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SCIENTIFIC AND TECHNICAL INFORMATION

CAMERON STATION, ALEXANDRIA, VIRGINIA

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FTD-TT· 62-1763

TRANSLATION

PHOSPHIDES

By

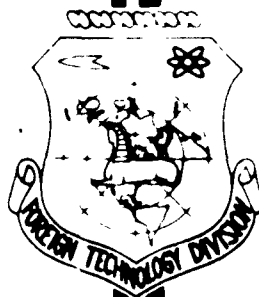G. V. Samsonov and L. L. Vereikin

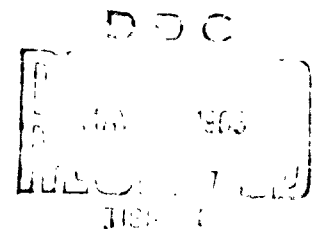# FOREIGN TECHNOLOGY DIVISION

AIR FORCE SYSTEMS COMMAND

WRIGHT-PATTERSON AIR FORCE BASE

OHIO

D D C

UNEDITED ROUGH DRAFT TRANSLATION

PHOSPHIDES (SELECTED PARTS)

BY: G. V. Samsonov and L. L. Vereikin

English Pages: 27

SOURCE: Russian Book, Fosfidy, Izdatel'stvo AN Ukrainskoy
         SSR, Kiev, 1961, pp. 3-4, 45-54, 68-70, 114-118

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Among the numerous classes of inorganic compounds, particular
interest is elicited by the direct combinations of metals with such
nonmetals as boron, carbon, nitrogen, silicon, phosphorous, sulphur -
so-called borides, carbides, nitrides, silicides, sulphides, phosphides
- many of which are distinguished by a high refractive index, hardness,
chemical stability, specific electrical and magnetic properties and
in connection with these, they are widely used in many branches of
technology. However, the study of these compounds has not been uniform -
the properties of the borides, carbides, nitrides, and the silicides,
the ways of obtaining them, the particularities of their crystalline
and electronic structure, all are described in quite some detail in
literature (1-5). The sulfides and phosphides have received much less
study, while this research and the determination of the areas in which
they would be useful has been complicated by the fact that data about
them is widely dispersed throughout numerous sources and also often
contradictory. This also gave rise to the present work, dedicated to
the properties, methods of obtaining and areas of application of the
phosphides for which, considering the brevity of the exposition, there
is a fairly voluminous bibliography which might be useful for making
a more profound and detailed acquaintance with the individual problems.

It should be observed that a study of the alloys of metals and
nonmetals with phosphorous presents a theoretical as well as a practical
interest. Recent years have seen a quite detailed study of the elec-
tronic and crystalline structure of the phases formed by metals with
nonmetals of the first period of Mendeleev's table (boron, carbon,
nitrogen, oxygen), by which it was established that many of the
physical properties of these phases are determined by the correspondence
between the distribution and the energetic characteristics of the metal

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atoms (by the blanks in the d and f electron shells of the atoms in the case of the transitional metals and the ionizing potentials in the nontransitional metals) and by the ionizing possibilities of the non-metallic atoms (6-9). The relationships set up make possible a synthesis of compounds of this type with previously established propeties. The same beginning is also gradually being spread to complex alloys of these compounds.

Much more complex is the nature of the electronic structure of phases formed by the metals and nonmetals of the second period with silicon (see [4], for instance), phosphorous, and sulphur. Crystallo-chemical and metallo-chemical studies of the phosphides were begun only quite recently, in particular by the works of Schonberg (Sweden), thus at present it is impossible to give any complete presentation whatsoever of the phosphides. It is, however, possible to note the basic direction of the studies which ought to lead to a clarification of the nature of these compounds.

Much interest is centered in the practical use of the phosphides-- addition of phosphorous to the melts of ferrous and nonferrous metals for alloy purposes, into alloys used for soldering, etc. The semi-conductive properties of the phosphides are particularly interesting, especially compounds of the type $A^{III}B^{V}$ which, unlike the already common compounds of antimony and arsenic, etc., may be used under condi-tions of extreme temperatures.

The present work does not pretend to exhaust the field, however, the authors hope that, in spite of all its omissions and shortcomings (for the indication of which they would be grateful to their readers), it may prove useful to scientists and engineers working in the areas of inorganic chemistry, metallurgy, and the synthesis of semiconductor compounds as well.

Chapters I and XI.   ·ov, chapters II -
XI by G. V. Samsonov and L. L. Vereikin, and chapter XII by L. L.
Vereikin. V. V. Pen'kovski and N. A. Samsonova took part in preparing
this book for press, for which the authors wish to express their
gratitude to them.

We also feel duty bound to express our gratitude to B. Aronsson
for submitting copies of several important works.

PHOSPHIDES OF METALS OF THE SUBGROUP V A
(VANADIUM SUBGROUP)

Vanadium phosphides. In the V-P system there are, according to the fundamental work of Tsumbush and Bil'tts [101], three compounds-- VP_2, VP, and the subphosphide V_3P, while works [39, 102, 103] indicate the existence of yet another low phosphide, V_2P. However, careful X-ray studies run by Schonberg [10] on alloys of the compositions $VP_{0.2}$, $VP_{0.4}$, $VP_{0.6}$, $VP_{0.8}$, $VP_{1.0}$, and $VP_{1.2}$, i.e., in the range from V to $VP_{1.2}$, disclosed only the existence of the monophosphide VP.

