92] conclusively confirmed its composition as $FeBe_{12}$ and a face-centred tetragonal structure.

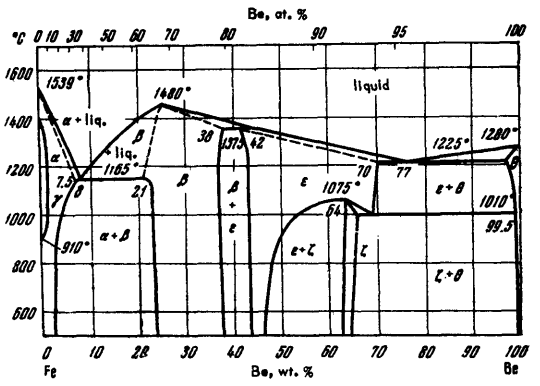


Fig. 12. Equilibrium diagram of the beryllium–iron system.

Table 13 gives the main information about the properties of the iron beryllides. The maximal solubility of Fe in Be is 0.0092 at.% (5.46 wt.%) at the eutectic temperature 1225°. [115]

Cobalt beryllides. After Köster and Schmid [116] who worked out the part of the Be–Co diagram up to 10 wt.% Be, Venturello and Burdese proposed the complete diagram of this system (Fig. 13). [117] In accordance with this diagram, the system contains the compounds CoBe [23,117,118] and Co_5Be_{21}, [117] however, according to Batchelder and Raeuchle [92] the lines of the X-ray diagram of this phase can

TABLE 13. Properties of the iron beryllides.

Property	Beryllide		
	$FeBe_2$	$FeBe_5$	$FeBe_{12}$
Be content, wt. %	24.5	44.6	66.3
Structure	hex.	cub.	tetr.
Structural type	$MgZn_2$	$MgCu_2$	$ThMn_{12}$
Lattice parameters, Å			
a	4.212 [113]	5.878 [113]	7.253 [92]
c	6.834	—	4.232
c/a	1.62	—	0.583
Density, g cm^{-3}	4.65 [113]	3.272 [114]	2.45 [89]
Melting point, °C	1480 [111,112]	~1375 [111,113]	~1300 [111,113,114]

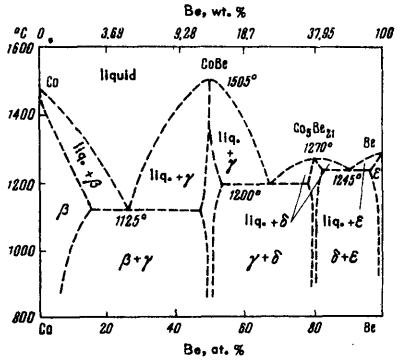


Fig. 13. Equilibrium diagram of the beryllium–cobalt system.

TABLE 14. Properties of the cobalt beryllides

Property	Beryllide		
	CoBe	$CoBe_2$	$CoBe_{12}$
Be content, wt. %	13.26	43.4	65.1
Structure	b.c.c.	f.c.c.	tetr.
Structural type	CsCl	$MgCu_2$	$ThMn_{12}$
Lattice parameters, Å			
a	2.615 [118]	5.852 [92]	7.237 [92]
c	—	—	4.249
c/a	—	—	0.587
Density, g cm^{-3}	—	—	2.49 [92]
Melting point, °C	1505	—*	—

* The melting point of the "Co_5Be_{21}" phase is reported [117] to be 1270°.

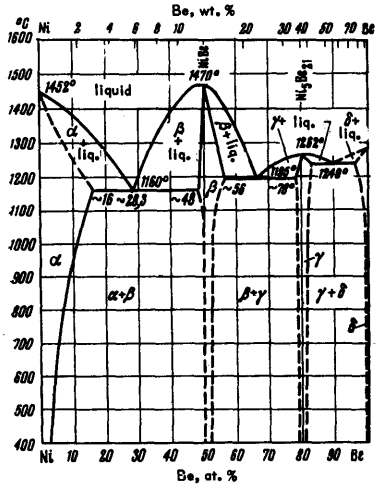


Fig. 14. Equilibrium diagram of the beryllium–nickel system.

be ascribed to $CoBe_{12}$ and $CoBe_5$, analogous to the corresponding iron beryllides, which seems more probable. CoBe is reported [23] to have an ordered b.c.c. lattice and Co_5Be_{21} has been investigated repeatedly [1,15,16]; Jahn [119] has given its equilibrium diagram in the most complete form (Fig. 14). nents under inert gas in an electric resistance furnace. Table 14 gives the main properties of the cobalt beryllides.

On heating mixtures of beryllium and cobalt powders, reaction between them starts at 670°. [20]

Nickel beryllides. The beryllium–nickel system has been investigated repeatedly [1,15,16]; Jahn [119] has given its equilibrium diagram in the most complete form (Fig. 14). According to this diagram the system contains the compounds NiBe and Ni_5Be_{21}, which have not very wide homogeneity regions and melt congruently. The maximal solubility of nickel in beryllium is 4.93 at.% at the eutectoidal temperature, 1065°. [115] The existence of Ni_5Be_{21} is probably doubtful (as is the analogous compound in the Be–Co system) but there have been no investigations in this direction and a phase of this composition has to be accepted at present. The structures of NiBe and Ni_5Be_{21} were investigated by Misch [113] and by Losana and Goria [120] and the results of the latter workers are considered [1] to be the most reliable data on the lattice parameters. The NiBe

TABLE 15. Properties of nickel beryllides.

Property	Beryllide	
	NiBe	Ni_5Be_{21}
Be content, wt. %	13.31	39.21
Structure	b.c.c.	cub.
Structural type	CsCl	Ni_5Zn_{21} (γ-brass)
Lattice parameter, Å		
a	2.621 [120]	7.625 [120]
Melting point, °C	1472 [119]	1262 [119]

phase is responsible for the precipitation hardening during the aging of Be–Ni alloys [121]. Beryllium–nickel alloys are made by melting in an inert gas or under a flux layer in BeO or MgO crucibles [15]; reaction between nickel and beryllium powders is reported [20] to start at 732°. Table 15 gives the properties of nickel beryllides.

2. Beryllides of Metals of the Platinum Group

Ruthenium beryllides. The existence of $RuBe_2$ has been established [23], but the precise composition and structure of this compound have not been determined. The compound Ru_3Be_{17} has been observed [119] on heating a mixture of ruthenium and beryllium powders in a BeO crucible under argon at 1480°. It was found to be f.c.c. with a = 11.337 Å, and to be isomorphous with the corresponding osmium compound. Its melting point is ≃ 1635°. [122]

Rhodium beryllides. Misch [23] indicated the possibility of the existence of $RhBe_2$ or another compound with Rh : Be = 1 : 2; its X-ray diagram is analogous to that of $IrBe_2$.

