On Metallic Phases in the Ti-P-O and Zr-P-O Systems

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METALLIC PHOSPHIDES

In a recently published paper about transition metal phosphides¹ the present author found that phosphide phases with a nonmetal content up to 50 atom-% have structures analogous to the metallic carbides and nitrides of the transition metals. The interatomic metal-metal bonds are weaker in the phosphides than in the carbides and nitrides, but the metal-phosphorus bonds seem to be strong, probably of a partial ionic nature.

TiP¹ and β -ZrP¹ are isomorphous with γ' -MoC² and NbN^{3,4}. α -ZrP¹ exists at the approximate composition ZrP_{0.9} and is of the B1 type. According to Biltz, Rink and Wiechmann⁵ a titanium "subphosphide" exists at the approximate composition Ti₂P. In the present study this compound was prepared from the elements in the same way as described earlier¹, and the composition was found to correspond to the formula Ti₃P rather than Ti₂P. The Ti₃P phase is of the Fe₃P^{6,7} structure, with the unit cell dimensions $a = 10.00$ Å, $c = 5.017$ Å; $c/a = 0.502$ ($V = 501.7$ Å³). A zirconium "subphosphide" also seems to exist, but its composition and structure is unknown^{8,1}.

METALLIC OXIDES

Besides the earlier known TiO phase^{9,10} of the NaCl structure Wang and Grant¹¹ have recently observed the existence of a phase (designated by δ) which is reported to be formed by a peritectoid reaction of the α -Ti and TiO phases at temperatures below 925° C.

Cubiciotti¹² and Domagala and Mc Pherson¹³ did not find any traces of a ZrO phase in their investigations of the Zr—O system. They prepared the samples starting from the pure metal and the dioxide. Only the α -Zr, β -Zr and ZrO₂ phases are shown in the equilibrium diagrams published by them. This was confirmed in the present study, when the corresponding preparation method was used, *i. e.* mixtures of Zr (degassed zirconium hydride from Metal Hydrides Inc.) and ZrO₂ (Baker's Analyzed) were heated in zirconia crucibles in a high frequency vacuum induction furnace at temperatures between 1200° C and 1700° C. But if the metal was carefully oxidized with steam in the presence of hydrogen in great excess at temperatures between 600° C and 800° C a phase

of B1 type and with a cubic edge length varying between $a = 4.584 \text{ \AA}$ and $a = 4.620 \text{ \AA}$ was obtained¹⁴. The presence of hydrogen in the lattice is most unlikely because heating *in vacuo* at 1000°C for two hours did not cause any structural change. The existence of ZrO is also confirmed by the fact that this phase could be found in many samples where Zr was oxidized *in vacuo* by means of different oxides of the metals Fe, Co, and Ni.

Because of the ease with which ZrO_2 is formed it was not possible to prepare ZrO in a pure state. The homogeneity range of ZrO seems to be comparatively large, but the limits are unknown. In contrast to ZrO it is fairly easy to prepare TiO, VO and NbO from the metals and, for instance, the oxides TiO_2 , V_2O_5 and Nb_2O_5 respectively.

METALLIC PHOSPHIDE-OXIDES

In order to search for metallic ternary Ti—P—O and Zr—P—O phases, phosphide samples of different compositions were prepared by heating metal (degassed hydride from Metal Hydrides Inc.) and red phosphorus (Kahlbaum, *pro analysi*) in evacuated and sealed silica tubes at 700°C for about one week. The powdered samples were then cautiously oxidized with steam in the presence of hydrogen at various temperatures between 600° and 800°C .

The phase analysis of the specimens was performed by means of powder photographs taken with Cu-K α radiation in a focussing camera of the Guinier type. For measurements of the high-angle reflections additional photographs were taken with Hagg-Phragmén type focussing cameras.

Besides the binary phosphide and oxide phases the interpretation of the photographs revealed the existence of a ternary phase in each system, in both cases of a structure related to a B1 type lattice. The purest samples of these ternary compounds were obtained for the metal/phosphorus ratio equal to 3/1. Because of the difficulty of obtaining these phases in a pure state it was not possible to determine the oxygen content with any accuracy. The structure determination, however, shows the value of the metal/phosphorus ratio to be 3/1 and further makes an oxygen content of 33 atom % or slightly less very probable. The formulae are therefore written Ti_3PO_2 and Zr_3PO_2 respectively. The two phases are isomorphous and appear as black powders.

