# THE PREPARATION AND PROPERTIES OF SOME TRANSITION PHOSPHIDES

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#### SUMMARY

The monophosphides of some transition metals in Groups IV, V, VI, and VII were prepared by reacting calcium phosphide with metal powders or metal chlorides. The densities, oxidation resistances, thermal stabilities, and hardnesses of the monophosphide powders and compacts were measured to further characterize these compounds. Niobium phosphide, the most stable phosphide of those studied, decomposed at  $1,730^{\circ}$ C, while MnP, the least stable phosphide, decomposed at  $1,100^{\circ}$ C. The monophosphides appear metallic, have high electrical conductivities, and are about as hard as hard steel.

## INTRODUCTION

Phosphides of the transition metals have been prepared by several methods. The most widely used synthesis is based on the reaction of metal powders and red phosphorus in sealed tubes at 600 to 1,000°C. BILTZ and co-workers have prepared the monophosphides of titanium<sup>1</sup>, zirconium<sup>2</sup>, vanadium<sup>3</sup>, niobium<sup>4</sup>, tantalum<sup>5</sup>, chromium<sup>6</sup>, molybdenum<sup>6,7</sup>, tungsten<sup>6,7</sup> and manganese<sup>8</sup> in this way. Although high-purity products were obtained, the synthesis was lengthy because the reactions were slow and sometimes involved intermediate crushing operations.

ANDRIEUX, CHENE and co-workers produced monophosphides of vanadium<sup>9-11</sup>, chromium<sup>10,11</sup>, molybdenum<sup>10,12</sup>, tungsten<sup>10,11</sup>, manganese<sup>10,13</sup>, and cobalt<sup>10,11</sup> by employing fused salt electrolysis. Titanium monophosphide and zirconium diphosphide were obtained by GEWEKE<sup>14</sup> who reacted the tetrachlorides with phosphine.

In this study the monophosphides of titanium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese and cobalt were prepared by a convenient new synthesis. Calcium phosphide was reacted with the metal powders or metal chlorides at elevated temperatures. The unreacted calcium phosphide and calcium or calcium chloride formed were removed from the phosphide product by leaching with hydrochloric acid. These monophosphides were shown to possess properties similar to those of the corresponding nitrides. They are metallic in appearance, good conductors of electricity, moderately hard, and stable at temperatures in the range 1,100 to 1,800°C.

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# EXPERIMENTAL

# Materials

The calcium phosphide used was a Fisher technical grade reagent containing 63% calcium and 34.5% phosphorus. The metal powders were obtained from the Union Carbide Metals Company and were over 99% pure and less than 100 mesh in particle size. The CrCl<sub>3</sub> and TaCl<sub>5</sub>, obtained at the same source, were sublimed prior to reaction. The MnCl<sub>2</sub> was prepared by chlorinating electrolytic manganese metal.

# Apparalus

Calcium phosphide and  $CrCl_3$  or  $MnCl_2$  were reacted by heating the powdered mixture in an alumina crucible protected with argon in a Vycor envelope. Tantalum phosphide was prepared from the pentachloride by passing the pentachloride vapors through a vertical Vycor tube containing 1/4-in. lumps of  $Ca_3P_2$  at the desired reaction temperature. The metal powders were reacted with calcium phosphide powder by heating alumina crucibles, containing the mixed reactants, in a zirconium silicate tube under argon.

Thermal stability tests were made by inductively heating a carbon crucible, in which the samples were suspended in molybdenum cups, under a flow of argon in a Vycor envelope. The oxidation resistances of the monophosphides were determined on a Stanton Thermobalance programmed at a 6°C/min temperature rise up to 1,420 °C. The samples were held in small alumina crucibles.

In order to obtain sintered bodies of the monophosphides for electrical resistance measurements, the phosphides were ground to -325 mesh, moistened with water, pressed to about 5,000 p.s.i. in 3/8-in. diameter dies, and sintered in molybdenum cups with induction heating. The specific electrical resistances were measured in a Wheat-stone Bridge circuit.

Standard pycnometric procedures, using water as the liquid medium, were utilized in determining the densities. A vacuum dessicator and pump aided in removing adsorbed gases from the powders during the density measurements.

For microhardness measurements, the phosphide powders were mounted in a thermoplastic resin and polished metallographically. Microhardness values were obtained with a Reichert microhardness tester.