In Bil'tts' work [101], there is described the preparation of vanadium phosphides by synthesis from pulverized metal and red phosphorous in carefully evacuated quartz tubes with a great abundance of phosphorous relative to the vanadium (4:1). The mixture was heated very slowly in several stages at a reaction-range temperature for the metal of 720-1030°C, and for the phosphorous of 480-550°, total duration of the synthesis--42 hours. Between the heats, the phosphidization product was carefully powdered in an atmosphere of argon or other inert gas for the prevention of oxidization to which these intermediate products are particularly sensitive. The powder thus obtained was homogenized by heating for three days at 650-680°, after which its reddish color, ascribed to the presence of free phosphorous, had changed to black. To finally bring the composition of the preparation to correspond to the formula VP_2, it was mixed with an abundant quantity of phosphorous again, and the mix was heated in a sealed quartz ampoule for 20 hours more with a slow increase of temperature from 500 to 800-850°, finally decreasing it to 700°.

Tensimetric analysis of such a phosphide, corresponding to the formula $VP_{1.90}$, shows that at 326° a curve of the isotherm with a tendency to change to constant pressure is noted at composition $VP_{\sim 2}$, and the isotherm 680° shows the same curve at composition $VP_{\sim 1}$, which

proves the existence of mono- and diphosphides of vanadium, to which also correspond individual X-ray diffraction patterns.

Upon further dissociation of VP_2 or VP, according to [101], the low phosphide V_3P is obtained.

Much simpler is the formation of the monophosphide by direct synthesis, according to Schonberg [10], who uses lower temperatures for this, but, it is true, longer duration (see chapter II).

Vanadium monophosphate may also be prepared by passing phosphine over powdered metallic vanadium heated to 800-850° [10], or by electrolysis of melted mixtures of V_2O_5 and sodium phosphate or metaphosphate [39, 102, 103]. By varying the concentration of V_2O_5 in a bath, Andriya was also able to obtain the vanadium sub-phosphide V_3P.

V_3P may also be prepared by direct synthesis at the stoichiometric ratio of the components. However, this process is very complex and is not distinguished by satisfactory repeatability.

The most stable phosphide of vanadium, VP, has a hexagonal crystal lattice of the nickel-arsenide type with a very narrow area of homogeneity and spacing of a = 3.18; c = 6.22 angstrom units; c/a = 1.96. Schonberg [10] calls attention to the very large value of the c/a ratio for VP. For other nickel-arsenide structures, c/a fluctuates between 1.2 and 1.7. The X-ray diffraction density of VP equals 4.72, the pycnometric (specific in kerosene) 4.75 - 4.84 gr/cm³ [101].

The subphosphide V_3P crystallizes into a tetragonal system (type Fe_3P) [104].

The diphosphide of vanadium is black, the mono- and subphosphides gray-black.

The solubility of vanadium phosphides in concentrated sulphuric acid increases as their phosphorous content decreases. In dilute hydrochloric and sulphuric acids this phosphide is practically indissoluble. After long boiling in nitric acid and aqua regia an incomplete

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dissolution of the vanadium phosphides takes place. They break down completely when fused with alkalis. A summary of the properties of the vanadium phosphides is given in table 13.

TABLE 13
PROPERTIES OF THE PHOSPHIDES OF VANADIUM NIOBIUM, AND TANTALUM

Property	Phosphide					
	V_3P	VP	α-NbP	β-NbP	α-TaP	β-NbP
Phosphorous content, %	16.86	37.81	25.0	25.0	14.62	14.62
Structure	Hexagonal	Hexagonal	Hexagonal	Tetragonal	Tetragonal	Tetragonal
Lattice spacing, angstrom units						
a	--	3.18 [10]	3.32 [10]	3.325 [10]	3.320 [10]	3.330 [10]
c	--	6.22	5.69	11.38	5.69	11.39
c/a	--	1.96	1.71	3.42	1.71	3.42
Volume of unit cell of metal atom, angstrom units	--	27.20	31.35	31.46	31.35	31.57
Density, gr/cm^3						
calculated. . . .	--	5.00	6.40	6.54	11.04	11.15
pycnometric	--	4.72	5.91 [105]	6.15 [10]	--	10.3 [10]
Area of homogenity.	--	Narrow	Narrow	Lacking	Narrow	Lacking

Niobium phosphides. The niobium phosphide NbP was first produced by Heinert and Bil'tts in work [105] with combining niobium with an abundance of phosphorous in a closed ampouseat 550°.

In [101] , the existence of two phosphides, NbP_2, and NbP, in the Nb-P system was established with the aid of tensimetric and X-ray diffraction analyses. Unlike the V-P system, the Nb-P system discloses no subphosphide of niobium. Further, Schonberg [101] showed that niobium monophosphide exists in two crystal modifications-- and β NbP.