Palladium beryllides. Fig. 15 shows the equilibrium diagram of the beryllium–palladium system after Winkler [22]. There is a large number of beryllides in this system: there are five between palladium and the compound PdBe and at least another two between PdBe and beryllium; $PdBe_5$ and $PdBe_{12}$. According to Misch [23], PdBe has the ordered CsCl type of structure with a = = 2.813 kX; these results were confirmed by Belov [123]. $PdBe_5$ has the $MgCu_2$ type f.c.c. structure (like $FeBe_5$ [23,24]) with a = 5.969 Å, [24] pyknometric density 4.56, X-ray density 4.62 g cm^{-3}. $PdBe_5$ does not exhibit superconductivity up to 0.30°K. Yet another phase has been reported [24],

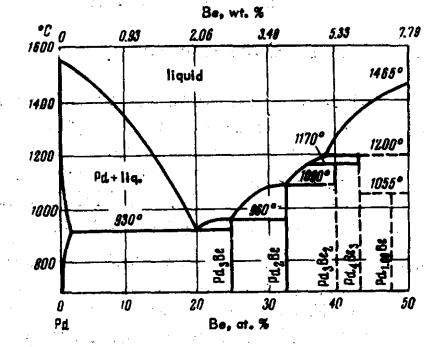


Fig. 15. Part of the equilibrium diagram of the beryllium–palladium system.

$PdBe_{12}$, isomorphous with $MoBe_{12}$, body-centred tetragonal, with a = 7.271 Å, c = 4.251 Å, c/a = 0.585, X-ray density 3.18 g cm^{-3}. The melting points are reported[22] to be: Pd_3Be 960°, Pd_2Be 1090°, Pd_3Be_2 1250°, Pd_4Be_3 1330°, $Pd_{13}Be_{12}$ 1450°, and PdBe 1465°.

Osmium beryllides. According to Misch[23], osmium forms the compound $OsBe_2$ with beryllium.

Iridium beryllides. According to the same author[23], there is the compound $IrBe_2$, the structure of which has not been established,

Platinum beryllides. Platinum and beryllium form the compounds $Pt_{15}Be$ and $PtBe_{12}$. $Pt_{15}Be$ was observed[124] and obtained by reducing a mixture of beryllium oxide and platinum powder at 1150°; it is hexagonal with a = 22.13, c = 27.12 Å. The compound $PtBe_{12}$ has[24] a face-centred tetragonal structure of $MoBe_{12}$ type with a = = 7.237, c = 4.252, c/a = 0.588, X-ray density 4.53 g cm^{-3}. Furthermore, in the same work[24] the possibility of there being a beryllide $PtBe_5$ was mentioned, f.c.c. with a = = 6.004 Å. According to older information[23] there is also a phase Pt_5Be_{21} with the structure of a deformed γ-brass (γ-Ni_5Zn_{21} type). However, the beryllides whose existence has been found most probably and reliably are $Pt_{15}Be$ and $PtBe_{12}$.

G. BERYLLIDES OF THE ACTINIDES

Thorium beryllides. The beryllium–thorium equilibrium diagram, earlier worked out only partially[1] has recently been supplemented considerably[125] (Fig. 16). This system contains the compound $ThBe_{13}$ (92.86 at.% Be) observed earlier by Baenziger and Rundle[40]. Babaeva and Kuznetsova[125] obtained it, like other alloys of the system, by melting 99.3% beryllium with 99.7% thorium in an arc furnace with a tungsten electrode and cooled copper hearth; the atmosphere was chemically pure argon. This compound is f.c.c. ($NaZn_{13}$ type) with a = 10.395 Å[40] (Babaeva and Kuznetsova[125] give a = 10.383 Å). The $ThBe_{13}$ structure has been confirmed[126]. $ThBe_{13}$ melts at ~ 1930°[125] and has good resistance to oxidation in a stream of dry air[79]. The microhardness of $ThBe_{13}$ is[125] ~ 950 kgf × × mm^{-2}. Reaction between compacted beryllium and thorium powders starts at 705°.[20]

Uranium beryllides. The equilibrium diagram of the beryllium–uranium system was developed mainly by Buzzard[127] and Hansen and Anderko's interpretation[16] is shown in Fig. 17. The system includes the compound UBe_{13} with an $NaZn_{13}$ type f.c.c. lattice. Reaction between uranium and beryllium in the form of compacted powders starts at 355°;[20] the compound UBe_{13} can be isolated from uranium-rich alloys by electrolytic dissolution in 10% chromic acid.

However, the main methods of obtaining UBe_{13} are powder metallurgy and vacuum induction melting[128]. In the former, uranium (or uranium hydride UH_3) and beryllium powders are used and the mixtures are sintered at 950–1050° (when beryllium and finely dispersed uranium powders are sintered in pure hydrogen the sintering temperature usually is 1300° and sometimes it reaches 1550°). Vacuum induction melting is done at 1130° (in a quartz container in argon at 1 atm) with subsequent addition of a 10% excess of beryllium (to compensate for the loss of beryllium by vaporisation) and brief homogenisation annealing at 1200–1300°.[128] For the preparation of compact articles of UBe_{13}, the products from sintering or melting are finely ground, pressed in a hydraulic press into blanks of the required shape, which are then sintered in argon at 1550° to give articles with a density > 97%.

Table 16 gives the principal physical properties of uranium beryllide; it must also be added that it exhibits marked brittleness[127]. The microhardness for the "UBe_{12}" phase is reported[59] to be 1300 kgf mm^{-2}.

In chemical respects UBe_{13} reacts with oxygen more slowly than do uranium carbides, nitrides, borides, and metallic uranium itself; it is especially resistant to oxidation at temperatures up to 500°. The oxidation at first follows a linear law and then slowly, by an exponential law, $k = 1.98 \times 10^8 \exp(-26\,200/RT)$ mg cm^{-2} s^{-1}. UBe_{13} behaves similarly with nitrogen, $k = 5.1 \times 10^4 \exp(-25\,800/RT)$, and with water vapour, $k = 5.46 \times 10^4 \exp(-25\,800/RT)$. The change in weight after treatment with water at 100° is 2.2 mg cm^{-2}, in addition to which water brings about rather marked intercrystalline corrosion of uranium beryllide.

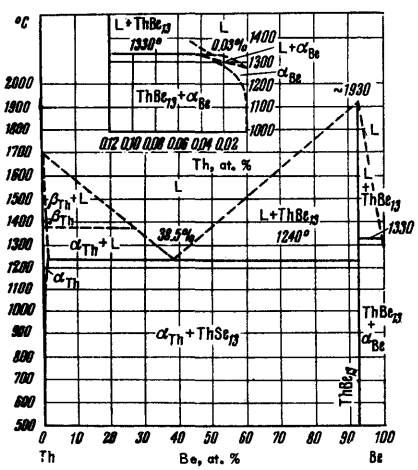


Fig. 16. Equilibrium diagram of the beryllium–thorium system.