## ANALYSES

For analysis, the phosphides were converted into phosphates and metallic oxides and salts by fusion with a mixture of sodium carbonate and sodium peroxide and dissolving the fusion in water or acid. These solutions were analyzed for phosphorus after precipitating the vanadium as a cupferrate or after adding citric acid in the case of chromium. The phosphorus was precipitated as magnesium ammonium phosphate and ignited to magnesium pyrophosphate. Titanium, niobium, and tantalum were estimated gravimetrically by precipitating as cupferrates and igniting to the oxides. Vanadium, chromium, and manganese were determined by standard ferrous sulfate titrations after suitable oxidations. Molybdenum and tungsten were determined by the alpha benzoine oxime and chinchonine methods used for steels. Cobalt phosphide was dissolved in fuming nitric acid and the cobalt determined electrolytically. Oxygen was determined by a vacuum fusion analysis, similar to that used for steels<sup>15</sup>. The samples were fused with an iron-tin alloy in high-purity graphite crucibles.

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# RESULTS AND DISCUSSION

Monophosphides of several transition metals were prepared in almost 100% yields, based on the metal, by reacting metal powders and  $Ca_3P_2$  (mole ratio  $Ca_3P_2/metal = {}^{3}/_{4}$ ) in argon at 1,200°C for 2 h. Manganese phosphide could not be prepared by this synthesis in yields over 15% in the temperature range 1,000 to 1,200°C. The excess calcium phosphide and calcium were removed from the phosphide product by leaching the cooled reaction mass with 0.1 N hydrochloric acid. Because of phosphine evolution, leaching was done in a hood. The surface of the leaching solution was protected with an inert gas to prevent oxidation of the metal phosphide product while the phosphine burned.

The analyses of the monophosphides are given in Table I.

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CHEMICAL ANALYSES OF MONOPHOSPHIDES PRODUCED BY THE REACTION BETWEEN METAL POWDERS AND CALCIUM PHOSPHIDE

Metal phosphide	Metal(%)		Phosphorus(%)		0	Atomic ratio P/M	
	Experi- mental	Theo- retical	Experi- mental	Theo- retical	(%)	Experimental	Theoretical
TiP	60.4	62.0	37.6	38.0	0.25	0.960	0.95
VP0.95	60.4	62.2	38.8	37.8	0.54	1.06	1.00
$\beta$ -NbP	74.4	74.9	24.9	25.1	0.14	1.00	1.00
β-TaP	85.3	85.4	14.1	14.6	0.54	0.965	1.00
CrP	62.2	62.6	36.6	37.4	0.25	0.985	1.00
MoP	75.5	75.6	24.4	24.4	0.31	1.00	1.00
WP	85.6	85.6	14.2	14.4	0.20	0.985	1.00
MnP	60.8	63.9	37.8	36.1	0.30	1.10	1.00
CoP	66.3	65.5	33.6	34.5		0.960	1.00

Equation (1) illustrates the reaction of metal powders with calcium phosphide at 1,200°C, where M represents titanium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, or cobalt.

$$2M + Ca_3P_2 \rightarrow 2MP + 3Ca \tag{I}$$

The phosphorus-to-metal ratio obtained for titanium phosphide and its X-ray pattern correspond to those of  $\alpha$ -TiP<sub>0.95</sub> reported by BILTZ<sup>1</sup>. Both niobium and tantalum phosphides were produced in the beta forms. The X-ray diffraction patterns were identical with chose reported by BILTZ<sup>4,5</sup> and SCHÖNBERG<sup>16</sup>. The X-ray patterns of the monophosphides of vanadium, chromium, molybdenum, and tungsten produced in these experiments were identical to those reported in the literature<sup>3,6,7,16</sup>.

Metal phosphides were also produced by the reaction of metal chlorides with calcium phosphide. Equation(2), written for  $CrCl_3$ , illustrates this reaction.

$$2\mathrm{CrCl}_3 + \mathrm{Ca}_3\mathrm{P}_2 \rightarrow 2\mathrm{CrP} + 3\mathrm{CaCl}_2 \tag{2}$$

With  $CrCl_3$  and  $MnCl_2$  the reactions were carried out by heating the anhydrous metal chloride powder with powdered calcium phosphide (ratio  $Ca_3P_2$  to  $MCl_x = x/3$ ) to 800°C in argon. To produce tantalum phosphide,  $TaCl_5$  was vaporized into a bed of

 $Ca_3P_2$ , which was packed in a vertical Vycor tube and held at 800°C. The phosphides were freed from the CaCl<sub>2</sub> and excess  $Ca_3P_2$  by leaching with hydrochloric acid. The analyses of the products are given in Table II.

The tantalum and manganese phosphides produced by this technique are mixtures of the monophosphides and diphosphides. This mixture may be converted to the pure monophosphide by thermal decomposition, as indicated by the literature<sup>16</sup>.