The strongest diffraction lines, which were in some cases slightly broadened, could be indexed as coming from face-centered cubic lattices. The lattice constants were found to be $a = 4.415 \text{ \AA}$ and $a = 4.779 \text{ \AA}$ for the Ti_3PO_2 and Zr_3PO_2 phases respectively. Besides these reflexions a series of comparatively weak lines were visible, indicating a true unit cell of hexagonal symmetry containing three metal atoms, *i.e.* one formula unit Ti_3PO_2 or Zr_3PO_2 , and with the axial ratio close to that characteristic for an ideal cubic close-packing, $c/a = \sqrt{6} = 2.449$. Some "superlattice" reflections are of such an intensity that they must be due to a displacement of the metal atom positions from the rhombohedral ones — *i.e.* 0,0,0; $1/3, 2/3, 1/3$; $2/3, 1/3, 2/3$ — and not only to an ordering of the nonmetal atoms. Starting from the assumption that the non-metal atoms occupy fixed positions in the lattice and that the interatomic

metal-phosphorus distances are about 0.4 Å longer than the metal-oxygen distances the most likely configuration for the phases will be obtained in the space-group $D_{3d}^3-P\bar{3}m$ with the following arrangement of the atoms:

- 1 Ti (Zr) in 1(a) 0,0,0
 2 Ti (Zr) in 2(d) $1/3, 2/3, z$; $2/3, 1/3, \bar{z}$; with $z < 1/3$
 1 P in 1(b) 0,0,1/2
 2 O in 2(d) $1/2, 2/3, z$; $2/3, 1/3, \bar{z}$, with $z > 5/6$

The best agreement between the observed intensities and the calculated p/F^2 values was obtained for $z_{Ti} = 0.28$ and $z_{Zr} = 0.29$. As the nonmetal atoms will be situated at the centres of metal atom octahedra the parameter values for the O atoms are assumed to be $\bar{z}_{Ti}/2$ and $\bar{z}_{Zr}/2$ for Ti_3PO_2 and Zr_3PO_2 respectively.

The intensities calculated and observed for the Ti_3PO_2 phase are compared in Table 1. The axial ratio $c/a = 2.453$ deviates to such a small extent from that characteristic of a cubical close-packed arrangement that the diffraction lines belonging to certain groups with hexagonal indices * will coincide in spite of the excellent resolution of the photographs. The cubical indices corresponding to the rhombohedral ones are given in Table 1 under the heading "B1 — indices".

Table 1. Calculated and observed intensities for the Ti_3PO_2 phase.

<i>hkl</i>	<i>I</i> _{calc}	<i>I</i> _{obs}	"B1-indices"	<i>hkl</i>	<i>I</i> _{calc}	<i>I</i> _{obs}	"B1-indices"
0,0,1	7	5		1,1,5	7	0	
0,0,2	2	0		2,1,0	1	0	
1,0,0	1	0		1,0,7	3		
0,0,3	3			2,0,5	12	30	3,3,1
1,0,1	42	50	1,1,1	2,1,1	14		
1,0,2	101	100	2,0,0	1,1,6	3	50	4,2,0
0,0,4	12	10		2,1,2	49		
1,0,3	21	15		0,0,8	2	0	
1,0,4	25			2,1,3	15	10	
1,1,0	68	100	2,2,0	2,0,6	13	10	
0,0,5	4	0		1,0,8	10		
1,1,1	1	0		2,1,4	14	50	4,2,2
1,1,2	1	0		3,0,0	20		
2,0,0	0	0		1,1,7	19	15	
1,0,5	23			3,0,1	0	0	
1,1,3	6	50	3,1,1	3,0,2	0	0	
2,0,1	12			0,0,9	1		
0,0,6	1			2,0,7	2		3,3,3
2,0,2	41	50	2,2,2	2,1,5	18	30	5,1,1
1,1,4	33	30		3,0,3	3		
2,0,3	13	10		1,1,8	6	0	
1,0,6	22	15		3,0,4	22	15	
2,0,4	13	15	4,0,0	1,0,9	9	0	
0,0,7	5	0		2,1,6	35	30	

* If $c/a = \sqrt{6}$ the quadratic formula for the hexagonal unit cell can be written as $\sin^2\theta = 8C(h^2 + k^2 + hk) + Cl^2 = 9Cn$ for $h + k + l = 3m$. As an example, the reflexions 0,0,9; 3,0,3; 2,1,5; 2,0,7 will coincide, all of them giving $n = 9$.

Table 2. Interatomic distances in the Ti_3PO_2 phase.

Atom	Surrounding atoms	Interatomic distance, Å
Ti in 1(a)	6 Ti in 2(d)	2.80
	6 Ti in 1(a)	3.12
	6 O	2.09
Ti in 2(d)	3 Ti in 1(a)	2.80
	3 Ti in 1(a)	3.82
	6 Ti in 2(d)	3.12
	3 P	2.47
	3 O	2.09
P	6 Ti in 2(d)	2.47
	6 P	3.12
	6 O	3.29
O	3 Ti in 1(a)	2.09
	3 Ti in 2(d)	2.09
	3 P	3.29
	3 O	2.80

The interatomic distances in the Ti_3PO_2 and Zr_3PO_2 phases are listed in Table 2 and Table 3, respectively.

