

New Phases in the Hf-As System

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The Hf-As system has previously been investigated by Jeitschko and Nowotny.¹ They prepared hafnium arsenides by reacting the component elements in evacuated silica tubes at temperatures about 1000°C and investigated the products by X-ray powder diffraction methods. The occurrence of three intermediate phases was reported. The diarsenide, HfAs₂, was found to crystallize with the PbCl₂-type structure and the monoarsenide, HfAs, with the TiP-type structure. The third phase was stated to have the approximate composition Hf₄As. The powder diffraction pattern was not interpreted.

A re-investigation of the Hf-As system has been started at this Institute and the present communication gives some preliminary results. The samples were prepared by reacting turnings of zone-refined polycrystalline hafnium bars, containing 3% zirconium (Koch-Light laboratories Ltd., claimed nonmetallic impurities less than 10 ppm C, 10 ppm H₂, 10 ppm N₂ and 50

ppm O₂) and arsenic (Koch-Light) in evacuated and sealed silica tubes for 3 days at 900°C. The reaction products were subsequently arc-melted under purified argon.

X-Ray powder diffraction examination of the samples was made using Guinier-Hägg type focussing cameras with CuK_α₁ or CrK_α₁ radiation. Single crystals picked from the arc-melted alloys were examined using Weissenberg cameras with filtered CuK or MoK radiation. The unit cell dimensions, as determined from powder diffraction films using silicon ($a=5.43054$ Å) as the internal calibration standard, were refined by means of a least-squares program.² (The standard deviations given in Table 1 are calculated without considering possible systematic errors).

In the reaction products obtained from the silica tubes, the only intermediate phases observed were HfAs and HfAs₂. The structure types for these compounds as reported by Jeitschko and Nowotny¹ were confirmed, and the cell dimensions were in agreement with those previously reported. Small variations observed for the cell dimensions of HfAs may possibly indicate a limited range of homogeneity.

For several binary systems containing Group IV and V transition metals and phosphorus or arsenic, it has been observed that new intermediate phases are formed when products obtained by the silica tube technique are subjected to heat treatments

Table 1. Crystallographic data for some hafnium arsenides.

Phase	Structure type	Space group	Cell dimensions and their standard deviations (Å)	Cell volume (Å ³)
Hf ₂ As	Ta ₂ P	<i>Pnmm</i>	$a = 15.3606 \pm 0.0006$ $b = 12.4892 \pm 0.0006$ $c = 3.6498 \pm 0.0002$	700.2
Hf _{1.67} As		<i>Pnma</i>	$a = 27.3884 \pm 0.0013$ $b = 3.6114 \pm 0.0002$ $c = 12.3049 \pm 0.0005$	1217.1
Hf ₃ As ₂	Hf ₃ P ₂	<i>Pnma</i>	$a = 10.4362 \pm 0.0009$ $b = 3.6521 \pm 0.0002$ $c = 10.1465 \pm 0.0005$	386.7
HfAs	TiP	<i>P6₃/mmc</i>	$a = 3.7681 \pm 0.0003$ $c = 12.7034 \pm 0.0017$	156.2
HfAs ₂	PbCl ₂	<i>Pnma</i>	$a = 6.7739 \pm 0.0008$ $b = 3.6763 \pm 0.0002$ $c = 8.9382 \pm 0.0008$	222.6

at higher temperatures.³⁻⁵ The Hf-As system was found to exhibit this behaviour, and the arc-melted alloys contained a number of phases not observed in the silica tube samples. The powder patterns of the arc-melted alloys were often highly complex and have not yet been completely interpreted. However, the compounds Hf_2As , $\text{Hf}_{1.67}\text{As}$, and Hf_3As_4 have been characterized by a combination of powder and single-crystal diffraction methods. Hf_2As crystallizes with the Ta_2P -type structure,⁶ and Hf_3As_4 is isostructural with Hf_3P_4 , the structure of which was recently determined by Lundström.⁷ Weissenberg films obtained for crystals of the $\text{Hf}_{1.67}\text{As}$ phase showed that the symmetry is orthorhombic, space group $Pnma$ or $Pn2_1a$. The very strong similarities between the layer lines $h0l$ and $h2l$ obtained by rotating the crystals about the b axis, indicate that the atoms most probably occupy $4c$ positions in space group $Pnma$. From the phase-analytical results and the volume of the unit cell it appears likely that the ideal composition of this compound is Hf_2As_3 , and the unit cell contains 8 formula units. A comparison of the Weissenberg films for $\text{Hf}_{1.67}\text{As}$ with those obtained by Hassler⁸ for a compound in the Nb-P system immediately showed that the two compounds are isostructural. A complete single crystal structure analysis of the niobium phosphide is in progress and will be reported later. With the aid of Hassler's powder diffraction results for the niobium phosphide, the powder pattern for $\text{Hf}_{1.67}\text{As}$ could be indexed, and accurate cell dimensions were determined.

Crystallographic data for the five well-established phases in the Hf-As system are collected in Table 1. In addition to these compounds there are further intermediate phases in the system. A crystal picked from one of the arc-melted alloys was found to be isostructural with Nb_7P_4 as determined by Rundqvist,⁹ but it has not yet been possible to identify the Hf_7As_4 phase with certainty in the powder photographs.

Another phase occurs at the approximate composition Hf_3As . Single crystal films of this phase indicate that the structure is related to that of Fe_3P . However the crystals studied appeared to be twinned, producing a pseudotetragonal symmetry on the Weissenberg films, and the interpretation of the single crystal and powder films is still incomplete.

It appears that the phase equilibria in the Hf-As system are rather complex, and the arc-melting technique used in the present investigation is not well suited for obtaining reliable results. A series of experiments with long annealing treatments of the alloys at temperatures much higher than 1000°C , followed by either slow cooling or rapid quenching, has therefore been started, and the results will be reported later.

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1. Jeitschko, W. and Nowotny, H. *Monatsh.* **93** (1962) 1284.
2. Tegenfeldt, J. Institute of Chemistry, Uppsala. *Unpublished*.
3. Rundqvist, S. *Nature* **211** (1966) 847.
4. Lundström, T. *Acta Chem. Scand.* **20** (1966) 1712.
5. Lundström, T. and Tansuriwongs, P. *Acta Chem. Scand.* **22** (1968) 704.
6. Nylund, A. *Acta Chem. Scand.* **20** (1966) 2393.
7. Lundström, T. *Acta Chem. Scand.* **22** (1968) 2191.
8. Hassler, E. Institute of Chemistry, Uppsala. *To be published*.
9. Rundqvist, S. *Acta Chem. Scand.* **20** (1966) 2427.

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