

New Phases in the Ti–P and Ti–Cu–P Systems

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An investigation of the Ti–P and Ti–Cu–P systems has disclosed new phases. The phases were studied using X-ray diffraction and electron microprobe techniques. The results obtained are reported in the present communication.

The Ti–P alloys were prepared by reacting filings of titanium and red phosphorus (Koch-Light Laboratories Ltd, Colnbrook, England, claimed purity 99.95 and 99.999 %, respectively) in evacuated and sealed silica tubes at 800 °C for at least three days. The reaction products were subsequently arc-melted under a purified argon atmosphere. In a similar manner copper-rich ternary samples were prepared by initially reacting lumps of copper

(Outokumpu Oy, Pori, Finland, as analyzed better than 99.99 %) and red phosphorus in silica tubes and subsequently melting the reaction products together with lumps of titanium in a cold crucible induction furnace or an arc furnace. Prior to the synthesis, surface oxides on the starting materials were removed. Parts of the samples were heat-treated at 800 and 900 °C for 11–12 days. Metallographic examination of the solidified copper-rich melts revealed small primary crystals (needles, plates, octahedra) in the copper matrix. The crystals were isolated by dissolving the matrix in nitric acid and were examined using single crystal as well as powder X-ray diffraction methods.

The single crystal fragments were examined in Weissenberg cameras with filtered $\text{CuK}\alpha$ radiation. Powder diffraction films were recorded in Guinier-Hägg cameras with $\text{CuK}\alpha_1$ radiation ($\lambda = 1.540598$ Å). Semiconductor grade silicon ($a = 5.431065$ Å) was used as internal calibration standard. The unit cell dimensions were refined by means of a least-squares program.¹ The standard deviations given in Table 1 were calculated without considering possible systematic errors.

Table 1. Crystallographic and electron microprobe data of binary and ternary phases. Unit cell dimensions in Å units with standard deviations in parentheses. Microprobe data in atomic percent, normalized to 100, HFM = High Frequency Melting.

Phase	Space group	Structure type	Cell dimensions	No. refl.	Heat treatment	Micro-analysis	Crystal shape
Ti_7P_4	$C2/m$	Nb_7P_4	$a = 14.614(1)$ $b = 3.4060(2)$ $c = 13.6196(6)$ $\beta = 104.650(4)$	24	Arc melted	--	--
$(\text{Ti}_{1-x}\text{Cu}_x)_7\text{P}_4$ $x = 0.033$	$C2/m$	Nb_7P_4	$a = 14.583(1)$ $b = 3.4084(2)$ $c = 13.6137(6)$ $\beta = 104.633(4)$	50	12d, 800°C after HFM	Cu 2.1 Ti 61.4 P 36.5	Twinned needles
$\alpha\text{-Ti}_5\text{P}_3$	$Pnma$	$\beta\text{-Yb}_5\text{Sb}_3$	$a = 9.7539(4)$ $b = 7.4263(3)$ $c = 6.5032(2)$	54	Arc melted	--	--
$\alpha\text{-}(\text{Ti}_{1-x}\text{Cu}_x)_5\text{P}_3$ $x = 0.011$	$Pnma$	$\beta\text{-Yb}_5\text{Sb}_3$	$a = 9.7475(5)$ $b = 7.4403(3)$ $c = 6.5056(5)$	15	12d, 800°C after HFM	Cu 0.7 Ti 62.5 P 36.8	Pseudo- octahedra
$\beta\text{-}(\text{Ti}_{1-x}\text{Cu}_x)_5\text{P}_3$ $x = 0.025$	$Pnma$	Nb_5P_3	$a = 24.843(2)$ $b = 3.4258(3)$ $c = 11.2228(7)$	20	12d, 800°C after HFM	Cu 1.6 Ti 61.5 P 36.9	Needles
$(\text{Ti}_{1-x}\text{Cu}_x)_{1.6}\text{P}$ $x = 0.034$	$Pnmm$ or $Pnn2$	$\text{Zr}_{1.6}\text{P}$	$a = 15.529(1)$ $b = 25.602(2)$ $c = 3.4796(2)$	47	12d, 800°C after HFM	Cu 2.1 Ti 60.3 P 37.6	Needles
$(\text{Ti}_{1-x}\text{Cu}_x)_{1.5}\text{P}$ $x = 0.069$	$Pbam$ or $Pba2$	--	$a = 18.531(2)$ $b = 9.3873(4)$ $c = 3.4418(3)$	24	12d, 800°C after HFM	Cu 4.1 Ti 55.4 P 40.5	Needles
TiCu_2P	$I4_1/amd$	--	$a = 3.5149(1)$ $c = 33.562(1)$ ($c = 8 \times 4.195$)	28	11d, 900°C after arc melting	Cu 47.6 Ti 25.2 P 27.2	Plates

The composition of the phases were determined using an electron microprobe (ARL-SEM). Single crystals were mounted in epoxy resin and after metallographic preparation covered with a thin layer of gold to facilitate electron conduction. A single crystal of Ti_3P was used as standard sample for the determination of titanium and phosphorus while elemental copper of high purity was used as standard for the determination of copper. The microprobe intensity data were corrected for the effects of atomic number, fluorescence and absorption using the program MAGIC.² The estimated relative errors in the microanalysis are approximately 1% for titanium and for copper in $TiCu_2P$ and 2% for phosphorus. Low copper concentrations were obtained with much larger relative error.

