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The interaction of phosphorus with titanium and molybdenum

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Abstract

The interaction between the components in the ternary system Ti–Mo–P has been investigated using X-ray structure analysis. The isothermal section of the phase diagram at 1070 K has been built in the range 0–0.67 at.% phosphorus. Considerable solid solution ranges exist for the binary phosphides Ti_3P and Mo_3P. The solubility of the third component in the other binary compounds is insignificant. The existence of the earlier known ternary phosphide $TiMoP_2$ has been confirmed and a new compound $(Ti,Mo)_{12-x}P_7$ has been found to be exist in a concentration region described by the chemical formula $Ti_{7.1-4.5}Mo_{4.2-6.8}P_7$. The atomic parameters are refined by the full-profile Rietvelt method for a sample of the $Ti_{4.5}Mo_{6.8}P_7$ composition (space group $P\bar{6}$, lattice parameters $a=0.96834(3)$ and $c=0.33091(1)$ nm, $R=0.092$). The crystal structure of the investigated phosphide is intermediate between the $Cr_{12}P_7$ and $Zr_2Fe_{12}P_7$ types.
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Keywords: Transition metal compounds; Crystal structure; Phase diagram; X-ray diffraction

1. Introduction

Partial investigations of the Ti–Mo–P system have shown the existence of the ternary compound $TiMoP_2$ (structure type NiAs, $a=0.325$ and $c=0.621$) having a homogeneity range described by the formula $Ti_{0.5-0.3}Mo_{0.5-0.7}P$ and solid solution ranges for the binary phosphides MoP (WC[1], limiting composition $Ti_{0.1}Mo_{0.9}P$) and TiP (TiAs, limiting composition $Ti_{0.95}Mo_{0.05}P$) [1,2]. The purpose of present work is a systematic study of the interaction between the components in the Ti–Mo–P system in the range of 0–0.67 at.% P.

2. Experimental procedure

Samples for investigation were synthesized using powders of metals and red phosphorus with a stated purity higher than 99.9 wt.%. Powders of the components were mixed in the respective stoichiometric ratio and pressed into pellets. Samples containing less than 0.33 at.% phosphorus were then melted in an arc furnace with a tungsten electrode in a protected atmosphere of purified argon. Samples with higher P contents were sealed into evacuated quartz ampoules and gradually heated (100 K per day) up to 1170 K and kept at this temperature during 300 h. The ampoules were then slowly cooled to room temperature within the furnace. Subsequently, the samples were crushed, pressed into pellets and again sintered at 1070 K during 300 h. Samples containing 0.33–0.40 at.% phosphorus were remelted in an arc furnace. For reaching the equilibrium condition all samples were homogenized by annealing in quartz ampoules at 1070 K during 1000 h and quenched in cold water. The phase compositions of the samples with high titanium contents were determined using powder diffractograms (diffractometer DRON-3M, Cu Kα or Co Kα radiation; $2\theta=15–130°$, scanning with a step of 0.05° of 2θ and exposition time 10 s in each point). For those with low titanium contents we used the Deby–Sherrer technique (chamber RKD-57.3, Cr K radiation). The crystal structure of the compound was studied by X-ray powder diffraction. All calculations were performed using CSD software [3].

3. Binary systems

In the Ti–Mo system we have confirmed that α-Ti practically does not dissolve molybdenum. The solid

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[1] Structure type of the compound is given in parentheses.

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solution of molybdenum in β-Ti is limited by the compositions $Ti_{0.94-0.82}Mo_{0.06-0.18}$. The solution of titanium in molybdenum reaches the composition $Mo_{0.68}T_{0.32}$, which is in good agreement with the data reported in Refs. [4,5]. The lattice parameters of the limit compositions of these phases are listed in Table 1.

In the systems Mo–P and Ti–P, in the range of 0–0.67 at.% phosphorus, we have confirmed the binary phases with structures and compositions listed in Table 1.

4. Phase equilibria in Ti–Mo–P system

Using the results of phase analysis of the samples synthesized and annealed at 1070 K, the phase equilibria in the Ti–Mo–P system have been established and the isothermal section of the system in the range of up to 0.67 at.% P has been built (Fig. 1).