TABLE II

#### PHOSPHIDES PRODUCED BY REACTIONS BETWEEN CALCIUM PHOSPHIDE AND METAL CHLORIDES

3.4.1.7.7.7.7.7.3	Product analysis (%)			Phosphorus-to-metal	
Metal chloride -	Metal	Phosphorus	Oxygen	aiomic ratio	
TaCl <sub>5</sub>	79.19	20.76		1.53	
CrCl <sub>3</sub>	61.0	37.0	0.10	1	
MnCl <sub>2</sub>	55.2	41.3	1.8	1.32	
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# Properties

Density. The densities of the monophosphides, with the compositions listed in Table I, were measured pycnometrically using water as the liquid medium. In Table III these pycnometric densities are compared with those calculated by SCHÖNBERG<sup>16</sup> from X-ray measurements.

TABLE III

MEASURED DENSITIES OF PHOSPHIDES COMPARED TO SCHÖNBERG'S CALCULATED X-RAY DENSITIES

Phosphide	Measured density (g/cm <sup>3</sup> )	Calculated density (g/cm <sup>3</sup> )	
TiP	4.08	4.27	
VP	4.98	5.00	
$\beta$ -NbP	6.48	6.54	
$\beta$ -TaP	10.9	11.15	
CrP	5-35	5.49	
MoP	7.33	7.50	
WP	12.0	12.40	
MnP	5.60	5.34*	

\* Measured density value from literature<sup>21</sup>.

Oxidation resistance. The monophosphide powders (---100 mesh) were tested for oxidation in air at high temperatures on the thermogravimetric balance. The temperatures at which 1% and 5% weight gains occurred are given in Table IV. The sample weights were from 0.2 to 1.0 g.

During the oxidation of TiP, MnP, and TaP, loss of weight occurred at temperatures of 750 to 820, 1,120 to 1,140, and 910 to 950°C, respectively, probably as a result of the volatilization of an oxide of phosphorus. A sintered tungsten phosphide cylinder, 3/8 in. in diameter and 1 in. long, was also tested. Slow oxidation began at about 400°C,

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and at  $900^{\circ}$ C the increase in weight was about 4.5%. At this higher temperature, oxidation ceased because of the formation of a protective coating. At 1,200°C, oxidation of the body resumed and continued to completion.

Phosphide	Temperature at 1% gain of weight (°C)	Temperature at 5% gain of weight (°C)	Particle size	Product of oxidation
TiP	570	640	100 M × D	semi-glass
$\mathbf{VP}$	630	690	100 M $\times$ D	glass
$\beta$ -NbP	720	850	100 M $\times$ D	powder
β-TaP	880	1,030	100 M $ imes$ D	powder
CrP	690	880	100 M $\times$ D	glass
MoP	540	590	10 µ	glass
WP	730	780	10 µ	glass
MnP	530	700	60 M × D	semi-glass

TABLE IV OXIDATION RESISTANCE OF MONOPHOSPHIDE POWDERS

Thermal stability. In the thermal stability tests the temperatures at which phosphorus was first evolved from the samples were determined by observing the presence of burning phosphorus in the exiting argon gas. In view of the lack of high temperature data for these compounds, it was considered that these data, however crude, have some value. These decomposition temperatures are given in Table V.

TABLE V

DECOMPOSITION TEMPERATURES OF TRANSITION METAL MONOPHOSPHIDES

Phosphide	Decomposition temperature (°C)	
TiP	1,580	
VP	1,320	
NbP	1,730	
TaP	1,660	
CrP	1,360	
MoP	1,480	
WP	1,450	
MnP	1,100	

In thermobalance tests, the temperatures at which manganese, chromium, and vanadium monophosphides first lost weight in argon were 1,100, 1,370 and 1,320°C, respectively. These temperatures for initial decomposition agree closely with those given in Table V. According to a calculation made from the thermogravimetric curve, manganese monophosphide decomposed at 1,100°C to  $Mn_3P_2$  which was thermally stable above 1,420°C.

By comparing the thermal stabilities of the nitrides and phosphides in relation to metal-to-metal distances and crystal structure, we note that the nitrides of Groups IV and V are more stable than the corresponding phosphides. These nitrides have cubic NaCl-type structures, while the phosphides have hexagonal structures with the exception of  $\alpha$ -ZrP. The larger diameter of the phosphorus atom results in larger metal-to-metal distances. Therefore, lower bond energies and thermal stabilities are expected for the phosphides than for the nitrides of Groups IV and V metals. For example, niobium nitride, with a mean intermetallic distance 6% greater than in the pure metal, decomposes at its melting point, 2,050°C, while niobium phosphide, with a mean intermetallic distance 15% greater than in the pure metal, decomposes at about 1,730°C.