It ought to be mentioned that the "superlattice" reflections could not be traced in the photographs for the cases when the reflections corresponding to a B1 type lattice were broad and diffuse. This may be caused by a more or less random distribution of the P and O atoms over the metalloid positions leading to mean parameter values $z_{Ti(Zr)} = 1/3$ and $\bar{z}_O = 1/6$. When these disordered samples are heated *in vacuo* for a sufficient long time at the same temperatures as that used for their preparations the lines turn sharper and the "superlattice" lines appear.

Table 3. Interatomic distances in the Zr_3PO_2 phase.

Atom	Surrounding atoms	Interatomic distance, Å
Zr in 1(a)	6 Zr in 2 (d)	3.09
	6 Zr in 1(a)	3.38
	6 O	2.29
Zr in 2(d)	3 Zr in 1(a)	3.09
	3 Zr in 1(a)	3.99
	6 Zr in 1(d)	3.38
	3 P	2.61
	3 O	2.29
P	6 Zr in 2(d)	2.61
	6 P	3.38
	6 O	3.53
O	3 Zr in 1(a)	2.29
	3 Zr in 2(d)	2.29
	3 P	3.53
	3 O	3.09

Table 4. Comparison between the volumes, nonmetal-metal and metal-metal distances of some metallic phases in the Ti-P-O and Zr-P-O systems.

Phase	Structure type	Axial values Å	Vol./metal atom Å ³	O-metal dist. (6-coord.) Å	P-metal dist. (6-coord.) Å	Metal-metal dist. (12-coord.) Å	Increase of metal-metal dist., %
α -Ti	A 3	$a = 2.952$ $c = 4.732$	17.85			2.93	—
α -Ti(O)*	L' 3	$a = 2.961$ $c = 4.806$	18.24	2.09		2.96	0.5
TiO	B 1	$a = 4.162$ $c = 4.232$	18.02— 18.95	2.08— 2.12		2.94— 2.99	0.3— 2.0
Ti ₃ PO ₂	Ti ₃ PO ₂	$a = 3.120$ $c = 7.652$	21.50	2.09	2.47	3.08	5.1
TiP	TiP	$a = 3.487$ $c = 11.65$	30.67		2.48	3.45 **	17.5
α -Zr	A 3	$a = 3.223$ $c = 5.127$	23.07			3.20	—
α -Zr(O)*	L' 3	$a = 3.268$ $c = 5.244$	24.25	2.30		3.25	1.7
ZrO	B 1	$a = 4.584$ $c = 4.620$	24.08— 24.65	2.29— 2.31		3.24— 3.27	1.4— 2.2
Zr ₃ PO ₂	Ti ₃ PO ₂	$a = 3.380$ $c = 8.279$	27.29	2.29	2.61	3.35	4.8
α -ZrP	B 1	$a = 5.270$	36.62		2.64	3.73	16.6
β -ZrP	TiP	$a = 3.677$ $c = 12.52$	36.65		2.64	3.65 **	14.2

* At the oxygen-rich phase limit (800° C).

** The metal atoms have 10-coordination.

The unit cell dimensions found in the present study for the metallic phases in the Ti—P—O and Zr—P—O systems (with the exception of the subphosphides) are listed in Table 4. The mean interatomic nonmetal-metal and the mean metal-metal distances are calculated from those data. The former ones vary very slightly for a given metal. The latter ones increase with increasing amount of phosphorus. The relative increase in relation to the intermetallic distances in the pure metals is shown in the last column of the table. These numbers may show the weakening of the metallic properties.

SUMMARY

The metallic corners of the Ti—P—O and Zr—P—O systems (nonmetal/metal ratio ≤ 1) have been investigated by means of X-ray methods.

The structures of the monophosphide phases are known earlier. Ti₃P is isomorphous with Fe₃P.

Attempts to prepare ZrO from Zr and ZrO₂ were in vain, but this phase (B1 type) could be identified in samples where Zr was oxidized by means of steam in the presence of hydrogen or with oxides of Fe, Co and Ni.

The ternary metallic phases Ti_3PO_2 and Zr_3PO_2 are isomorphous with each other and are of an interstitial structure type with the nonmetal atoms in ordered positions at the centres of metal atom octahedra. The three metal atoms in the hexagonal unit cell are displaced to a slight extent from the positions corresponding to a cubic close-packing.

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