Considerable solid solution ranges with mutual substitution of titanium and molybdenum are formed for the binary phosphides Ti_3P and Mo_3P. The solid solutions $(Ti–Mo)_3P$ (Ti_3P) and $(Mo,Ti)_3P$ (α-V_3S) reach the limiting compositions $Ti_{1.6}Mo_{1.4}P$ and $Mo_{1.6}Ti_{1.4}P$, respectively. Plots of the lattice parameters are shown in Fig. 2. The solid solution range of MoP (WC) does not include the $Ti_{0.1}Mo_{0.9}P$ composition, which is indicated by a slight increase of the lattice parameters in the two-phase sample ($TiMoP_2$+MoP) compared to the molybdenum monophosphide. The solid solution range of TiP reaches the composition $Ti_{0.95}Mo_{0.05}P$, which is in agreement with Ref. [2]. The decreasing of the lattice parameters of TiP_2 ($PbCl_2$) in two-phase samples (TiP_2+MoP_2) indicates a small solubility of molybdenum in titanium diphosphide, not exceeding the $Ti_{0.9}Mo_{0.1}P_2$ composition. The slight decrease of the unit cell parameters of Ti_2P (Ti_2P) and Ti_7P_4 (Nb_7P_4) in two- and three-phase samples and the increase of the lattice constants of Mo_4P_3 in three-phase samples shows the existence of insignificant solid solution

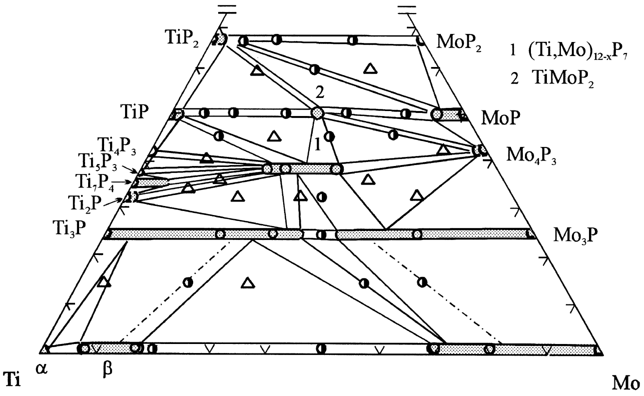

Fig. 1. Phase diagram of the Ti–Mo–P system in the range of 0–0.67 at.% P at 1070 K; (○, ◑, △) one-, two- and three-phase samples, respectively, (- · -) direction of connode.

Table 1
Lattice parameters of binary phases in the Ti–Mo–P system

Phase	Structure type	Lattice parameters (nm)			Refs.
		a	*b*	*c*	
α-Ti	Mg	0.29506		0.46788	[6]
α-$Ti_{0.99}Mo_{0.01}$ [a]		0.29405(9)		0.4651(2)	b
β-($Ti_{0.94-0.82}$ $Mo_{0.06-0.18}$)[a]	α-Fe	0.3179(1)– 0.3164(4)			
		0.3258			b
$Ti_{0.89}Mo_{0.11}$					[7]
$Mo_{0.68}Ti_{0.32}$ [a]	α-Fe	0.3238			[7]
		0.3150(1)			b
Ti_3P	Ti_3P	0.99592		0.49869	[5]
		0.9953(2)		0.4994(4)	b
Ti_2P	Ti_2P	1.15314		0.34575	[5]
Ti_7P_4	Nb_7P_4	1.4614	0.34060 β=104.65°	1.36196	[5]
Ti_5P_3	Yb_5Sb_3	0.97475		1.1676(5)	[5]
Ti_4P_3	anti-Th_3P_4	0.74298			[5]
TiP	TiAs	0.3499		1.1750	[5]
TiP_2	$PbCl_2$	0.61812	0.33455	0.82578	[5]
Mo_3P	α-V_3S	0.9794		0.4827	[5]
		0.9794(3)		0.4822(3)	b
Mo_4P_3	Mo_4P_3	1.2428	0.3158	2.0440	[5]
MoP	WC	0.3223		0.3191	[5]
MoP_2	MoP_2	0.3145	1.1184	0.4984	[5]

[a] Limiting compositions of solid the solution ranges of α-Ti, β-Ti and Mo.

