

An X-Ray Study of the Tantalum-Nitrogen System

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The preparation and properties of a compound TaN were described by July¹, who also maintained, that Ta₃N₅ and TaN₂ exist. However, later investigations have shown that nitrides with a higher nitrogen content than that corresponding to the stoichiometric composition 1 : 1 are most unlikely to occur. Van Arkel² suggested a hexagonal structure probably of wurzite type for TaN. Achermann, Friedrich, Justi and Kramer³, however, found that this nitride did not correspond to the composition 1 : 1, but was analogous to and had almost the same unit dimensions as the compound Nb₂N prepared by Brauer⁴. Besides this hexagonal close-packed Ta₂N, a tantalum nitride of complex nature has been described by, among others, van Arkel², Becker and Ebert⁵, Horn and Ziegler⁶. The latter gave *d/n* values and relative intensities for the strongest reflections in the diffraction pattern of a nitride with 50.2 atom-% of nitrogen. But they pointed out that "the complexity of the diffraction spectrum is consistent with the results of other investigations, but there is no general agreement in *d/n* values or relative intensities".

EXPERIMENTAL

As starting materials in the preparation of the nitrides powdered tantalum metal (Fansteel) and tantalum hydride (Metal Hydrides Inc.) were used. Ammonia was used instead of nitrogen for the nitriding, partly because it is considerably more effective for this purpose and partly because of the difficulty of purifying commercial nitrogen. After drying with calcium oxide a constant and relatively fast stream of the gas was passed through a silica tube furnace, in which the specimen was placed in an alumina boat. The tube was packed with asbestos pellets containing zirconium powder in order to prevent possible traces of oxygen and water reacting with the tantalum and thus producing oxides or ternary phases.

The nitriding process was performed at various temperatures between 700° C and 1 100° C and for times varying between an hour and two weeks. In order to homogenise the product and to detect the possible presence of high temperature modifications of the nitrides, the samples were heated in evacuated and sealed silica tubes at temperatures between 600° C and 1 100° C and then quenched in cold water.

The phase analysis and structure determinations were made from powder photographs taken with Cu-K α radiation in Guinier type cameras using bent quartz and aluminium monochromators. For measurements of the high-angle reflections additional photographs were taken with Hägg-Phragmén type focusing cameras.

It was not possible to obtain single crystals of any of the intermediate phases.

The nitrogen content of the specimens was determined by means of the Kjeldahl method.

THE STRUCTURE OF THE PHASES

The interpretation of powder photographs and the nitrogen content determination of samples resulting from nitriding of tantalum metal and tantalum hydride with ammonia indicated four intermediate phases.

 β phase: $\text{TaN}_{\sim 0.05}$

The tantalum atoms of this phase occupy a cubic lattice which is only slightly different from the body-centred cubic lattice of pure tantalum (α).

For pure tantalum the cube edge was found to be $a = 3.311 \text{ \AA}$ ($V = 36.30 \text{ \AA}^3$). The body-centred cubic sublattice of the β phase invariably gives an edge with $a = 3.369 \text{ \AA}$.

Besides the strong lines of the sublattice a series of weak superlattice lines occur. These can be explained by a cubic lattice having an edge three times as long as that of the sublattice, *i. e.*, $a = 10.11 \text{ \AA}$.

The occurrence of the superlattice is probably related to the fact that the nitrogen atoms can hardly be accommodated in the largest interstices of the undeformed body-centred cubic lattice. The introduction of a few nitrogen atoms (about 5 atomic %) can only take place after a slight deformation of the metal lattice.

In this connection it may be of interest that, in order to investigate metallic tantalum oxides⁷, tantalum hydride was oxidized with steam in an excess of hydrogen at about 600°C . In this way oxygen atoms were introduced into the body-centered tantalum lattice, causing a deformation. The dimensions of the resulting rhombic unit cell were found to vary slightly around the values $a = 3.61 \text{ \AA}$, $b = 3.27 \text{ \AA}$, $c = 3.21 \text{ \AA}$ ($V = 37.89 \text{ \AA}^3$), as compared with the cube edge of tantalum $a = 3.311 \text{ \AA}$ ($V = 36.30 \text{ \AA}^3$). The upper composition limit of this bluish black oxide corresponds to the formula Ta_4O .

