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# Ternary Metallic Phases in the Ta—C—N, Ta—C—O, and Ta—N—O Systems

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During the last thirty years or so a great amount of data about tantalum carbides has been published. On the basis of microscopic and X-ray investigations and of melting point determinations on tantalum carbide specimens, Ellinger [1] established a phase diagram of the Ta—C system. The Ta—N and Ta—O systems have recently been studied by the present author [2].

The structures and compositions of the metallic binary phases are thus known, and the present study was undertaken in order to discover possible metallic ternary phases. Tantalum metal powder (Fansteel) and tantalum hydride (Metal Hydrides Inc.) were used for the preparation of carbides and nitrides as starting materials. The carbide samples — $Ta_2C$ and TaC — were obtained from the reaction between the metal or metal hydride and carbon (soot) in a graphite tube vacuum resistance furnace [3] at a temperature of about 1 800° C. The nitride samples — $Ta_2N$ ($\gamma$), $TaN_{0.80-0.90}$ ($\delta$), and TaN ($\varepsilon$) — were prepared by nitriding with dry oxygen-free ammonia at various temperatures between 700° and 1 100° C.

The phase analysis was performed by means of powder photographs taken in focussing cameras of Guinier type using monochromatized Cu$K\alpha$ radiation. The carbon and nitrogen contents of the samples were determined by means of combustion and Kjeldahl methods respectively, and the metal content by weighing the pentoxide formed after oxidation of the samples with oxygen.

## The Ta — C — N system.

Tantalum carbides were nitrided with dry ammonia, and the nitrides were carburized with dry methane at about 1 100° C. No ternary phase was found to exist.

The unit cell dimensions of $Ta_2C$ were found to vary between $a = 3.094$ Å, $c = 4.918$ Å, $c/a = 1.590$ ($V = 40.78$ Å$^3$) and $a = 3.111$ Å, $c = 4.948$ Å, $c/a = 1.590$ ($V = 41.46$ Å$^3$) and those of $Ta_2N$ between $a = 3.041$ Å, $c = 4.907$ Å, $c/a = 1.614$ ($V = 39.29$ Å$^3$) and $a = 3.048$ Å, $c = 4.918$ Å,

$c/a = 1.614$ ($V = 39.57$ Å$^3$). The lattice constant values of $Ta_2(C,N)$ specimens indicate a continuous solid solution series $Ta_2C$—$Ta_2N$.

The solubility of TaC in the $TaN_{0.80-0.90}$ phase ($\delta$) is of the order of 5 at.-%. Whereas the unit cell dimensions of the $\delta$-nitride are $a = 2.925$—$2.938$ Å, $c = 2.876$—$2.883$ Å, $c/a = 0.983$—$0.981$ ($V = 21.31$—$21.55$ Å$^3$), those of a sample with the approximate composition $TaN_{0.85}C_{0.15}$ were found to be $a = 2.938$ Å, $c = 3.071$ Å, $c/a = 1.045$ ($V = 22.96$ Å$^3$).

The solubility of TaC in TaN could not be determined because of the difficulty of obtaining homogeneous samples. It is probably fairly small. The replacement of some nitrogen with carbon in the TaN lattice causes an increase of the cell dimensions from $a = 5.158$ Å, $c = 2.908$ Å, $c/a = 0.561$ ($V = 67.70$ Å$^3$) to $a = 5.206$ Å, $c = 2.914$ Å, $c/a = 0.560$ ($V = 68.38$ Å$^3$). A volume decrease would be expected, however, as the corresponding volumes per metal atom of the TaN and TaC phases are 22.57 and 21.34—22.15 Å$^3$ (for TaC, $a = 4.403$—$4.456$ Å) respectively. The solubility of TaN in TaC is not known.

## The Ta — C — O system.

The samples were prepared in two ways:

*A.* Tantalum carbides were oxidized by means of steam in the presence of hydrogen in great excess at about 700° C.

*B.* Tantalum pentoxide was reduced with carbon (soot) in a graphite tube vacuum furnace at about 1 800° C.

One metallic ternary phase and two phases of unknown properties and compositions were obtained. One of the latter compounds has a face-centered cubic unit cell with an axial value of $a = 10.41$ Å. The ternary metallic phase was only obtained in the presence of rather great amounts of $Ta_2C$ or TaC and has a tetragonally deformed NaCl structure with the lattice constants $a = 4.303$ Å, $c = 4.097$ Å, $c/a = 0.952$ ($V = 75.53$ Å$^3$). A comparison between the cell volumes of $Ta_4O$, TaO, $Ta_2C$, and TaC makes the approximate formula $Ta_2(C,O)$ probable. The C/O ratio is unknown. Phases with an analogous structure have earlier been found in the Mo—N [4] and Nb—N—O [2] systems.

## The Ta — N — O system.

Tantalum nitride samples were oxidized with steam in a similar manner to that used for the preparation of Ta—C—O samples. They could be prepared in fairly pure states. The compound most rich in nitrogen was only formed by the oxidation of TaN, while three other compounds were obtained when TaN ($\varepsilon$) or $TaN_{0.80-0.90}$ ($\delta$) were used as starting materials.

The volumes per metal atom of the different oxide-nitrides are compared in Fig. 1.

1. $TaN_{\sim 0.90}O_{\sim 0.10}$. Besides the strong reflections of the $\varepsilon$ phase a series of weak superlattice reflections were visible in the powder photograph, indicating a doubling of the $a$-axis as well as the $c$-axis of the hexagonal TaN sublattice: $a = 10.34$ Å, $c = 5.802$ Å, $c/a = 0.561$ ($V = 537.1$ Å$^3$, $Z = 24$). The weakness of the "extra" lines shows that the deviation from the "ideal" atomic positions (in TaN) is very small.