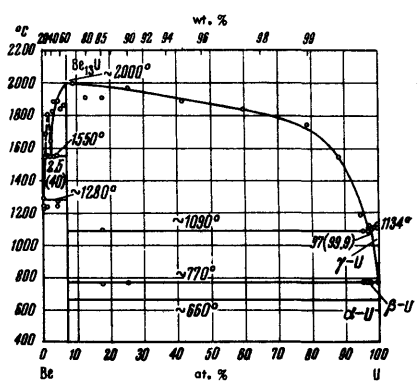


Fig. 17. Equilibrium diagram of the beryllium–uranium system.

TABLE 16. Properties of uranium beryllide.

Property	UBe_{13}
Be content, wt. %	32.9
Structure	f.c.c.
Structural type	$NaZn_{13}$ [40]
Lattice parameter, Å	10.256 [40]
Density, g cm^{-3}	4.373 [40]
Melting point, °C	~2000 [129]
Heat of formation, kcal $mole^{-1}$	37.8 [128]
	39.3 [129]
Thermal conductivity, cal cm^{-1} s^{-1} deg^{-1}	
100°	0.050 [128]
300°	0.058
500°	0.062
650°	0.064
Coefficient of thermal expansion × 10^6 (20°–1000°), deg^{-1}	16.7 [128]
Knoop microhardness, kgf mm^{-2}	
fused	960 [128]
sintered	1155 [128]

Neptunium beryllides. In the reduction of neptunium fluoride by beryllium in a vacuum at 1100–1200°, the compound $NpBe_{13}$ (33.09% Be) was obtained [130]. This is isomorphous with the corresponding phases of thorium and uranium and is f.c.c. ($NaZn_{13}$ type) with a = 10.266 (on the beryllium side) to a = 10.256 Å (on the neptunium side), that is, there is some region of homogeneity. The melting point is above 1400°.

Plutonium beryllides. Plutonium also forms a compound with beryllium of composition $PuBe_{13}$ (32.63% Be) (Fig. 18) [131–133]; it is f.c.c. ($NaZn_{13}$) with a = 10.284 (on the beryllium side) to a = 10.278 Å (on the plutonium side) [130] in the limits of the homogeneity region; according to Konobeevskii [131] a = 10.274 Å. The microhardness of $PuBe_{13}$ [131] is 947 kgf mm^{-2}, the density [131,132] 4.35–4.36 g × × cm^{-3}. The compound is an active source of neutrons [131]. Its m.p. is 1600° and heat of formation 35.7 ± 3.3 kcal × × $mole^{-1}$. [134] $PuBe_{13}$ can be made by melting a mixture of pieces of metallic plutonium and beryllium powder in BeO crucibles under argon in a high-frequency furnace [135].

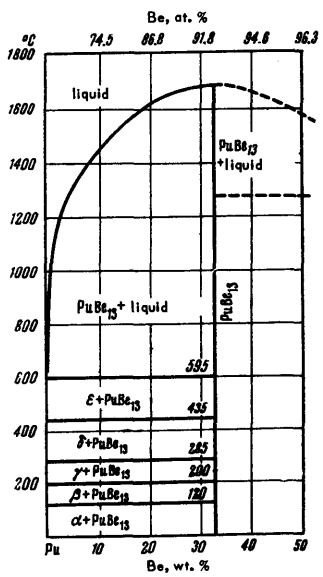


Fig. 18. Part of the equilibrium diagram of the beryllium–plutonium system.

The beryllide $PuBe_{13}$ corresponds to the maximal neutron emission in the Be–Pu system, 67 × 10^6 neutrons × × kg^{-1} s^{-1}. [136]

Americium beryllides. Runnals and Boucher [137] prepared a beryllide, $AmBe_{13}$, by reducing AmF_3 with beryllium in a vacuum (the reaction starts at 900° and proceeds rapidly at 1125°). Like the other beryllides of this composition, it is f.c.c.; a = 10.283 Å (on the beryllium side of the homogeneity region). Its m.p. is 1375°, density 4.376 g cm^{-3} (according to a review [138] 4.35 g cm^{-3}). It has mainly been studied as a source of neutrons [125].

IV. COMPLEX BERYLLIDES

In addition to two-component beryllides, several multicomponent complex beryllides have now been discovered and investigated; they are of considerable scientific and practical interest.

Nowotny and coworkers [88] discovered the ternary beryllides ZrBeSi and HfBeSi, with lattices of the nickel arsenide type ($B8_2$). The compound ZrBeSi has a certain region of homogeneity, within the limits of which the lattice parameters vary from a = 3.722, c = 7.232 Å (at the silicon-rich side) to a = 3.718, c = 7.217 Å (at the beryllium-rich side); for HfBeSi the lattice parameters are equal§: a = 3.693, c = 7.135 Å.

It has been found [139] that there is a continuous series of solid solutions between the compounds $ThBe_{13}$ and UBe_{13} in the Be–Th–U ternary system. An investigation of the physicochemical properties of the solid solution of composition $(Th_{0.9}U_{0.1})Be_{13}$ showed [140] that on oxidation in air at 482° the change in weight of specimens of this alloy is from 0.234 mg cm^{-2} (oxidation time 8 h) to 0.623 mg cm^{-2} (oxidation time 24 h). The physico-technical properties of alloys of (Th, U)Be_{13} with uranium have been described in detail [79].

A ternary compound of the idealised composition AlBeB has been observed [141] in the Al–B–Be system; it is a dark, finely crystalline substance, which crystallises with an antifluorite lattice, the sites of the metal atoms in which are occupied by ordered atoms of Be and Al.

The lattice parameters vary between 4.952 and 4.925 Å, owing to the partial formation by this ternary beryllide of solid solutions with Be_2B.

In the Be–Co–Mn system [142] a ternary phase of composition $MnCo_{0.8}Be_{1.2}$ is found, with the structure of a cubic Laves phase ($MgCu_2$ type) and a = 6.20 Å.

Several complex beryllide phases have been described in reviews [143,144]. In ternary systems with participation of binary beryllides the equilibrium has been described in the systems Be–Fe–P [145] (Fe_2P–$FeBe_2$ and Fe_3P–$FeBe_2$ sections); Be–C–U [146] (UC–Be_2C section); Al–Be–Zr [147] ($ZrBe_9$–Zr_4Al_3, $ZrBe_9$–$ZrAl_2$, $ZrBe_2$–$ZrAl_2$, $ZrBe_{13}$–$ZrAl_{13}$, $ZrBe_{13}$–Al, and $ZrAl_3$–Be sections); Be–Fe–Si [148] (compounds were found: FeSiBe, melting congruently at 1160° and $FeSiBe_3$, melting congruently at 1240°); Be–Cu–Mn [149,150] (Cu–$MnBe_2$); Be–Cu–Ti [150] (Cu–$TiBe_2$ section); Be–Co–Cu [150] (Cu–CoBe section); Cu–$CrBe_2$ [150]; Cu–$FeBe_2$ [150]; Al–Be–Cu [151]; and Be–Cu–Ni [152] (Cu–NiBe section).

§ Presumably on each side of the homogeneity region (Ed. of Translation).