 γ phase: $\text{TaN}_{\sim 0.40}$ — $\text{TaN}_{\sim 0.45}$

In agreement with earlier investigations³, this nitride was found to be of the interstitial type common among the carbides and nitrides of the transition metals with the metal atoms in a close-packed hexagon and the nonmetal atom in one of the two octahedron centres of the unit cell. The unit cell dimensions were found to vary between $a = 3.041 \text{ \AA}$, $c = 4.907 \text{ \AA}$, $c/a = 1.614$ ($V = 39.29 \text{ \AA}^3$) and $a = 3.048 \text{ \AA}$, $c = 4.918 \text{ \AA}$, $c/a = 1.614$ ($V = 39.57 \text{ \AA}^3$). This phase could not be obtained in a pure state, and the nitrogen analyses therefore give only roughly approximate values for the homogeneity limits. The formula may be written as Ta_3N or as Ta_2N , but by analogy with the great number of related carbide and nitride phases the proposed formula may be convenient. The following are mean interatomic distances: Ta — 6Ta 3.02 \AA , Ta — 6Ta 3.05 \AA , Ta — 3N 2.14 \AA , N — 6Ta 2.14 \AA .

 δ phase: $\text{TaN}_{\sim 0.80}$ — $\text{TaN}_{\sim 0.90}$

The powder photographs of a pure phase with the composition $\text{TaN}_{0.83}$ (45.4 atom-% of N) indicated a simple hexagonal cell with the stacking sequence AAA... of the metal atoms. The only nitride of this type earlier

known is MoN^8 , but recently the following isomorphous phases have been found: $\text{NbN}_{0.8}$, WN , $(\text{Ti}_{0.7}\text{Co}_{0.3})\text{N}$, $(\text{Ti}_{0.7}\text{Ni}_{0.3})\text{N}$, $(\text{Mo}_{0.8}\text{Co}_{0.2})\text{N}_{0.9}$ and $(\text{Mo}_{0.8}\text{Ni}_{0.2})\text{N}_{0.9}$ ⁷. From space considerations the most likely position of the nitrogen atom must be in one of the centres of the two trigonal metal atom prisms in the unit cell. The space-group is $D_{3h}^1-P\bar{6}m2$ with 1 Ta in 1(a) 000 and ~ 0.85 N in 1(d) $1/3\ 2/3\ 1/2$ or 1(f) $2/3\ 1/3\ 1/2$.

The phase analysis indicated a homogeneity range from about $\text{TaN}_{0.80}$ to about $\text{TaN}_{0.90}$, corresponding to the cell dimensions $a = 2.925\ \text{\AA}$, $c = 2.876\ \text{\AA}$, $c/a = 0.983$ ($V = 21.31\ \text{\AA}^3$) and $a = 2.938\ \text{\AA}$, $c = 2.883\ \text{\AA}$, $c/a = 0.981$ ($V = 21.55\ \text{\AA}^3$) respectively. The mean interatomic distances are: Ta — 2Ta $2.88\ \text{\AA}$, Ta — 6Ta $2.93\ \text{\AA}$, Ta — ~ 5 N $2.22\ \text{\AA}$, N — 6Ta $2.22\ \text{\AA}$ (as compared with the corresponding distances in Ta_2N , $2.14\ \text{\AA}$).

The calculated density for the composition $\text{TaN}_{0.88}$ is 14.95. The observed value was 14.1.

ϵ phase: TaN

The end product of the nitriding was found to be homogeneous at the stoichiometric composition TaN. It was easily obtained in a pure state for instance, at a temperature of 1000°C over three days — if sufficient care was taken to exclude oxygen from the reaction. Traces of oxygen, however, caused the formation of ternary Ta-N-O phases and/or tantalum oxides. The diffraction pattern of the compound TaN published by Horn and Ziegler⁶ is not in any way related to the patterns of the δ or ϵ phases. But it agrees rather well with the observed positions and relative intensities of the diffraction lines of two ternary Ta-N-O phases. The present author has prepared at least four such phases, which will be described elsewhere. All the tantalum nitrides have a greyish black metallic lustre but the colours of these nitride — oxides varies from greyish brown to dark red, and three of them have been found to have metallic properties.

The photographs indicate a hexagonal cell for TaN, related to the unit cell of the δ phase as well as to that of the γ phase. The dimensions were invariably found to be $a = 5.185\ \text{\AA}$, $c = 2.908\ \text{\AA}$, $c/a = 0.561$, ($V = 67.70\ \text{\AA}^3$). The similarity to the lattice of the δ phase is seen if the latter is described with an axial system of type H. The dimensions are then $a = 5.08\ \text{\AA}$, $c = 2.88\ \text{\AA}$, $c/a = 0.57$ ($V = 64.34\ \text{\AA}^3$) and the coordinates of the metal atoms 000; $1/3\ 2/3\ 0$, $2/3\ 1/3\ 0$. As reflections with $h-k \neq 3n$ and $l = 2n$ are absent, the three tantalum atoms in TaN have to be placed in the positions 000; $1/3\ 2/3\ 1/2$; $2/3\ 1/3\ 1/2$. This atomic grouping can perhaps be regarded as a mixture between the "simple" hexagonal stacking AAA... and the hexagonal close-packing ABAB..., and seems to be unique. There is only one possibility for the positions of the three nitrogen atoms, namely, at the centres of three deformed metal atom octahedra.