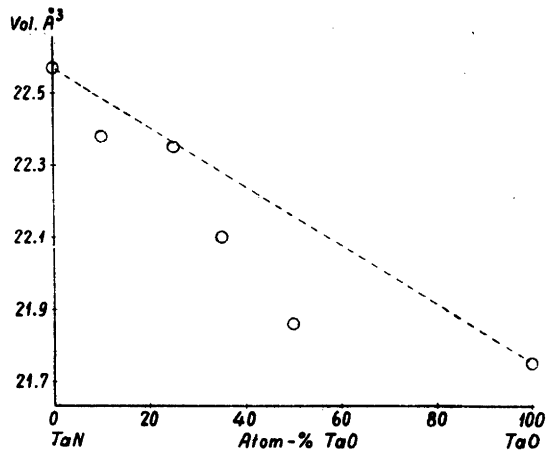


*Fig. 1. The volumes per metal atom of the phases in the pseudo-binary* TaN—TaO *system.*

2. $TaN_{\sim 0.75}O_{\sim 0.25}$ ($Z = 4$). This phase is closely related to the hexagonal $\delta$ phase in the Ta-N system, as indicated by the intensity distribution in the diffraction pattern. Comparatively weak reflections indicate a superlattice with $a \sim 2a_\delta$ and $c \sim c_\delta$. The lengths of the axes are: $a = 5.988$ Å, $c = 2.879$ Å, $c/a = 0.481$ ($V = 89.39$ Å$^3$; $Z = 4$).

3. $TaN_{\sim 0.65}O_{\sim 0.35}$ ($Z = 12$). This compound, like the last one, has a $\delta$ phase superstructure. But in this case $a \sim 2\sqrt{3}\ a_\delta$ and $c \sim c_\delta : a = 10.34$ Å, $c = 2.864$ Å, $c/a = 0.277$ ($V = 265.2$ Å$^3$).

4. $TaN_{\sim 0.50}O_{\sim 0.50}$ The strongest reflections in the powder photograph of this phase correspond to a hexagonal sublattice with the dimensions: $a = 5.939$ Å, $c = 2.866$ Å, $c/a = 0.483$ ($V = 87.54$ Å$^3$), containing four formula units $TaN_{0.5}O_{0.5}$. The intensity distribution shows that the atomic arrangement is different both from that in the $\delta$ and from that in the $\varepsilon$ phase in the Ta—N system. All reflections can be indexed, if a hexagonal superlattice with $a' = 2a$ and $c' = 6c$ is chosen. But the absence of a great many lines in the pattern makes such a big unit cell ($Z = 96$) unlikely. The symmetry may be lower and the cell content then smaller that that corresponding to 96 metal atoms.

The colour of the oxide-nitrides changes continuously from black for $TaN_{\sim 0.90}O_{\sim 0.10}$ to reddish black for $TaN_{\sim 0.50}O_{\sim 0.50}$. The interatomic distances probably differ very slightly from those observed for the nitrogenrich tantalum nitrides [2].

The solubility of N in the TaO phase is not known.

The approximate outline of the "metallic" corner of the Ta—N—O system is drawn in Fig. 2.

If ammonia was led over $Ta_2O_5$ samples at 1 100° C, besides small amounts of the $\varepsilon$ phase in the Ta—O system a black ternary phase was obtained. Its structure is complicated, as indicated by the powder photograph. Metallic oxide-nitrides could not be prepared in this way.

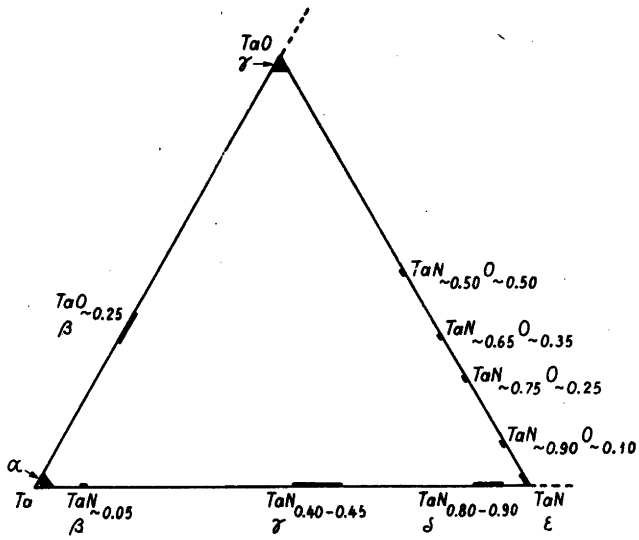


*Fig. 2. An outline of the* Ta—N—O *system with the* (N,O) / Ta *ratio* $\leq 1$.

## SUMMARY

Ta—C—N, Ta—C—O, and Ta—N—O samples with the nonmetal / metal ratio $\leq$ 1 have been prepared with different methods.

No ternary phase has been found in the Ta—C—N system. Solid solubility ranges have to some extent been determined in this system.

At least one metallic phase exists in the Ta—C—O system: a compound with the approximate composition $Ta_2(C,O)$ has a tetragonally deformed NaCl structure.

Four metallic phases with the following approximate compositions have been prepared in the Ta—N—O system: $TaN_{0.90}O_{0.10}$, $TaN_{0.75}O_{0.25}$, $TaN_{0.65}O_{0.35}$, and $TaN_{0.50}O_{0.50}$. The stucture for the nitrogen-richest compound is closely related to that of $\varepsilon$-TaN, and the following two oxide-nitrides have $\delta$-TaN superstructures.

An outline of the part of the Ta—N—O system with the (N,O) / Ta ratio $\leq$ 1 has been drawn.

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