

New Ternary Phosphides of the $Nb_5Cu_4Si_4$ Type

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In an attempt to pick a crystal of TaNiP suitable for X-ray structure refinement from a sample of this nominal composition, a single crystal was found which exhibited tetragonal symmetry. The ternary Ta–Ni–P system has not been exhaustively examined, and the identity of the new phase was established only after new alloys approaching this composition had been prepared. It then emerged that the ideal composition of the new compound ought to be $Ta_5Ni_4P_4$, the phase being isostructural with $Nb_5Cu_4Si_4$.¹ An analogue was also found in the Nb–Ni–P system.

Experimental. Two methods were used for preparing $Ta_5Ni_4P_4$, either heating the elements in a silica tube or melting TaP together with elemental nickel in an induction furnace. The niobium analogue was prepared by silica-tube synthesis only.

X-Ray powder photographs produced by a Guinier-Hägg focusing camera were used for the phase analyses, and the cell dimensions, as presented in Table 1, were determined using silicon ($a = 5.431065 \text{ \AA}$) as internal calibration standard.² The radiation was strictly monochromatic $CuK\alpha_1$.

Results and discussion. The two Ta–Ni–P samples also contained TaNiP and TaP. As can be seen from Table 1, the cell dimensions of $Ta_5Ni_4P_4$ were found to vary. This was also the case for the TaNiP phase, as observed by Rundqvist and Nawapong.³ Only a single-crystal structure deter-

mination can ascertain whether the noted deviations are due to vacancies or substitution at the crystallographic sites. A refinement of the $Ta_5Ni_4P_4$ structure has been started, the results of which will be published later. Calculations of powder intensities using the positional parameters of Ganglberger¹ gave excellent agreement with the observed data, and there can thus be no doubt as to the structure type assignment even though no complete phase analysis of the investigated systems has been made.

The presence of NbNiP was also ascertained in the Nb–Ni–P sample, but extra lines found could not be indexed.

The $Nb_5Cu_4Si_4$ structure can formally be derived from that of Ti_5Te_4 ⁴ by the addition of eight atoms to the cell. In a similar way, V_3As_2 is generated by adding two atoms per cell,⁵ and there is also an accompanying space-group change.

Attempts to prepare analogous compounds in the Nb–Cu–P and the Nb–Co–P systems were not successful. This outcome can hardly be explained by considering the relative atomic sizes but rather indicates an electron concentration factor for the stability.

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Table 1. Least-squares refined cell parameters of $Ta_5Ni_4P_4$ and $Nb_5Ni_4P_4$, space group $I4/m$.

Phase	Cell dimensions/Å	
	~ 1050 °C	~ 1600 °C
$Ta_5Ni_4P_4$	$a = 9.8918(3)$ $c = 3.5141(2)$	9.8693(3) 3.5076(2)
$Nb_5Ni_4P_4$	$a = 9.9288(3)$ $c = 3.5238(2)$	