Niobium diphosphide   ~~prepared by direct synthesis~~ in the presence
of an abundance of phosphorous (Nb:P = 1:4) by heating for two-three
days with reaction tube temperature for the boat of metal of 650-750°
and for the phosphorous of 450-500° with subsequent homogenization at
750-800°. When heated in a vacuum, niobium diphosphide starts to lose
phosphorous at 430° and changes into monophosphide at 650°.

Niobium monophosphide may be obtained by dissociation of the
diphosphide or by direct synthesis [10] by the regime described in
chapter II, or by passing phosphine gas over niobium, heated to 800-
850°, for eight hours. The reaction product is subjected to homo-
genization in an evacuated quartz ampoule at 800°.

The monophosphide -NbP (the composition $NbP_{0.95}$ was actually
obtained) has a face-centered tetragonal unit cell with two formula
units. The lattice spacing is a = 3.32, c = 5.69 angstrom units [10],
the calculated density is 6.54 gr/cm^3, the area of homogeneity is
narrow. The Nb-Nb and P-P distances constitute 2.6 and 3.1 angstrom
units respectively.

The β-NbP has a face-centered elementary unit cell of the type
D_4^{10} with eight formula units and spacing of a = 3.325, c = 11.38
angstrom units. The calculated density is 6.54 gr/cm^3. The composi-
tion of β-NbP corresponds exactly to the ratio Nb:P = 1:1.

Dilute hydrochloric and sulphuric acids do not break down niobium
phosphides, while long boiling in nitric acid and aqua regia produces
incomplete dissolution and fusing with alkalis breaks them down rapidly
and completely.

Tantalum phosphides. The first attempts to produce tantalum
phosphides were made by Heinert and Bil'tts who established that at a
temperature of 500° these elements react only very incompletely [105].
In the later work of Stroesser and Bil'tts [101] was established the

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existence of two phosphides--the diphosphide TaP$_2$ and the monophosphide TaP.

Tantalum diphosphide is prepared by direct synthesis in an evacuated quartz ampoule at a temperature for the metal of 750° at the start and then 950-1100°, and for the phosphorous, 450-530°. The thermal stability of tantalum diphosphide is higher than those of the diphosphides of vanadium and niobium.

Tantalum monophosphide may be obtained directly using Schonberg's synthesis [10] described in chapter II, or by passing phosphine over powdered tantalum heated to 850°.

The monophosphide has two modifications: α - and β-TaP [10].

α-TaP is isomorphic with α-NbP and its composition is TaP$_{0.95}$. There has yet been no success in isolating this phase from the reduction composition. The area of homogeneity is narrow. β-TaP is an isomorph of β-NbP and homogeneous at Ta:P = 1:1, i.e., the area of homogeneity in it is completely lacking.

The chemical properties of tantalum phosphides are analogous to those of niobium phosphide. In dilute hydrochloric and sulphuric acids the phosphides of tantalum do not dissolve, in concentrated nitric acid and aqua regia an incomplete breakdown . occurs after long boiling, and they break down completely when fused with alkalis.

PHOSPHIDES OF THE METALS OF THE VI A SUB-GROUPS
(CHROMIUM SUB-GROUP)

Chromium phosphides. The existence of chromium monophosphide CrP, was established by the works of Grenier [106] and Marroneau [107], while Deekman and Hanff [108] by direct synthesis obtained a phosphide of the composition Cr$_3$P$_2$, which according to data [105] loses its phosphorous and becomes Cr$_3$P when heated.

A systematic stud, ... with phosphorous

was carried out by Faller and B.l'tts [109] who obtained and studied

by X-ray diffraction the phosphides CrP_2, CrP, Cr_2P, and Cr_3P. The

presence of the phosphide CrP is also confirmed by the data of works

[77, 110] and of the phosphide Cr_2P by the data of [110, 111]. The

existence of the phosphide Cr_3P_2 is much more doubtful.

Chromium diphosphide, CrP_2, is obtained by direct synthesis with

a superabundance of phosphorous by heating at temperature of 850-1000°

for the metal and 450-500° for the phosphorous for many days. When

the diphosphide is heated in a vacuum, it dissociates, giving off

phosphorous and forming the monophosphide, whose existence is confirmed

by the data of tensimetric analysis. The breakdown of the diphosphide

practically terminates at 700°, which follows from the temperature-

pressure relationship of phosphorous to the diphosphide:

Temperature, degrees C	594	628	660	673
Pressure, mm. of mercury	72	117	268	411

Thus, chromium monophosphide, CrP, is obtained either by the

thermal breakdown of CrP_2 at 700° [109], or by direct synthesis ac-

cording to Schonberg (see chapter II), or by passing phosphine over

chromium heated to 850° [10]. The authors obtained chromium mono-

phosphide by passing phosphine over chromium powder, heated to 850°,

for a period of 6 hours.

CrP has a rhombic lattice with two formula units in an elementary

unit cell isomorphic with MnP, FeP, and CoP, and a spacing group of

D_{2h}^{16} (the deformed rhombic structure of nickel arsenide).