The space-group is thus $D_{6h}^1-P6/m\ m\ m$ with 1 Ta in 1(a) 000, 2 Ta in 2 (d) $1/3\ 2/3\ 1/2$; $2/3\ 1/3\ 1/2$, and 3 N in 3(f) $1/2\ 0\ 0$; $0\ 1/2\ 0$; $1/2\ 1/2\ 0$. TaN is thus of the B 35-type. Calculated and observed relative intensities are compared in Table 1, and the values of interatomic distances are given in Table 2. The calculated density is 14.34, and the observed value was 13.6.

Table 1. Observed and calculated intensities for TaN (c).

| <i>h k l</i> | Intensities | |
|--------------|-------------|------|
| | Calc. | Obs. |
| 001 | 9 | 10 |
| 110 | 175 | 175 |
| 101 | 133 | 115 |
| 111 | 18 | 15 |
| 201 | 60 | 50 |
| 300 | 48 | 50 |
| 211 | 81 | 75 |
| 002 | 15 | 15 |
| 301 | 9 | 10 |
| 220 | 40 | 50 |
| 112 | 80 | 75 |
| 221 | 8 | 10 |
| 311 | 65 | 75 |
| 401 | 24 | 25 |
| 302 | 54 | 50 |
| 410 | 41 | 35 |
| 321 | 36 | 35 |
| 003 | 1 | 0 |
| 222 | 41 | 35 |
| 103 | 18 | 15 |
| 411 | 9 | 10 |
| 113 | 4 | 0 |
| 203 | 13 | 15 |
| 330 | 18 | 15 |
| 501 | 20 | 15 |
| 213 | 37 | 35 |
| 331 | 6 | 0 |
| 421 | 50 | 50 |
| 303 | 6 | 0 |
| 412 | 112 | 115 |

SUMMARY

Tantalum nitrides have been prepared by ammonia nitriding of tantalum powder and tantalum hydride at 700—1100° C. The phase analysis was performed by X-ray methods, and the nitrogen content of the samples determined by the Kjeldahl method. Four intermediate nitrides have been found to exist.

Nitrogen is practically insoluble in tantalum.

The β phase has the approximate composition $\text{Ta}_3\text{N}_{0.05}$, and a body-centered cubic sublattice of tantalum atoms is indicated. The diffraction data can be explained by a cubic superlattice having a cube edge three times as long as that of the sublattice. The exact structure has not been determined.

The γ phase has a composition closely corresponding to the formula Ta_2N , and the metal atoms are arranged in a close-packed hexagon.

The δ phase has a homogeneity range of about three atomic percent of nitrogen within the limits $\text{Ta}_3\text{N}_{0.80}$ — $\text{Ta}_3\text{N}_{0.90}$. The metal atoms form a simple hexagonal lattice.

Table 2. Interatomic distances in TaN (ϵ).

| Atom | Surrounding atoms | Interatomic distance, Å |
|------------|-------------------|-------------------------|
| Ta in 1(a) | 2 Ta in 1(a) | 2.908 |
| | 12 Ta in 2(d) | 3.402 |
| | 6 N in 3(f) | 2.593 |
| Ta in 2(d) | 2 Ta in 2(d) | 2.908 |
| | 3 Ta in 2(d) | 2.994 |
| | 6 Ta in 1(a) | 3.402 |
| | 6 N in 3(f) | 2.204 |
| N in 3(f) | 4 Ta in 2(d) | 2.204 |
| | 2 Ta in 1(a) | 2.593 |

The ϵ phase is homogeneous at the stoichiometric composition TaN. The hexagonal unit cell contains three formula units TaN in the space-group D_{6h}^{17} — $P 6/m m m$ with 1 Ta in 1(a) 000, 2 Ta in 2(d) $1/3 2/3 1/2$, $2/3 1/3 1/2$ and 3 N in 3(f) $1/2 0 0$; $0 1/2 0$; $1/2 1/2 0$ (B 35-type).

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