[b] Data of present work.

Table 2
Lattice parameters of ternary phases in the system Ti–Mo–P

Phase	Structure type	Lattice parameters (nm)		
		a	*b*	*c*
$Ti_{1.6}Mo_{1.4}P^{a}$	Ti_3P	0.9793(5)		0.4982(2)
$Mo_{1.6}Ti_{1.4}P^{a}$	α-V_3S	0.9885(4)	1.0441(4)	0.4939(2)
$\sim Ti_{1.9}Mo_{0.1}P^{a}$	Ti_2P	1.1471(5)		0.3435(3)
$\sim Ti_{6.5}Mo_{0.5}P_4{}^{a}$	Nb_7P_4	1.4125(5)	0.3582(3) β=104.33(5)°	1.3147(7)
$\sim Mo_{3.8}Ti_{0.2}P_3{}^{a}$	Mo_4P_3	1.2423(2)	0.31736(6)	2.0396(4)
$Ti_{0.9}Mo_{0.1}P^{a}$	WC	0.32191(7)		0.31995(8)
$Ti_{0.95}Mo_{0.05}P^{a}$	TiAs	0.34933(8)		1.1676(5)
$Ti_{0.9}Mo_{0.1}P_2{}^{a}$	?bCl_2	0.6190(6)	0.3329(3)	0.8260(6)
$TiMoP_2$	NiAs	0.3228(2)		0.6413(5)
$Ti_{7.1-4.5}Mo_{4.2-6.8}P_7$	$Cr_{12}P_7$	0.9690(2)– 0.96834(3)		0.33399(8)– 0.33091(4)

[a] Limiting composition of the solid solution.

Table 3
Atomic coordinates and thermal parameters ($nm^2 \times 10^2$) in the crystal structure of the $(Ti,Mo)_{12-x}P_7$ phosphide of $Ti_{4.5}Mo_{6.8}P_7$ composition, space group $P\bar{6}$

Atom	Position	Occupancy	*x*	*y*	*z*	*B*
Ti1	1(*c*)	0.14(2)	1/3	2/3	0	0.4(1)
Ti2	1(*f*)	0.12(2)	2/3	1/3	1/2	0.4(1)
M1	3(*j*)	0.73(1)Ti+0.27(1)Mo	0.0162(9)	0.2599(8)	0	0.55(5)
M2	3(*k*)	0.69(1)Ti+0.31(1)Mo	0.7759(8)	0.0083(9)	1/2	0.55(5)
Mo1	3(*j*)	0.850(7)	0.3698(6)	0.5040(7)	0	0.68(3)
Mo2	3(*k*)	0.84(1)	0.4977(9)	0.1263(9)	1/2	0.68(3)
P1	1(*a*)	1.0	0	0	0	1.4(3)
P2	3(*j*)	1.0	0.435(1)	0.254(1)	0	0.55(8)
P3	3(*k*)	1.0	0.160(1)	0.467(2)	1/2	0.55(8)

ranges for the corresponding phosphides. The limiting compositions of these solid solutions could not be established. The lattice parameters of all mentioned solid solutions in the Ti–Mo–P ternary systems are listed in Table 2.

In the section with 0.5 at.% phosphorus we have confirmed the ternary phosphide $TiMoP_2$ with NiAs structure, but in contrast to the data reported in Ref. [2], we did not observe a considerable homogeneity range for this compound. The unit cell parameters of $TiMoP_2$ are listed in Table 2. In the twice sintered and remelted samples of the Ti–Mo–P system in the range of 0.35–0.40 at.% P we have found a new ternary phosphide of the approximate composition $Ti_6Mo_6P_7$.