The subphosphide of chromium, Cr_3P, synthesized by Deekman and

Hanff [108] is isomorphic with Fe_3P (tetragonal lattice, spacing group

S_4^2) which is also confirmed and discussed by Aronsson [112].

The polyphosphide, Cr_2P, according to the supposition of Novotnii and Khenglein [113] may exist stably only by replacing part of the chromium atoms in the lattice by iron atoms. Under this condition, it crystallizes into a rhombohedral unit cell C 32 (type D_3^2).

The physical properties of chromium phosphides are given in table 14.

Molybdenum phosphides. The Mo-P system discloses three compounds: MoP_2, MoP, and Mo_3P [109].

Molybdenum diphosphide, MoP_2, is obtained by direct synthesis in previously evacuated quartz tubes [105, 109] with a superabundance of phosphorous (Mo:P = 1:4) by long heating (42-46 hours) at 850-1000° for the metal and 525° for the phosphorous, and with a subsequent long homogenization. The diphosphide is isomorphic with WP_2, however its heat of dissociation is lower than that of tungsten diphosphide. At 1000° it breaks down completely, forming the monophosphide whose existence, as well as that of the diphosphide, is clearly proved by tensimetric analysis.

MoP was first obtained by Weller and Rautenberg [35] by carbon reduction of a blend of MoO_3 and phosphoric anhydride. Later MoP was prepared by direct synthesis [94] by passing phosphine over pulverized molybdenum heated to 850° [10], and by electrolysis of a fusion containing MoO_3 and sodium phosphate [116]. The authors [116], by varying the concentration of MoO_3 in the electrolyte, were also able to obtain the subphosphide Mo_3P.

The phosphide Mo_3P is isomorphic with Fe_3P (tetragonal lattice in an elementary unit cell containing four formula units).

The monophosphide MoP has the structure of WC, at which Mo:P = 1:1, the area of homogeneity is lacking [10]. The disposition of the phosphorous atoms recalls the structure of nickel arsenide. The thermal stability of MoP is relatively high--in a high vacuum at a temperature

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PROPERTIES OF THE PHOSPHIDES OF CHROMIUM, MOLYBDENUM AND TUNGSTEN

Properties	Phosphide								
	Cr_3P	Cr_2P	CrP	CrP_2	Mo_3P	MoP	MoP_2	WP	WP_2
Phosphorous content, %	16.56	22.94	37.33	54.36	9.74	24.40	39.93	14.41	25.19
Area of homogenity	None	None	Narrow	?	None	None	?	Narrow	?
Structure	Tetrag-onal	Rhombo-hedral	Rhombic	?	Tetrag-onal	Hexag-onal	?	Rhombic	?
Lattice spacing, angstrom units a	9.144 [10]	--	6.108 [10]	--	9.729 [10]	3.23 [10]	--	6.219 [10]	--
b	--	--	5.362	--	--	--	--	5.717	--
c	4.567	--	3.113	--	4.923	3.20	--	3.238	--
c/a	0.50	--	--	--	0.51	0.99	--	--	--
Volume of the unit cell of the atom of metal, angstrom units	15.91	--	25.11	--	19.42	28.64	--	28.78	--
Density, gr/cm³ calculated	6.51 6.25 [10] 6.02 [110]	--	5.49 5.25 [10] 5.3 [110]	-- 4.50 [109]	9.14 8.60 [10] 9.07 [110]	7.50 7.20 [10] 6.58 [110]	-- 5.21 [109] 5.30 [110]	12.40 11.7 [10]	-- 8.60 [105] 9.17
pycnometric	6.24 109	--	5.32 [109]	--	--	--	5.35	--	105

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TABLE 14--CONTINUED

Properties	Phosphide								
	Cr$_3$P	Cr$_2$P	CrP	CrP$_2$	Mo$_3$P	MoP	MoP$_2$	WP	WP$_2$
The temperature of complete dissociation at p = 760 mm. mercury.	--	--	--	700 [109]	--	--	1000 [109]	1050 [109]	1100 [109]
Melting point, degrees C	--	1600	--	--	--	~1500 [114]	--	--	-- 12
Heat of formation from MoP and white phosphorous, kilocalories .	--	--	--	6.6 [109]	--	--	[109]	--	[109]

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of 1200° it loses only part of its phosphorous, becoming a fusion with the conditional composition of $MoP_{0.8}$ (under similar conditions, tungsten monophosphide loses all of its phosphorous).

In work [114], there is given an ideal diagram for Mo-P (see figure 59). The Mo-P system has a eutectic character. Molybdenum monophosphide MoP forms a eutectic with molybdenum at 1063° and 12% P. MoP melts incongruently at approximately 1550°. Phosphorous dissolves in molybdenum to 5-7%. The remaining compounds of molybdenum with phosphorous in the diagram by Fogle and Horstmann were not studied.

Hot, concentrated nitric acid dissolves MoP with the formation of phosphonic and molybdenic acids. Chlorine interacts with the monophosphides beginning with only slight heating. A summary of the phosphides of molybdenum is given in table 14.