Crystallographic and microanalysis data are presented in Table 1. The micro-probe data are given in atomic percent, normalized to a sum of 100. The crystal shape is also given in the table. The axis of the needle-shaped crystals is in all cases coincident with the short crystallographic axis. For some of the phases in Table 1, in particular for $Me_{-1.5}P$, significant unit cell variations were found, indicating a range of homogeneity.

From a crystal structure refinement³ it has been established that $\alpha-Ti_5P_3$ crystallizes in the $\beta-Yb_5Sb_3$ type structure⁴ as was earlier proposed by Berger.⁵ This phase is identical to that denoted $Ti_{-1.7}P$ by Snell.⁶ Ti_7P_4 crystallizes in the Nb_7P_4 type structure⁷ and dissolves small amounts of copper as demonstrated by the microanalysis and the shrinkage of the unit cell volume (see Table 1).

The crystals of $\beta-Ti_5P_3$ gave diffuse and very weak intensities in Weissenberg as well as powder patterns. The crystals frequently consisted of several intergrown, very small ($< 3 \mu m$ in diameter) needles as demonstrated in a SEM study. The structural isotypism between $\beta-(Ti_{1-x}Cu_x)_5P_3$ and Nb_5P_3 ⁸ was inferred from the similarity of the unit cell dimensions of the two phases and a satisfactory agreement between the observed and calculated (using the atomic parameters of Nb_5P_3) intensities in the pattern of $\beta-(Ti_{1-x}Cu_x)_5P_3$. A comparison of the Weissenberg films for $(Ti_{1-x}Cu_x)_{-1.6}P$ with those for the compound ZrP_x ($0.5 < x < 1$) in the $Zr-P$ system⁹ immediately showed that the two compounds are isostructural. The space group of $(Ti_{1-x}Cu_x)_{-1.5}P$ was determined from Weissenberg films. The approximate compositions of $(Ti_{1-x}Cu_x)_{-1.6}P$ and $(Ti_{1-x}Cu_x)_{-1.5}P$ were obtained from crystallographic considerations of the unit cell content and from the microanalysis.

As can be seen from Table 1 the three phases $\beta-(Ti_{1-x}Cu_x)_5P_3$, $(Ti_{1-x}Cu_x)_{-1.6}P$ and $(Ti_{1-x}Cu_x)_{-1.5}P$ contain only a few atomic percent copper. It has not so far, been possible to prepare these

phosphides in the $Ti-P$ system using temperatures below $1100^\circ C$. One (or more) of the phases may be binary at high temperature and ternary at low temperature or it may be binary within the whole temperature region. In the latter case the formation of the phase is facilitated by crystallization from the copper melt.

The ternary compound $TiCu_2P$ crystallizes in the space group $I4_1/amd$. Its crystal structure can be described as a superstructure of a tetragonally deformed *f.c.c.* structure (Strukturbericht A1) with the *c* axis eight times larger than that of the sub-cell. The structure belongs to the $TiAl_3$ family.¹⁰ A structure determination of $TiCu_2P$ is currently being undertaken by the present authors.

Acknowledgements. The authors thank Mrs Gunilla Runnsjö, Swedish Institute for Metal Research, Stockholm, for valuable help with the microanalysis. This investigation was supported by Bergwall's Foundation and the Swedish Natural Science Research Council. One of us (W.C.-C.) is indebted to the Ford Foundation for financial support.

1. Lundgren, J.-O., Ed., *Crystallographic Computer Programs*, Institute of Chemistry, University of Uppsala, Uppsala 1975, UUIC-B13-04-02.
2. Colby, J. W. *Adv. X-Ray Anal.* 11 (1968) 287.
3. Carrillo-Cabrera, W. and Lundström, T. *To be published.*
4. Brunton, G. D. and Steinfink, H. *Inorg. Chem.* 10 (1971) 2301.
5. Berger, R. *Acta Chem. Scand. A* 31 (1977) 514.
6. Snell, P.-O. *Acta Chem. Scand.* 22 (1968) 1942.
7. Rundqvist, S. *Acta Chem. Scand.* 20 (1966) 2427.
8. Hassler, E. *Acta Chem. Scand.* 25 (1971) 129.
9. Lundström, T. *Acta Chem. Scand.* 20 (1966) 1712.
10. Raman, A. and Schubert, K. *Z. Metallkd.* 56 (1965) 44, 99.

Received March 26, 1979.