V. STRUCTURE AND PHYSICOCHEMICAL NATURE OF THE BERYLLIDES

Hardly anything has been published about the principles governing the formation of alloys of beryllium and of its compounds with other elements, if one discounts the very general contributions dealing mainly with the possibility of the formation of solid solutions by beryllium [153].

Because the beryllium atom is larger than the boron atom Parthé [154] considers that the beryllides should not be so refractory as the corresponding borides: he thinks that the highest melting points should be expected from the compounds of beryllium with the metals of the sixth period, and bearing in mind the small number of valence electrons of beryllium, with the metals of Groups V and VI, that is, with tantalum and tungsten.

In considering the physicochemical nature of the beryllides it is of prime importance to allow for the peculiar electronic structure of the beryllium atom. The electronic configuration of the beryllium atom is $1s^2 2s^2$; in the formation of crystals, beryllium and compounds are characterised by a single-electron $s \rightarrow p$ promotion [155] with the formation of the electronic configuration $1s^2 2s 2p$. The presence of sp valence electrons brings about the formation of relatively strong covalent bonds between the beryllium atoms, both in the crystal lattice of the metal itself and in the lattices of its compounds with other elements, particularly with metals. In the last instance the tendency of the beryllium atoms to form a covalent bond with one another brings about a statistical diversion to this bond of electrons from the M–Be and M–M bonds, which leads to their corresponding weakening. Corresponding to the formation of a covalent bond between the beryllium atoms, the latter tend to associate in the crystal lattices of the beryllides into more or less intricate structural complexes.

Above all, the peculiarities of the electronic structure of the beryllium atom and its high capability for $s \rightarrow p$ promotion with the formation of a stable sp configuration of the electrons shows in the properties of beryllium itself. As the sp configuration is energetically somewhat more stable than s^2, then on thermal excitation the original $s^2 \rightleftharpoons sp$ equilibrium is shifted to the right and with the prevalence of statistical weight of the sp configuration the crystal structure of the beryllium can be changed, which is also observed in reality [156¶]. The fact that the temperature of this $\alpha \rightarrow \beta$ transformation is close to the melting point of beryllium shows that the sp configuration is not much more stable than the s^2 configuration; this requires a rather high temperature to create the prevailing statistical weight of the sp states and the corresponding modification transformation. Beryllium exhibits the highest heat of fusion among the metals, which is undoubtedly brought about by the presence in it of sp states; this explains the high electronic work function of beryllium, which is not characteristic for ordinary metals with s valence electrons. The tendency of the sp configurations already existing in beryllium to trap electrons and to the formation of the sp^2 and especially sp^3 configurations, which are more stable energetically, brings about both the exceptional tendency of beryllium to contamination by various impurities and the difficulty of removing them, and also the high brittleness of the contaminated beryllium, which in this state contains an electron configuration analogous in energetic state and type to the electron configurations in diamond, silicon, and germanium. The chemical properties of beryllium, which tends, for example, to form compounds of both basic and acidic type, are also evidence of the dual nature of this element, which possesses simultaneously the attributes of a metal (on account of the s electrons) and of a non-metal (on account of the known statistical weight of the sp states).

Just the presence of the sp states, which tend to be stabilised into the states of a higher energetic order sp^2, sp^3, determines the formation by the beryllium atoms of complex elements of structure in compounds, especially with partners, the atoms of which are donors of electrons.

Alkali metal beryllides have the composition MBe_2 ($MgCu_2$ type, characterised by there being in each octant a regular tetrahedron of beryllium atoms, so that their centroids are at the centres of the octants) [157]. Hence the stable tetrahedral configuration of beryllium atoms corresponding to the electronic configuration sp^3 is realised in this structure, for the creation of which the abstraction of electrons from an alkali metal is necessary. In turn the ability of alkali metals to transfer electrons to the Be–Be bond is determined by their ionisation potentials, which decrease from lithium (5.37 eV) to caesium (3.36 eV). Evidently therefore a beryllide has been observed first for potassium [11,158] which has a low ionisation potential (4.32 eV) among those alkali metals whose compounds have been longest and most carefully investigated (Li, Na, K). Possibly, lithium and sodium beryllides either are not formed at all, because of the high ionisation potentials of these metals, or are formed under conditions of strong excitation (high temperatures, strong electrostatic or magnetic fields, electrolysis); on the other hand, the formation of rubidium and caesium beryllides should proceed relatively easily and the fact that it has not yet been observed may be due to the compounds of these rare metals having been insufficiently studied.

On the other hand the possibility of the formation of alkali metal beryllides can be interpreted by assuming that in the formation of metallic crystals from alkali metal atoms s^2 configurations are formed from the valence electrons of the atoms, whereas for the formation of the beryllides the destruction of these configurations is necessary, which is especially easy to complete for the alkali metals starting with potassium owing to the partial promotion of s electrons to the completely vacant d states. Since this promotion increases with the principal quantum number of the d states it is obvious that the most favourable conditions for the formation of a beryllide is with potassium, for which this transition is sharply expressed for the excitation of the s^2 configuration but does not lead to preferential promotion of the s electrons into the d states, owing to the low principal quantum number of the latter; therefore the transfer of some of the s electrons to the beryllium atoms is possible.

The diversion of alkali metal electrons to the Be–Be bond and the formation of covalently bound complexes of beryllium atoms in the beryllide structures should confer on the alkali metal beryllides the character of ionic-covalent compounds with strong asymmetric distribution of the electron density — to sharp displacement of the electrons of the bonds in the direction of the complexes of beryllium atoms. Evidently this asymmetry should increase with a fall in the ionisation potential of the metal

¶ Here, in accordance with the high energetic stability of the sp configuration, the β modification of beryllium based upon it is cubic, whereas the α modification which is based upon the s^2 states is hexagonal, that is, has a lower symmetry.

and with a decrease in the statistical weight of the s^2 configurations; one should expect a parallel reduction in the thermal stability of the beryllides in their disproportionation with formation of groups of beryllium atoms in the vapour state, probably in this instance analogous to the groupings of carbon atoms in the disproportionation of some carbides. It can also be suggested that in these beryllides regions of homogeneity are almost absent or are very narrow.

Beryllides of the metals of the copper subgroup. In the formation of the beryllides of the metals of this subgroup there again appears a tendency for beryllium atoms to form sp electronic configurations and corresponding structural elements of beryllium atoms in the lattices of the beryllides; this tendency is combined with the existence of a free s^1 electron of the metal which is comparatively easily transferred to the beryllium atoms. In this connection, copper ($3d^{10}4s^1$, ionisation potential 7.67 eV) readily forms beryllides CuBe, $CuBe_2$, $CuBe_3$ with a growing bridge structure of beryllium atoms in the crystal lattices; in particular, whereas in the structure of CuBe (closely resembling FeSi) the beryllium atoms are isolated, in the $CuBe_2$ structure they form regular tetrahedra situated in the vacancies of the octants of the $MgCu_2$ structure, alternating with magnesium atoms, which are arranged in a diamond-type structure [157]. The greater ease of removal of electrons from the silver atom ($4d^{10}4f^05s^1$, ionisation potential 7.58 eV) facilitates the formation of covalent bonds between the beryllium atoms and shifts the concentration of beryllium in the corresponding beryllides towards higher values $AgBe_2$ and $AgBe_{12}$. Gold forms an even greater number of beryllide phases (Table 1).