Tungsten phosphides. In old works [117, 118], it was accepted that tungsten forms no compounds with phosphorous. The first serious study of the W-P system was made by Faller and Bil'tts [109]. Two phosphides--WP and WP_2-were disclosed in the system.

Tungsten diphosphide is obtained by direct synthesis in an evacuated quartz ampoule in three steps, with a superabundance of phosphorous:

Step	W:P ratio	Temp. °C	Heating duration, hours
I	1:1.3	970	48
II	1:2.3	825	110
III	1:2.9	700	150

The heating temperatures given for the steps refer to the side of the tube in which is placed the boat with the metal; for the phosphorous the temperature constitutes 435-450° [109].

It is also possible to prepare WP_2 by precipitation out of the gaseous phase as the result of the reaction between PH_3 and WCl_6 [119] or by the interaction between WO_3 and red phosphorous at a temperature

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of 500° [105]. The existence of WP_2 and also the monophosphide WP are well confirmed by tensimetric analysis. By X-ray diffraction the phosphide WP_2 is comparable to MoP_2, but not isomorphic with CrP_2. At 1100°, the diphosphide breaks down, changing into the monophosphide [109]. WP_2 has a black color.

The monophosphide WP is also obtained by the reaction of WP_2 with a superabundance of metal at a temperature of 1200° [120,] by electrolysis of a melt containing WO_3 and sodium phosphate [119, 121, 122], and mainly, by passing phosphine over tungsten heated to 850° [10] or by direct synthesis [10], although by the data of [109], it is impossible to obtain the monophosphide by direct synthesis. WP has a rhombic lattice (type MnP), a spacing group of D_{2h}^{16} with two molecular units in the unit cell.

Those tungsten-phosphorous compounds which were mentioned in the literature and written with the formulae W_2P [109], W_4P [121], W_3P_4 [123], by the data of work [10], appear not to be individual phases, but rather mixtures of tungsten monophosphide with tungsten or with phosphorous.

On the basis of the preceding works, Schneider and Fogle [124] tried to set up an ideal diagram of the status of the W-P system (figure 26). Here C_p - L_1 represent the precipitation curve of tungsten-rich melts, respective to the curve C_p - L_1. There exist in the area V + L the vapors C_p - V_1 and the melts C_p - L_1. In an area of much lower temperatures, this field of the diagram is limited by the reaction between the vapor V_1, the melt (liquid) L_1 and the solid monophosphide WP proceeding along the diagram:

$$V_1 + L_1 \rightleftharpoons WP.$$
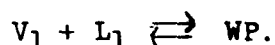
If the compositions of the molten alloys are distributed in the area WP - L_1, then the reaction terminates after exhaustion of vapor V_1. On the other hand, for compositions of the area V_1- WP there remain

abundant phases of V_1 and WP. The area V + WP represents an area of coexistence of the vapor V_1 - V_2 with the solid WP. Vapor V_2 coexists with the solids WP_2 and WP

$$V_2 + WP \rightleftharpoons WP_2.$$

Thus, crystals of WP_2 are formed when the temperature is lowered and break down when it is raised. If the liquid alloy is located in the concentrated area WP_2-WP of the last reaction, then after its termination, only phases WP and WP_2 are formed. If, however, the composition lies between vapor V_2 and WP_2, then WP is completely consumed and there occurs a transformation in the V + WP_2 field in which side by side with WP_2 there are formed vapors of the composition V_2 - V_3. The two-phase area V + P consists of a vapor (corresponding to the curve C - V_3) and a solid phosphorous. From the vapor V_3 there precipitates a mixture of P + WP_2. The area L represents a molten alloy. In the areas L + P there coexist alloys of the composition L_1 and WP, and in the field L + W', alloys of the composition L' and solid solutions of the compositions L' - W'. The molten alloy e solidifies by the eutectic reaction between WP and the solid solution W'.

Figure 26. An ideal diagram of the condition
of the W-P system 124 .

When heated to 1050° in a high vacuum, WP breaks down completely (unlike the diphosphides, the thermal stability of the monophosphides is reduced when passing from chromium to tungsten).

WP is stable in air under normal conditions, but when heated, it oxidizes intensely, forming WO_3. Hydrogen has no effect on WP up to a temperature of 900°, chlorine reacts with it when it glows cherry red and forms PCl_3 and WCl_6. Dilute HCl and HF do not break down WP, even after long boiling. Nitric acid slowly oxidizes WP when heated, the mixture HF+ HNO_3 and aqua regia break it down completely when heated. Also, solutions of alkalis hardly affect WP. Melted K_2CO_3, Na_2CO_3, $KHSO_4$, and a mixture of KNO_3 and K_2CO_3 oxidize WP with the formation of tungstenate and phosphate.

The phosphide WP_2 is chemically very little stable: a cold mixture of HF + HNO_3 breaks it down completely and sulphuric and nitric acids oxidize it, when heated, to WO_3.

WP_2 also breaks down when melted with potash, soda, a mixture of soda and saltpeter, or $KHSO_4$. It is not soluble in hydrochloric or hydrofluoric acids, alcohol, ether, carbon disulphide, chloroform, benzene [119], nor in ammonia and perhydrol [105].