5. Crystal structure of the $(Ti,Mo)_{12-x}P_7$ phosphide

The crystal structure of the $(Ti,Mo)_{12-x}P_7$ phosphide has been determined using the sample of $Ti_{4.5}Mo_{6.8}P_7$ composition. The powder diffractogram of the sample was well indexed with the hexagonal lattice parameters a=

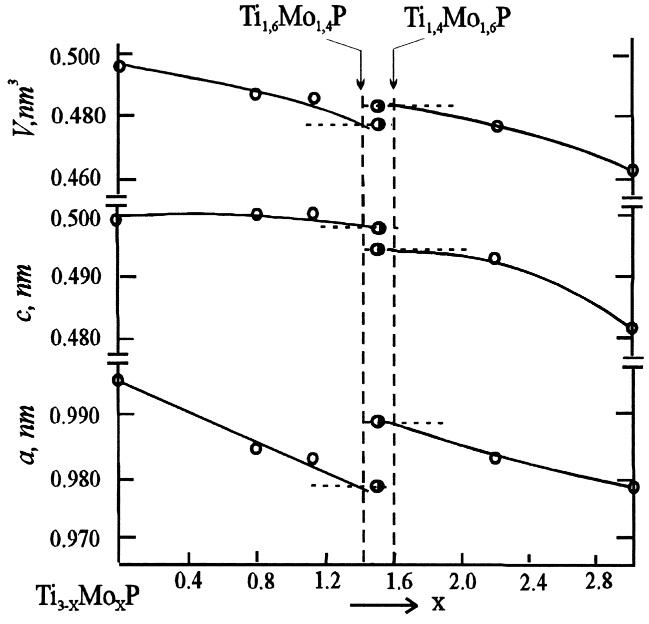

Fig. 2. Plot of lattice parameters of the solid solutions $(Ti,Mo)_3P$ and $(Mo,Ti)_3P$; (○, ◑) one- and two-phase samples.

0.96835(3) and $c=0.33091(1)$ nm. Proceeding from the initial composition of the sample, the refined unit cell constants and intensities of the reflections, we have supposed the crystal structure of the investigated compound to be related with the $Cr_{12}P_7$ type. Refinement of the atomic parameters in space groups $P6_3/m$ and $P\bar{6}$, taking into account a statistical distribution of molybdenum and titanium atoms in the crystallographic positions resulted in reliability factors of $R=0.12$ and 0.105, respectively. Proceeding from the lower R factor and also from the better values of the thermal parameters and interatomic distances, we prefer space group $P\bar{6}$ for the investigated phosphide. The calculation based on differential Fourier synthesis has shown additional electronic density maxima in positions 1(*c*) (1/3 2/3 0) and 1(*d*) (2/3 1/3 1/2). However, too short interatomic distances with neighbouring molybdenum atoms did not permit full occupancy of these positions. Taking into account the higher values of interatomic distances from atoms in 1(*c*) and 1(*d*) positions to the neighbouring phosphorus atoms and comparing with the corresponding distances between occupied positions 3(*j*) (Mo1) and 3(*k*) (Mo2), we suppose that the titanium atoms occupy the first two positions. Refinement of the occupancy factors gives total *G* values close to 1.0 for both pairs of partially occupied positions, which permits their simultaneous presence in the structure. Final refinement of atomic coordinates, thermal parameters and distribution of the atoms in the structure (Table 3) resulted in an R value of 0.092. Experimental and calculated diffractograms of the compounds and also their difference are shown in Fig. 3.

The interatomic distances in the crystal structure of $(Ti,Mo)_{12-x}P_7$ are close to the sums the of atomic radii of the corresponding components (Table 4). A slight shortening is observed between phosphorus and metal atoms, which can indicate some covalent bonding between these atoms ($\chi_P=2.1$, $\chi_{Ti}=\chi_{Mo}=1.6$) [8].

The investigated phosphide $(Ti,Mo)_{12-x}P_7$ has a homogeneity range which is described by the chemical formula $Ti_{7.1-4.5}Mo_{4.2-6.8}P_7$. The lattice parameters of the limiting compound in the homogeneity range are listed in Table 2.