In considering the number and nature of the beryllide phases formed by the metals of the copper subgroup, it must be borne in mind that whereas for copper the s electrons can be transferred to a partner without the destruction of the stable d^{10} configuration, with silver and gold the completely vacant corresponding $4f$ and $5f$ states appear, which can bring about partial abstraction of the electrons from the d^{10} configurations with destruction of the latter, and on going from silver to gold the probability of the transfer of the d electrons to the f states should increase owing to an increase in the energetic stability of the f states with rise in the principal quantum number [159]. However, the energetic stability of the d^{10} configuration rises simultaneously and to a greater extent, therefore metallic gold, in particular, has a melting point higher than that of silver, but lower than that of copper, for which (despite the low principal quantum number of the d electrons) the d electrons are not removed to the f states. In connection with the breakdown of the d^{10} configuration of silver and gold the loss of their stability due to the $d \rightarrow f$ transitions creates the possibility of both an increased transfer (compared with copper) of electrons of beryllium to form intricate structural complexes of them with high statistical weight of the sp^3 configurations, and also the possibility of covalent association of the silver or gold atoms with a tendency to the reduction of the destroyed d^{10} states, which brings about for gold the appearance of the lower beryllide phases Au_3Be and Au_2Be†. Analogously, it is to be expected that for silver also lower beryllide phases should be observed.

† On the contrary, in the higher beryllides of the $AuBe_{12}$ type the statistical weight of the d^5 configurations in the gold sublattice is probably very great.

Beryllides of magnesium and the alkaline earth metals. In accordance with the peculiarities of the structure of $NaZn_{13}$ type in which the only beryllium–magnesium compound ($MgBe_{13}$) crystallises, some of the beryllium atoms form icosahedra, the others are at the vertices, the centres of the faces, edges, and in the centre of the cell, and the magnesium atoms are isolated in the centres of the eight cubes into which the cell is divided. Hence in the $MgBe_{13}$ structure the structural motif of the beryllium atoms is particularly strongly expressed.

Beryllium, magnesium, and the alkaline earth metals (calcium, strontium, barium, and radium) have the s^2 configuration of the outer (valency) electrons, which is capable of being converted into the sp configuration by $s \rightarrow p$ promotion. As the stability of the sp states rises with fall in principal quantum number of the sp electrons, the probability of the $s \rightarrow p$ promotion with the formation of these states is much greater, as was shown above for beryllium. For magnesium, owing to the lower stability of the sp states the probability of the $s \rightarrow p$ promotion decreases, nevertheless magnesium also retains the feature of a certain dualism of properties, which leads to its separation from the group of alkaline earth metals proper. On passing further to calcium, this gradual fall in non-metallic properties is sharply accelerated with the appearance in calcium of completely vacant $3d$ shells into which s electrons can be transferred.

Hence the electronic transitions acquire the general form expressed by the scheme $d \rightleftharpoons s^2 \rightleftharpoons sp$. Therefore the lowering of the statistical weight of the sp configurations at calcium is due not only to the increase in the principal quantum number of its sp electrons, but mainly to $s \rightarrow d$ promotion, which sharply lowers the probability of that of the $s \rightarrow p$. Since the stability of the electron configurations which are converted into the d states increases with increase in the principal quantum number of the d electrons, then on going from calcium to strontium, barium, and radium the equilibrium $d \rightleftharpoons s^2 \rightleftharpoons sp$ is sharply displaced in the direction of the formation of the configurations of d electrons with a diminution in the statistical weight of the sp states; the metallic properties of these elements rise correspondingly sharply.

Therefore in the compound $MgBe_{13}$ the "more metallic"‡ magnesium emerges as a donor of s electrons and beryllium as an acceptor with the formation of sp configurations. The difficulty of making magnesium beryllide described above (see p. 341) is probably explained not only and not so much by the volatility of magnesium and the difficulty of its concentration in the reaction space of the furnace, as by the relative similarity of the electronic structure and energetic states of the beryllium and magnesium, in particular, by the presence in both metals of the difficultly-excited sp electronic configurations. In this connection, the calcium beryllide $CaBe_{13}$ is formed much more easily when it is also taken into account that the stable pairs of s^2 electrons are destroyed in consequence of the $s \rightarrow d$ promotion. Therefore $CaBe_{13}$ is also more stable in thermal respects than magnesium beryllide.

It is possible that the absence of such phases for strontium and the other alkaline earth metals is due not only to their having been little investigated, but to the principal considerations that as a result of the $s \rightarrow d$ promotion there is a strong bonding of the electrons and increasing difficulty in their transfer to the beryllium atoms; this

‡ Obviously it would be even better to say "less non-metallic".

difficulty should increase with increase in the principal quantum number of the d electrons, that is, from strontium to radium.

It should be noted that Laube and Nowotny[45] connect the formation of the structural type $NaZn_{13}$ (AB_{13}) with the great difference in the atomic radii r_A and r_B, by showing that this explains the existence of the phases AB_{13} for the beryllides (A = Mg, Ca, Sc, Y, La, Ce, Zr, Hf, Th, U, Pu), zincides (A = Na, Sr, Ba), cadmides (A = K, Rb), and for the same reason such phases are unknown for the magnides, where component B would be magnesium. It is evident that this purely "geometrical" standpoint does not reveal the actual reasons for the formation of beryllide phases of the type AB_{13}.

Beryllides of metals of the zinc subgroup. The increase in the ionisation potentials (up to 9–10.5 eV) compared with the metals previously considered and also the existence of rather stable electronic configurations for the atoms of these metals (type $d^{10}s^2$) greatly hinders the transfer of electrons to beryllium, therefore it is evident that corresponding beryllides have still not been observed, if we rule out the indication of the possibility of the formation of an amalgam $BeHg_2$ on electrolysis, that is, under conditions when there is a rather strong excitation of the mercury atoms (mercury cathode). Under ordinary conditions of heating, the metals of the zinc subgroup are almost inert towards beryllium.

Hence the difficulty or even impossibility of forming beryllides of the metals of the zinc subgroup can most probably be explained by the presence in the crystals of these metals of a high statistical weight of the stable s^2 configurations, which should be destroyed for transfer of some of the s electrons to the beryllium atoms. Such a destruction is mainly possible on account of the $s \rightarrow f$ transitions with cadmium and mercury, which are also realised with sufficiently strong excitation of the atoms of the latter.