THE PHOSPHIDES OF THE ACTINIDES

Thorium phosphides. Thorium phosphide Th_3P_4 is prepared by heating thorium tetrachloride in the vapors of phosphorous [187], by the interaction of thorium hydride with phosphine [188], by the action of phosphine on powdered thorium [189], and by direct synthesis [29].

For direct synthesis, it is sufficient to heat a mixture (Th:P = 1:3) in a sealed, evacuated quartz ampoule with a temperature of 450° at its cold end and 940° at its hot end for a period of 60 hours.

Th_3P_4 is a compound of steel-gray color crystallizing in the body-centered cubic lattice [98], spacing group T_d^6 with four molecular units

in the unit cell. Each atom of thorium is surrounded by eight atoms of phosphorous at a Th-P distance of 2.98 angstrom units.

Thorium phosphide is a thermally stable compound. When heated in air it changes to thorium phosphate [189], under the action of dilute acid it gives off phosphine, and it reacts practically not at all with water and alkalis.

When comparing thorium phosphide Th_3P_4 with higher phosphoric compounds of elements - homologues of IV group - attention is called to the gradual change from the metallic character of the compound SiP, through the semi-metallic (TiP and ZrP_2) to the salt-like (ionic) type of the bond in Th_3P_4.

Bil'tts, Stroesser and Maizel [29] indicate the existence of still another compound of thorium with phosphorous - the subphosphide $ThP_{0.6-0.75}$, which crystallizes in the cubic system (type NaCl), spacing group O_h^5, with four formula units in the unit cell.

A summary of the properties of thorium phosphide are given in table 18.

Uranium phosphides. X-ray diffraction has established the existence of two phases in the U-P system: UP and U_3P_4 [190, 191].

Uranium monophosphide UP is formed, according to Rammelsberg [192], by thermal breakdown of $UO_2(H_2PO_2)_2H_2O$, or by direct synthesis at a temperature for the metal of 800-900°, and for the phosphorous 425-450°.

U_3P_4 is formed by the action of phosphine on Na_2UCl_6 with an insignificant outflow [190]. The most simple way of preparing the phosphide U_3P_4 consists of introudcing aluminum phosphide into melted Na_2UCl_6 in an atmosphere of dry hydrogen. The product thus obtained is cleansed of NaCl and an unreacted double chloride by repeated washing with water.

TABLE 18

PROPERTIES OF THE PHOSPHIDES OF THORIUM, URANIUM, NEPTUNIUM, AND PLUTONIUM

Property	Phosphides					
	$ThP_{0.75}$	Th_3P_4	UP	U_3P_4	Np_3P_4	PuP
Phosphorous content, %.	9.09	15.10	11.50	14.90	14.84	11.40
Structure	Cubic face-centered	Cubic body-centered	Cubic face-centered	Cubic body-centered	Cubic body-centered	Cubic face-centered
Lattice spacing, angstrom units.	5.818 [29]	8.60 [98]	5.60 [14]	8.22 [14]	?	5.649 [257]
Density, gr/cm3 calculated.	6.96	8.59	9.68	9.83	--	10.18
pycnometric	--	8.44 [29]	9.69 [98]	--	--	--

UP crystallizes in the cubic system, type NaCl, with four formula units in the unit cell. U_3P_4 has a cubic body-centered lattice of the type Th_3P_4 (see page 15), also with four molecular units in the unit cell.

U_3P_4 oxidizes slowly in air. It breaks down very slowly in water. Dilute hydrochloric acid, HNO_3, aqua regia, and melted alkalis easily break this phosphide down.

Neptunium phosphides. Sheft and Freid [193] obtained the phosphide Np_3P_4 by heating metallic neptunium with a super abundance of red phosphorous. The pipe temperature for the metal was kept at a constant 750°, for the phosphorous, 425-450°. The process of obtaining phosphide under these temperature conditions took 16 hours. X-ray diffraction of the product showed that Np_3P_4 is an isomorph of Th_3P_4 (see page 68). The lattice spacing of trineptunium phosphide has not yet been determined.

Np_3P_4 is insoluble in water but dissolves easily in six-molar hydrochloric acid.

Plutonium phosphides. Plutonium phosphide PuP has, as do the other monophosphides of the actinides, a cubic face-centered lattice of the sodium chloride type. The phosphide melts and breaks down at approximately 2000°.

XIII. THE AREAS IN WHICH THE ALLOYS OF PHOSPHOROUS ARE
EMPLOYED IN TECHNOLOGY

Use of phosphides as semiconductors. The most fruitful perspective for the use of the phosphides of many metals and nonmetals is in the field of semiconductors.

Particular attention is called to the class of phosphides related to the class of semiconductive compounds of type $A^{III}B^V$. Studies have shown that these compounds may be applied in such devices, acting on new principles, as the Hall emf sensors, and semiconductor tetrodes--

spacistors, thermal elements for solar batteries, devices for transonic aviation, and infrared receivers [365].

Gallium phosphide has been successfully used for making diodes [359] and semiconductor spacistors [360] the application of which allows passing beyond the limiting frequency barrier of the germanium apparatus (about 100 megacycles per second). It is proposed that such devices might work effectively at frequencies right up to 10,000 megacycles per second at temperatures up to 500° and will find wide application in guided missiles, rockets, and also in radio and television receivers.