6. Discussion

The small difference in atomic radii of the metals ($r_{Ti}=0.1462$, $r_{Mo}=0.1400$ nm [6]) and their identical electronegativities ($\chi_{Ti}=\chi_{Mo}=1{,}6$) [8]) leads to the formation in the Ti–Mo–P system of considerable solid solution ranges for the M_3P phosphides by mutual substitution of metal atoms. However, besides the solid solutions, two ternary compounds are formed in the system: the earlier known $TiMoP_2$ (NiAs) and $(Ti,Mo)_{12-x}P_7$. As regards the character of the interaction between the components, the Ti–Mo–P system exhibits some similarity with the systems Ti–Cr–P [1,2,5,9] and Ti–W–P [1,2,5]. Ternary

Table 4
Interatomic distances (δ, nm) in the structure of $Ti_{4.5}Mo_{6.8}P_7$

Atoms	δ
Ti1–6 P3	0.246(1)
2 Ti1	0.33091(1)
3 M1	0.3585(9)
6 Mo1	0.3757(3)
Ti2–6 P2	0.2573(8)
2 Ti2	0.33091(1)
3 M2	0.3789(8)
6 Mo2	0.3790(5)
M1–1 P2	0.233(1)
2 P3	0.243(1)
1 P1	0.2442(7)
2 Mo2	0.270(1)
2 M2	0.282(1)
2 M2	0.2901(9)
1 Mo1	0.304(1)
1 Mo1	0.3173(8)
2 M1	0.33091(1)
1 Ti1	0.3585(7)
M2–2 P2	0.247(1)
2 P1	0.2762(7)
1 P3	0.277(1)
2 M1	0.2822(9)
2 Mo1	0.2872(9)
2 M1	0.2901(9)
1 Mo2	0.315(1)
2 M2	0.33091(1)
1 Mo2	0.341(1)
1 Ti2	0.3789(8)
2 M2	0.383(1)
Mo1–2 P3	0.238(1)
2 P3	0.251(1)
Mo1–1 P2	0.280(1)
2 M2	0.2872(8)
2 Mo2	0.301(1)
1 M1	0.304(1)
2 Mo1	0.3080(9)
1 M1	0.317(1)
2 Mo1	0.33091(1)
2 Ti1	0.3757(3)
Mo2–2 P2	0.232(1)
1 P3	0.244(1)
2 M1	0.270(1)
2 P2	0.274(1)
2 Mo1	0.3010(9)
1 M2	0.315(1)
2 Mo2	0.320(1)
2 Mo2	0.33091(1)
1 M2	0.341(1)
2 Ti2	0.790(4)
P1–3 M1	0.2442(8)
6 M2	0.2762(6)
P2–2 Mo2	0.232(1)
1 M1	0.233(1)
2 M2	0.247(1)
2 Ti2	0.257(1)
2 Mo2	0.274(1)
1 Mo1	0.280(1)
P3–2 Mo1	0.238(1)
2 M1	0.243(1)
1 Mo2	0.244(2)
2 Ti1	0.246(1)
2 Mo1	0.251(1)
1 M2	0.277(2)

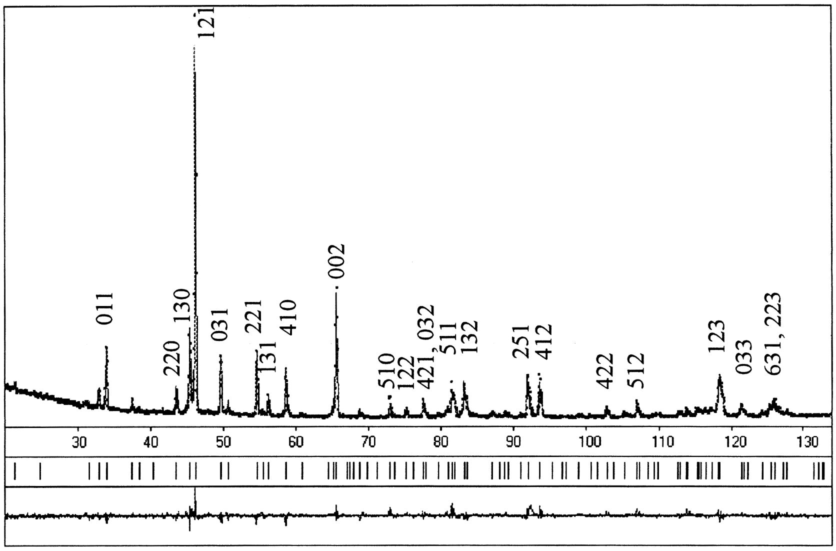

Fig. 3. Experimental (· · ·) and calculated (- - -) diffractogram of the $(Ti,Mo)_{12-x}P_7$ ($Ti_{4.5}Mo_{6.8}P_7$ composition) and their difference. The indices shown are the strongest ones.

compounds of the NiAs structure type are formed in all mentioned systems. Taking into account that only a partial investigation of the Ti–W–P system has been performed, one can suppose the existence of a ternary compound isotypic with $(Ti,Mo)_{12-x}P_7$ in this system.