Beryllides of the rare-earth metals. It is evident that the picture of the nature of the chemical bond in the rare-earth beryllides is the same in principal as for the beryllides of the alkaline earth metals, owing to the high ionisation potentials (6–7 eV [160]) and the existence of paired outer s electrons for all the lanthanides. In this context, all the r.e.e. beryllides form beryllide phases of the same composition MBe_{13} with $NaZn_{13}$ structure (as do the alkaline earth metal beryllides), but scandium, as a typical d transition metal, forms (in addition to $ScBe_{13}$) also phases of composition Sc_2Be_{17} and $ScBe_5$, which are characteristic of zirconium and hafnium. However, the formation of beryllide phases by the r.e.e. proceeds more easily than that by the alkaline earth metals, apparently owing to the higher energetic position of the $6s^2$ electrons, and also the rather strong screening of the incomplete $4f$ electron shells of the lanthanides. Nevertheless, it must be suggested that their physical properties should differ rather appreciably, owing to a difference in ability to make $f \rightarrow d$ electron transitions and the possibility of the establishment of $5d$ states ($4f^n \rightarrow 4f^{n-1}\,5d^1$) [161,162], the probability of which should rise from gadolinium, on the one hand to lanthanum, and on the other to lutetium. The lattice parameters of the lanthanide beryllides MBe_{13} decrease almost monotonically with rise in atomic number [55] in accordance with the well-known lanthanide contraction. In this the usual breakdown of this monotonicity for europium and ytterbium is essentially not observed, for in the beryllides all the lanthanides behave as formally bivalent metals, and a high statistical weight of stable sp^3 electron configurations of beryllium atoms is formed.

Simultaneously, with increase in the number of electrons in the f shell of the isolated lanthanum atom there is a rise in the statistical weight of the stable f^7 (for elements with seven or less f electrons) or f^{14} (for elements with more than seven f electrons) configurations; correspondingly there should be a drop in the fraction of electrons changing into a delocalised state. Therefore for beryllides with a high statistical weight of f^7 and f^{14} states under the condition of simultaneous localisation of the beryllium valence electrons in stable sp configurations, the appearance of an energy gap and the corresponding semiconducting properties can be expected. The energetic isolation of configurations of electrons localised in the metal and beryllium atoms, with a corresponding decrease in the fraction of non-localised electrons leads to less breakdown of the lattice than would correspond with the relatively high melting points of the lanthanide beryllides, their high hardness, and also ability to disproportionate on melting or vaporisation, as all these features should increase with increase in the statistical weight of the stable f^7 or f^{14} configurations respectively of the atoms of the metal sub-lattice, as is actually observed (Table 2).

It has been noted [55] that the unit-cell volumes of the beryllides MBe_{13} are larger, which is associated with their high beryllium content (92.86 at.%), in which these volumes do not correspond with the rule of the additivity of the metal and beryllium volumes shown by Matyushenko [163] for the beryllides of all simple metals. In other words, since the MBe_{13} beryllides fit the additivity rule for the volumes of the components, then the volume of the beryllium atom should be decreased by ~ 0.23 Å^3 for most beryllides. This can be imagined to be the result of exceptional "close packing" (localisation) of the electrons of the skeletal beryllium atoms associated with the above-mentioned high statistical weight of stable sp electron configurations.

It must be noted that for $ScBe_{13}$ because of the high donor capability of the poorly filled d shell of the scandium atom the formation of the stable electronic configurations of the beryllium atom is accompanied by the appearance of a higher concentration of delocalised electrons, which should involve a lower melting point for this beryllide, more sharply expressed metallic properties, and a lower vapour pressure in thermal dissociation, owing to the greater fraction of electrons passing into the delocalised state and to the more symmetrical distribution of the electron density in the lattice.

Beryllides of the d transition metals. In considering the physicochemical nature and the electronic and crystal structures of the transition metal beryllides with incomplete d electron shells, we must consider the concept of the unimportant difference in distribution of the charge of the d electrons in a metal crystal from that in an isolated atom [164], the possibility of the formation of stable electron configurations of atoms of metals and non-metals [159], the possibility of electron promotion and transfer, and data on the distribution of electrons in the crystals of transition metals into covalently bound and delocalised [165–167]. The scheme of the bonds in the beryllides can be represented in the general form thus:

where M–Be is a predominantly metallic bond, effected by delocalised electrons, the bond Be : Be of predominantly covalent character, and the bond M+M mixed covalent--metallic. Evidently the fraction of the individual types of bonds in metal beryllides depends firstly on the ability of the d shells of these metals to accept or donate electrons with the formation of one or another configuration of localised electrons.

In accordance with ideas about the formation and breaking of stable electronic configurations which have been advanced[159,168,169,176] the stable states formed by the d electrons appear to be d^0, d^5, and d^{10}, the greatest stability being exhibited by the d^5 configuration, and the energetic stability of any configuration of the d electrons increases with increase in the principal quantum number of the d electrons.

For transition metals which possess in the state of isolated atoms the d^1s^2 configuration of valence electrons (scandium and yttrium) and also d^2s^2 (the metals of subgroup IVa) the most probable is the transfer of some of the valency electrons to partners with the formation of a high statistical weight of the d^0 state and a fall in the statistical weight of the d^5 state§. On passing to the metals of Groups V and VI (d^3s^2, d^4s^1, d^4s^2, d^5s^1) with a number of d electrons close to 5, the statistical weight of the d^5 configurations rises and there is a corresponding fall in the donor and rise in the acceptor ability of the atoms, directed to the completion and stabilisation of the d^5 configuration. For the transition metals with more than five electrons in the d shell (Group VIII) the presence of two stable configurations is characteristic: d^5 and d^{10}, the statistical weight of which changes to the benefit of the d^{10} states with rise in the number of electrons in the d shell of the isolated atom.

It must accordingly be expected that the transition metals of Groups III–IV will mainly tend to transfer valency electrons to beryllium atoms with the formation in the metallic sub-lattice of a high statistical weight of the d^0 state, and in the beryllium sub-lattice of covalent groups of beryllium atoms stabilised by valence electrons transferred by the metal atoms. With increase in the relative concentration of beryllium atoms there will be a greater transfer of metal electrons from the valence state in the beryllium atoms which are combined in stable configurations and there is an associated decrease in the concentration of delocalised free electrons, a corresponding decrease in the loosening of the lattice, and a rise in melting point, hardness, and electrical resistivity (Tables 4 and 5). It is noteworthy here that the melting points increase on going from the titanium to the zirconium beryllides, and then decrease for the hafnium beryllides; this is because on going from titanium to hafnium there is a simultaneous change in the stability and the statistical weight of the d^5 configuration and the probability of the promotion of part of the d electron density of zirconium and hafnium to the f state, whereas with zirconium there is evidently a known optimum – with the rise in stability and statistical weight of the d^5 state (leading to a fall is the concentration of the delocalised electrons) for zirconium the process of $d \rightarrow f$ promotion is still not strong enough, leading to a fall in the statistical weight of the d^5 state, to a rise in the weight of the d^0 state with a corresponding increase in the concentration of delocalised electrons, resulting in loosening of the lattice.