There is significant interest in the use of solid solutions of phosphorous in silica for the creation of solar batteries which, in particular, would be used as sources of electrical energy in artificial satellites [248].

At the dawn of the development of semiconductor technology, junctions through the edge of electron- and hole-donor semiconductors were used for rectifying current. Subsequently such p-n junctions began to be made inside the crystal [233]. For a diagram of p-n junctions, see figure 66.
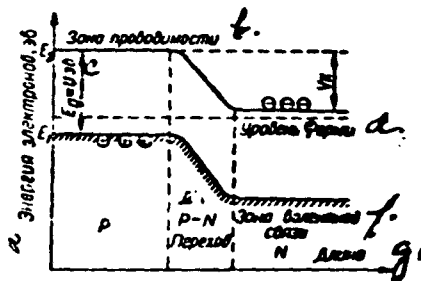

Figure 66. Diagram of the energy zones in the vicinity of p-n junctions
(a) Energy of electronics, electron volts; (b) Zone of conductivity; (c) V of Div; (d) Plane; (e) Junction; (f) Zone of valent bonds; (g) length.

For the creation of p-n junctions, the surface of a single crystal is exposed to ions of the N type, which create acceptor impurities, or

to rapid electrons. The processes of introducing impurities into the semiconductors during crystallization and of diffusion of impurities through their surfaces are also widespread. This later process is commonly used for creating solar batteries.

When the surface of the semiconductor is exposed to sunlight, there takes place the absorption of a photon and the creation of an electron-hole pair which in the absence of a p-n junction leads to increasing the concentration of current carriers and the appearance of photoconductivity.

In the presence of a p-n junction in the semiconductor, the holes and electrons created by exposure to photons diffuse toward this junction at which the electrons freely cross over the potential barrier V_k of the p-n junction into the region of electron conductivity of the crystal, charging it negatively, and the holes going into the area of hole conductivity and charging it positively. If the external circuit is closed, the current flows through it, this current being created by the carriers, the holes for instance, diffusing out of the n-region of the crystal into the p-region [302]. The creat. n of p-n junctions in silicon may be effected by diffusing boron onto the surface of a single crystal [302], or phosphorous - which is more effective. When making this thermal diffusion the phosphorous is obtained from the gaseous phase, which makes it possible to obtain junctions at an exactly given crystal depth. A schematic representation of a silicon photo-element with p-n junctions created by thermal diffusion of phosphorous is shown in figure 67. The field of a silicon photoelement, a film of 0.7-1 mm. depth, comprises 5-8 cm^2, separate elements being composed in series. The e.m.f. of the photoelements rapidly decreases as the temperature rises (figure 68) for which reason a solar battery, if it is to attain maximum power, must operate at sufficiently low inherent temperatures if it is not to present particular technical difficulties.
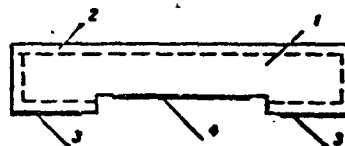
Figure 67. The construction of an experimental silicon photo-
element:
1. Silicon of p type; 2. Layer of silicon changed to n type by
thermal diffusion of phosphorous; 3. Annular electrode of n-
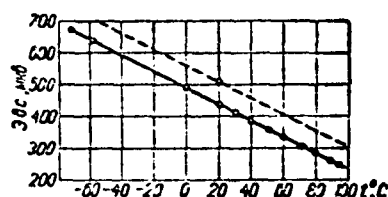type silicon; 4. Electrode of p-type silicon.

Figure 68. The temperature-e.m.f. ratio of silicon
photoelements:

_____ = photoelement of silicon with initial $\rho \cong 20$ ohm/cm;

- - - - - - = photoelement of silicon with initial $\rho \cong 0.6$ ohm/cm
(it is assumed that the curve is carried through one experimen-
tal point).

Use of phosphides in soldering techniques. Alloys of copper with

7 0 to 7.5% phosphorous are used for soldering brass pieces, instead of

the silver solder of the brand PSR-45 [303]. Copper-phosphorous

solder, unlike silver, has good wettability and fluidity and is self-

fluxing. And, it costs 20 to 30 times less than silver solder.

Use of phosphides in metallurgy. In most steels, phosphorous is a

harmful impurity, however, in a number of cases it is used as an alloy

component. The mutual effect of carbon and phosphorous on each other

in carbon steels and ferroalloys is interesting. Increasing the phos-

phorous content of ferrophosphorous results in a reduction of its

carbon content (figure 69) [305].

Hopkins and Tyler [294], when studying the Fe-P-C system, estab-

lished that the addition of phosphorous to ferrocarbon alloys resulted
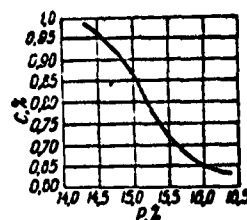
in increased strength.