The crystal structure of $Ti_{4,5}Mo_{6,8}P_7$ is closely related with the $Cr_{12}P_7$ type. Both structures consist of similar atomic blocks (Fig. 4), but in the former compound two additional crystallographic positions (1(*c*) and 1(*f*), space group $P\bar{6}$) are partially occupied by transition metal atoms (titanium). Besides, in $Ti_{4.5}Mo_{6.8}P_7$ two closely located to 1(*c*) and 1(*f*) positions are also partially occupied by molybdenum atoms and the other transition metal positions are occupied by a statistical mixture of titanium and

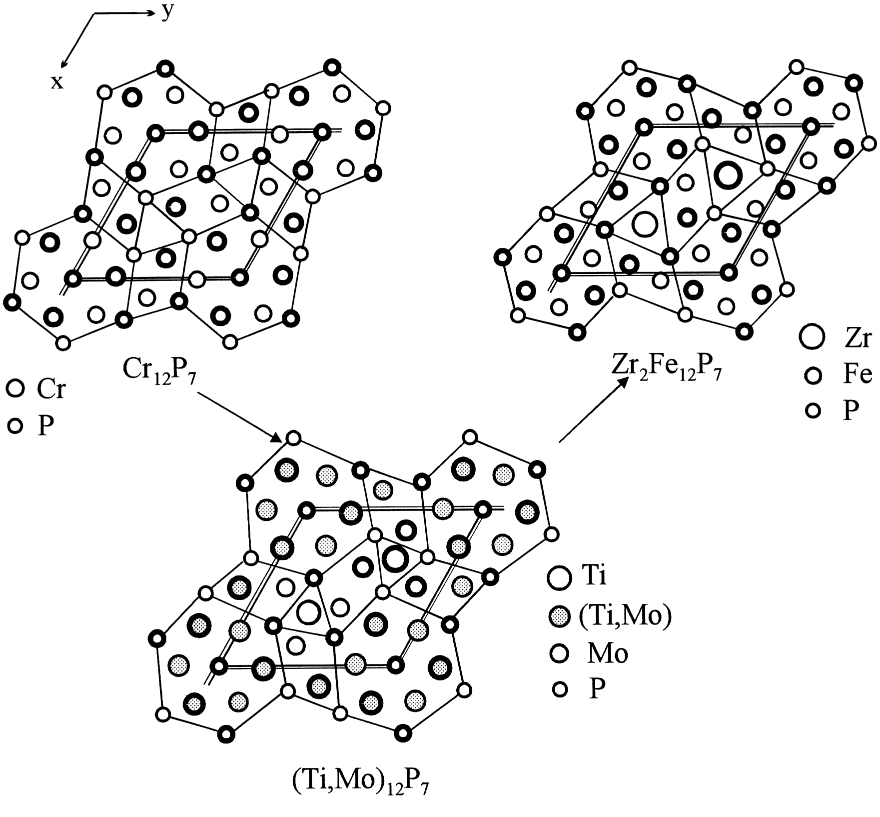

Fig. 4. Crystal structures of $Cr_{12}P_7$, $Zr_2Fe_{12}P_7$ and $Ti_{4.5}Mo_{6.8}P_7$.

molybdenum (shaded circles in Fig. 4). In the closely related $Zr_2Fe_{12}P_7$ structure, the atomic distribution is completely ordered and the atoms of largest size (zirconium) are located in different planes (displaced by 1/2 of the hexagonal constant *c*) compared to the neighbouring medium size atoms. The crystal structures of $Cr_{12}P_7$, $Zr_2Fe_{12}P_7$ and $Ti_{4,5}Mo_{6,8}P_7$ phosphides are shown in Fig. 4.

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