However, it was found that some of the phosphides of Group VI are more stable than the corresponding nitrides. According to KIESSLING AND LIU<sup>17</sup>, CrN is unstable above 1,180°C, and according to our thermogravimetric tests, Mo<sub>2</sub>N and WN decompose at 850 and 900°C, respectively. The nitrides were prepared by reacting the respective chlorides with liquid ammonia at -33.4°C and pyrolyzing the resulting ammoniates at 800°C. On the other hand, CrP, MoP, and WP are stable to 1,360, 1,475, and 1,450°C, respectively. SCHÖNBERG<sup>16</sup> reasoned from analyses of crystal structures that the stabilities of these phosphides are due largely to strong metal to phosphorus bonds (6-co-ordination) probably of a partial ionic character. In contrast, the bonding in nitrides is essentially metallic, with the nitrogen-metal bond contributing little to the stability.

*Hardness*. The metal phosphides are hard materials but not as hard as the corresponding carbides. The Diamond Pyramid microhardnesses found for several of the phosphides are given in Table VI.

Phosphide	Average hardness	No. of readings
TiP	718	3
VP	541	3
NbP	599	4
TaP	374	3
CrP	632	3
MnP	633	3

TABLE VI

# DIAMOND PYRAMID MICROHARDNESSES OF TRANSITION METAL PHOSPHIDES (17-g load)

These phosphides are about as hard as hardened high-carbon steel, which has a value of about 600, but are softer than titanium carbide, which has a hardness of 1,700 on the same scale.

According to HÄGG<sup>18,19</sup>, when the radius ratio non-metal/metal is below 0.59, the structure of the intermetallic compound is simple and compact and the compounds are usually hard. When this radius ratio is above 0.59, the structure is complicated and the compounds are still metallic in character but not so hard. The radius ratios of the phosphides that we prepared were between 0.749 and 0.880 indicating that the phosphides are not so hard as the corresponding nitrides and carbides which have simple cubic structures.

*Electrical resistivity.* Sintered compacts of the monophosphides were prepared by cold pressing the minus 325-mesh powders and heating the compacts in argon to just below their decomposition temperatures. The approximate resistivities of these

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compacts as determined with a Wheatstone Bridge circuit are given in Table VII. These results are not highly accurate because the sintered compacts had less than theoretical density and contained small cracks. However, they show that the products are metallic conductors rather than semiconductors at the temperatures indicated.

Phosphide	Measur resistivity	ed specific v (ohm/cm)	Compact density % theoretical	Sintering temperature (°C)
	20°C	-197°C		
TiP	$3.4 \cdot 10^{-3}$	1.3.10-3	64	1,575
VP	9.7.10-3	•	60	1 225
NbP	$1.7 \cdot 10^{-3}$	0.4 · 10 <sup>-3</sup>	65	1,730
TaP	27.10-3	11.6.10-3	69	1,660
CrP	25.10-3	$14.2 \cdot 10^{-3}$	66	1,380
MoP	0.9.10-3	1.4 · 10 <sup>-3</sup>	53	1,475
$\mathbf{WP}$	1.8.10-3	0.46 10-3	57	1,450
MnP	2.5.10-3	1.10-3	78	1,075

TABLE VII

SPECIFIC RESISTIVITY OF SINTERED TRANSITION METAL PHOSPHIDES

The specific electrical resistivities of the nitrides of Groups IV and V are significantly lower than those of the phosphides. For example, according to MOERS<sup>20</sup>, TiN has a specific resistivity of  $0.0217 \cdot 10^{-3}$  ohm/cm at 25°C, and thus is 150 times more conductive than TiP according to our measurements. This is probably caused by the greater intermetallic distances in the phosphides with consequent dilution of the electron density of the metal atoms and also to the decreased metallic character of the bond of the phosphides.

#### CONCLUSIONS

The new syntheses presented for the transition metal phosphides appear to have some advantages over other methods. Large quantities of these phosphides can now be prepared readily without specialized equipment and utilizing available materials. The reactions are rapid and the phosphides produced have good stoichiometry.

Measurements of thermal stability, hardness, and electrical conductivity place the phosphides of the transition metals of Groups IV, V, and VI with carbides, borides, nitrides, and silicides in the so-called class of "hard metals". The thermal stabilities, hardnesses, and electrical conductivities of these compounds were correlated with the crystal structures calculated by previous investigators.

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