Similarly, for the metals of Group V the formation of beryllides should be connected with the breakdown of the electron configuration of beryllium and the transfer of the electrons to the transition metal atoms. However, owing to the tendency of beryllium to form stable electron configurations of type sp^3, it is evident that the same process of transfer of part of the valency electrons from the transition metal atoms to the beryllium occurs, but simultaneously strong covalent bonds are formed between the transition metal atoms[165–167], the more strongly the less they are destroyed by the transfer of electrons to the beryllium atoms. Therefore, for example, for the series of niobium beryllides (Table 6) the melting points of the corresponding phases do not decrease, but rise with increase in the relative proportion of metal, or with decrease in the relative proportion of beryllium. The same also occurs for the tantalum beryllides, and later in Group VI for the beryllides of molybdenum and apparently (judging by hardness)¶ – tungsten. It is interesting that tungsten and rhenium, which have quite stable and not readily excitable d^5 states (formed by d electrons which possess the highest principal quantum numbers, so that in tungsten these states are formed even in the metal crystal: $d^4s^2 \rightarrow d^5s^1$), form phases with the greatest relative amount of beryllium MBe_{22}, which is evidently connected with the considerable ease of transfer to beryllium of their s electrons of the stable d^5 states formed by the localised valence electrons.

For the transition metals having more than five electrons in the d shell of the isolated atom it is possible for both donor and acceptor properties to appear within wide limits, which gives rise to a wide variety of possible combinations of the bond functions and a correspondingly large number of compounds with beryllium, these being formed specially with the platinoids. Here, in those instances when the platinum metal is predominantly a donor, tending to give some of its electrons with a corresponding increase in the statistical weight of the d^5 configuration, phases with a high relative concentration of beryllium are formed predominantly (as for the transition metals of Groups IV–VI), for example, for ruthenium (d^7s^1), osmium (d^6s^2), and iridium (d^7s^2). When the metal is predominately an acceptor, tending to acquire electrons and increase the statistical weight of the d^{10} configurations, then phases with a high relative concentration of metal and a low relative concentration of beryllium are formed, which in this way is prevented from forming covalent groups because the metal atoms do not transfer to it the additional electrons. This occurs, for example, with palladium (d^{10}) and especially with platinum (d^9s^1), for which phases are formed with the lowest beryllium concentrations, right down to Be : M = 1 : 15. Nevertheless these metals, because they retain the probability of forming a type d^5 configuration, also form phases with a high relative concentration of beryllium.

X-Ray crystallographic studies of the beryllides TiBe, $TiBe_2$, Ti_2Be_{17}, and $TiBe_{12}$ have been made and they have

§ Using the results of the X-ray spectroscopic investigation of crystals of transition metals[165–167,177], the statistical weight of the d^5 configurations can be estimated for the metals (%): Sc 18, Y 22, La 23, Ti 43, Zr 52, Hf 55, V 63, Nb 76, Td 81, Cr 73, Mo 88, W 94.

¶ The more so, as hardness in these compounds of metallic type is determined by the concentration of delocalised electrons and by the degree of asymmetry of the electron density distribution, as in metals[170].

been compared with beryllium[66,171]. As a result it was found that for TiBe and $TiBe_2$ [171] the valence electrons of both atoms (titanium and beryllium) are delocalised, which ensures an essentially metallic type of bond with a small contribution from the donor–acceptor interaction of the 3*d* electrons of the titanium with the 2*p* electrons of the beryllium. In Ti_2Be_{17} [66] there is a marked weakening of the degree of overlap of the energy bands of the valence electrons of the components of the alloy and a substantial increase in the role of the interaction between the beryllium atoms, that is, apparently the appearance of strongly covalent Be–Be bonds, which the authors[66] designate as the difference in the "effective electronegativity" of beryllium from the electronegativity of titanium, instead of the practical equality of these quantities of the free atoms and their similar values for the phases containing less beryllium[171]. Hence the results of the X-ray studies of the titanium beryllides confirm well the nature of the change in the type of chemical bond with change in the relative concentration of beryllium atoms in the titanium beryllides.

Unfortunately, there has been no investigation of the superconducting properties of beryllium compounds which would permit several important conclusions about the electronic structure of these compounds to be drawn.

The dependence of the relative change in volume of beryllides of various compositions AB_x on atomic volumes of components A has been investigated[49,55] (Fig. 19). It is evident that the increase in the Be : M ratio leads to a decrease in the fraction of the volume associated with one atom of beryllium, that is, the significant growth in Be : Be covalent bonds and the corresponding packing of the structural complexes of beryllium atoms are again confirmed.

With increase in the Be : M ratio there is a corresponding increase in the coordination number of the M atoms: for the compounds MBe_2 (Laves phase type) the value 16 is characteristic; for the phases MBe_5 ($CaCu_5$ type), M_2Be_{17} (Th_2Zn_{17} type), and MBe_{12} ($ThMn_{12}$ type) 20; for the MBe_{13} phases ($NaZn_{13}$ type) 24. However, the coordination number of M for the MBe_{22} type phases is lower than in MBe_{12} and MBe_{13}, which agrees well with the formation here of the most complicated complexes from the beryllium atoms, which are structurally rather strongly isolated from the metal atoms (which in their turn, have a stable state with a high statistical weight of the d^5 configuration).

The electrophysical properties of the transition metal beryllides have hardly been studied at all, but the available data show that the beryllides of metals with a higher statistical weight of d^0 states and a correspondingly high concentration of delocalised electrons have the metallic type of conductivity with a temperature coefficient of resistivity which decreases with fall in the statistical weight of the d^0 state and increase in the weight of the d^5 state. The coefficients of thermal expansion of the beryllides tend to decrease, which is due to the great strength and rigidity of the bonds in their crystal lattices.

Hence the formation of covalent bonds, both between the transition metal atoms and also between the beryllium atoms, on simultaneous transfer of some of the valence electrons of the components into a delocalised state is characteristic of the transition metal beryllides. The transition metal beryllides then can be classified as covalent–metallic compounds with a wide variation in physical and chemical properties within these limits from being present in a predominantly covalent state (at a high statistical weight of stable electronic configurations of the metal and beryllium atoms) to metallic properties, determined by the lower statistical weight of the stable configurations and the large transfer of valence electrons of the components into a delocalised state.