Figure 69. The relationship between phosphorous- and carbon-content in carbon-containing ferrophosphorous

In steels with phosphorous content up to 0.36%, a significant coarsening of the grain is noted and this leads to reducing hysteresis loss. An insignificant reduction of the losses to eddy currents takes place thanks to some increase of unit electro resistance under the influence of phosphorous. Increasing the phosphorous content in steel shows up favorably by increasing magnetic penetration in weak and strong fields, [323].

Cast iron alloyed with phosphorous is used for fine machine and artistic casting (maximum phosphorous content in such cast iron--up to 3% by weight) [304]. Gray cast irons with increased phosphorous content are characterized by good wearing qualities.

It follows from the system diagram of Fe-P (see figure 29b) that there is a sharp reduction in the γ region when phosphorous is added to iron, and the absence of transformation in alloys with 0.6% P, right up to 1400°, making it possible to obtain large grains or single crystals of ferrite in the annealing process. And these remain even after cooling to room temperature. Using such single crystal models it is possible to study physical and mechanical properties. In work [306], single crystal ferrite was obtained by the power-metallurgy method by sintering iron powder with an addition of red phosphorous (compressed to a pressure of 6 tons per cm^2) in hydrogen at 1050-1350° for four hours (large crystals were formed at a sintering temperature above 1200°). Figure 70 shows models for tensile testing prepared in this manner and consisting of two or three large single crystals.
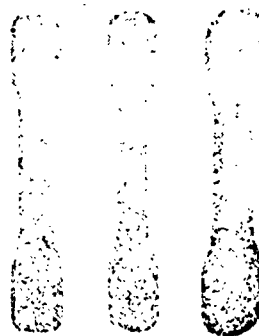
Figure 70. Specimens to be used for tensile testing,
made of large crystals of ferrite, etched

The tendency of phosphorous to liquate increases its negative
effect on the mechanical properties of steel together with a significant
embrittlement of ferrite. As confirmed by Moldavskii [324], this
influence may be weakened by applying deoxidizers or alloying elements
as, for instance, silicon, which reduce the liquation of phosphorous in
steel or increase its solubility in iron.

In pure ferrophosphorous alloys, when the phosphorous content is
increased to 0.5%, the limit of strength is increased. The yield point
also continues to rise as the amount of phosphorous is increased.

Phosphorous shows a favorable effect on the ability of structural
steels to resist atmospheric corrosion, particularly when the copper
content is high [339, 347].

Surface coverings. The creation of hard phosphide containing coat-
ings on steel improves the wear resistance of machine parts. In partic-
ular, a coating containing nickel phosphide is used for this purpose.
These coatings are gotten by the reduction of nickel from aqueous
solutions of its salts by the aid of hypophosphites and the use of
electric currents [352]. X-ray diffraction of films on KhVG steels
produced in this manner discloses the presence of a nickel phosphide,
the composition of which has not been completely established, but which
is distinct from Ni_2P and Ni_7P_3. This phosphide phase is stabilized by

thermal treatment of the coating, which, according to the data of [352], is most expeditiously produced by heating to 400-450° for 40 to 45 minutes. The layer of nickel phosphide is well bonded to the base and has, when subjected to the indicated heat treatment, a high hardness reaching 950 kg/mm^2 (on the scale of micro-hardness) and also a dense, amorphous structure.

Phosphides in chemistry and astrochemistry. The relatively weak mutual compensation of the bonds between metal atoms and phosphorous in a number of phosphides may be used in the process of heterogeneous catalyzation. In this matter, the phosphides of vanadium, niobium, tantalum, chromium, molybdenum, tungsten, and metals of the ferrous group show particular promise.

A study of the catalytic activity of the ferrophosphides FeP and Fe$_2$P [40] showed that in breaking down CO, the phosphide FeP was initially very little active catalytically, but after being maintained at 450° for five hours, there began a noteworthy acceleration of the reaction which dropped off completely 20 hours later. Fe$_2$P immediately reveals a higher activity after which the reaction speed of separation becomes constant for the following 12 hours. The question of the catalytic activity of the phosphides, as well as that of other similar classes of compounds (carbides, silicides, nitrides, and borides), has been little looked into and demands a serious all-round study which promises an interesting technological result.

In the last few years particular attention has been turned toward those phosphides which are unstable in moisture and are subject to hydrolysis, such as the phosphides of aluminum, manganese, and calcium, yielding compounds of phosphorous and hydrogen. Such phosphides may be used for disinfecting granaries, or other purposes [74, 204].

The discovery of iron phosphides and nickel in meteorites [292] in conjunction with the study of the conditions of their formation under

laboratory conditions makes it possible for the astrochemist to reconstruct the processes of their formation and behaviour in the cosmos.

Pyrotechnics. Sulphur phosphides, and in particular the phosphide P_4S_3 [355], find a wide employment as components in pyrotechnical compounds.

The ability of the phosphides of calcium, Ca_3P_2, and of magnesium, Mg_3P_2, to break down in moist air, giving off hydrogen phosphide which contains, besides PH_3, other phosphines as well (P_2H_2), and the spontaneous combustiveness of these phosphines in air, make it possible to use these compounds for special signal devices in the fleet [355].

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