VI. PROMISING FIELDS OF USE OF BERYLLIDES

The high strength of beryllides at high temperatures, especially of transition metal beryllides (Fig. 20), which is about ten times that of ceramics, in conjunction with high oxidation resistance and also high thermal conductivity (which is twice that of high-temperature materials based on oxides) suggests a promising use of beryllides as materials for heat-resistant and other high-temperature alloys with maximal operating temperatures up to 1700°.[172] The industrial use of beryllide heat-resistant materials has been described[80]. Thus, components of space vehicles and guided missiles made from such materials are capable of withstanding a temperature 1.5 times higher than the

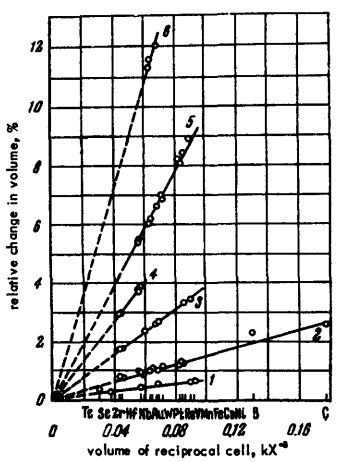


Fig. 19. Dependence of the relative change in the volume of the beryllides ABe_x on the atomic volumes of the components:
1) ABe; 2) ABe_2; 3) ABe_5; 4) $ABe_{8.5}$; 5) ABe_{12}; 6) ABe_{22}.

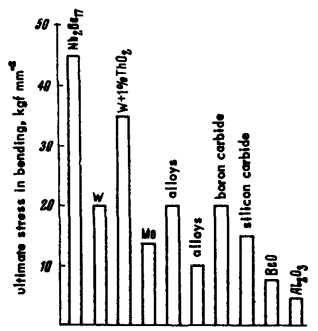


Fig. 20. Comparative strength of the beryllides and other refractory metals (at 1370°).

usual cobalt-, nickel-, and niobium-based alloys. The combination of high strength with low specific gravity (2.7 to 5–6) offers an especially promising use of beryllides in aviation and rocket technology. The resistance of beryllides to thermal shock at low rates of heat transfer and high-temperatures — which are higher than for most metal oxides, but lower than for graphite, fused silicon dioxide, and TiC-based cermets — is important for these fields of use; at high heat transfer rates the beryllides exhibit the same resistance to thermal shock as ThO_2, ZrO_2, and Al_2O_3.

The beryllides are of considerable practical interest for nuclear energy and energetics. Thus the beryllide UBe_{13} is liquid alkali metals is of interest as a nuclear fuel in heat liberating elements of the disperse type [173]. The Be–UBe_{13} dispersion systems have also been described [1,173]. The use of $NbBe_{12}$, YBe_{13}, and $ZrBe_{12}$ as moderators has been discussed [174]. The beryllide $PuBe_{13}$ is used as a neutron source, giving a stable yield of neutrons thanks to the long half-life of plutonium [131].

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The peculiarity of the electronic structure of the beryllium atom, which enables it to form either a metallic bond by means of the valence *s* electrons, or covalent bonds, by means of the *sp* electronic configuration, determines both the dualism of the properties of beryllium itself, which acts simultaneously as a metal and as a non-metal, or as a semi-metal, and also the wide variety of compounds of beryllium with other metals — the beryllides — and their physicochemical properties.

In turn, the variety of properties ensures a wide potential field of use of this important and complex class of chemical compounds, especially in the various branches of high-temperature technology, nuclear physics, semiconductor technology, and in catalysis.

The investigation of the nature of the chemical bond is beryllides is of considerable importance for the development of the principles of contemporary metal chemistry [175] and the creation of new inorganic materials with previously specified physico-technical characteristics.

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THE COLOUR OF DYES AND STERIC HINDRANCE IN THEIR MOLECULES

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Steric hindrance in the molecules of organic dyes has a marked influence on their colour, ability to fluoresce, solubility, and many other physical and chemical properties. The presence of steric hindrance in the molecule quite often makes a dye unsuitable for practical application. With direct dyes the rule exists [1,2] that factors — including steric hindrance — which disturb bond conjugation weaken the affinity of the dye for the fibre, and may result in complete loss of this affinity. Moreover, steric hindrance lowers the intensity of absorption, so that dyes having non-planar molecules yield weaker colours [3]. Steric hindrance in the molecules of cyanine dyes sharply diminishes their ability to sensitise a silver halide emulsion [4]. Thus the problem of steric hindrance in the molecules of organic dyes is of great practical importance.

The chief method for detecting steric hindrance in dye molecules, as in other organic compounds, consists in examining their absorption in the visible or the ultraviolet region of the spectrum.

The absorption spectra of organic compounds depend to a considerable extent on the spatial arrangement of the atoms in their molecules, and sometimes this factor is dominant. The intense and longer-wavelength absorption bands typical of dyes (Burawoy's *K* bands [5]) are associated with $\pi-\pi^*$ electronic transitions, and are caused by the presence in the molecule of an extended system of conjugated double and single bonds, the chromophore [6]. Henceforward we shall confine our discussion to these bands.

Hückel [7] and Pauling [8] showed that the maximum conjugation of multiple bonds is achieved when the molecule has a planar structure, since the axes of the *p* orbitals are then parallel, and the orbitals overlap to the maximum extent. This theoretical conclusion was subsequently confirmed by the X-ray examination of a large number of compounds containing systems of conjugated bonds (*trans*-stilbene, phthalocyanines, cyanine dyes, etc.).

According to the conclusions of quantum-mechanical theory and the results of X-ray structural analysis, the principal structural features of an organic dye molecule are: (1) atoms forming part of the conjugated bond system lie in the same plane; (2) the angles between the bonds involving atoms in the conjugated chain are close to 120°; (3) double bonds in conjugated chains are usually arranged in *trans-trans*-positions; and (4) the lengths of bonds between directly linked atoms in the conjugated chain lie within the range 1.34–1.48 Å (the lengths of bonds between carbon atoms in buta-1,3-diene).

These rules may break down when bulky substituents are present in the conjugated system or adjacent to it. The departures from the normal geometry of the molecule are due to steric hindrance and the mutual repulsion of atoms which are not directly interlinked. If normal angles and a planar structure had been preserved in the molecule, these atoms would have been very close together.

Repulsive forces fall off very rapidly with increase in the interatomic distance. When the latter exceeds the sum of the van der Waals radii, repulsion between the atoms dies away. The van der Waals radii correspond to the minimum distances between atoms in various molecules and molecular crystals, and can be determined from X-ray data.

According to Kitaigorodskii [9] the van der Waals radii of atoms and radicals remain constant to within 0.01 Å on passing from the molecule of one substance to that of another. The van der Waals radii of several atoms and radicals, determined by the above method, are listed in Table 1. [10]

It must be remembered, however, that, as a result of some compression of the electron clouds, atoms can approach, without any considerable consumption of energy, to distances less than the sum of the van der Waals radii. Magat [11] introduced the concept of "effective" radii of atoms and radicals as a limit closer than which atoms could not approach. These effective radii or radii of action depend on the temperature in the sense that the higher the temperature the greater the energy of the colliding atoms, and the more strongly are they deformed on collision.

Although repulsive forces begin to act at distances equal to the sum of the van der Waals radii, the radii of action are in practice more suitable for detecting steric hindrance

TABLE 1.

H 1.20 Å	S 1.85 Å
C 1.80 Å	CH_3 2.00 Å
N 1.50 Å	(C_6H_5) 1.70 Å*
O 1.40 Å	

* Half the thickness of an aromatic ring.