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Contributions to the Knowledge of the Molybdenum-Nitrogen and the Tungsten-Nitrogen Systems

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Schematic phase diagrams for the Mo—N and the W—N systems have been constructed by Hägg [1] on the basis of the X-ray diffraction study of his preparations. He nitrided fine and very pure metal powders with ammonia in a porcelain-tube furnace for up to two days. The reaction temperature was varied between 400° C and 725° C for the molybdenum nitrides and between 700° C and 800° C for the tungsten nitrides.

The following phases are recorded by Hägg [1]:

1. *The Mo—N system.*
   α phase (Mo). The solubility of nitrogen in molybdenum is very small.
   β phase. Stable only above 600° and containing about 28 atom-% of N. The metal atoms form a face-centered tetragonal lattice.
   γ phase. This phase has a narrow homogeneity range in the vicinity of 33 atom-% of N and hence corresponds to the formula Mo_2N. The metal atoms form a face-centered cubic lattice.
   δ phase. Exists at about 50 atom-% of N and hence corresponds to the formula MoN. The metal atoms form a simple hexagonal lattice but weak extra lines indicate the existence of a superlattice.

2. *The W—N system.*
   α phase (W). Nitrogen is practically insoluble in tungsten.
   β phase. Isomorphous with Mo_2N (γ phase).
   Kiessling and Liu [2] found a second W_2N-modification — a γ phase — which is formed by nitriding at 825°—875° C. It is cubic, probably with a distorted face-centered lattice.

The present author has confirmed the results of Hägg in all respects but could not verify the existence of the γ tungsten nitride reported by Kiessling and Liu. Here, therefore, it is only necessary to report some new facts about the two nitride systems.

The new information was obtained from preparations with a maximum nitrogen content. These were prepared by heating two porcelain boats con-

taining molybdenum (fine powder; Söderfors 99.9 %) and tungsten (fine powder; Lindberg, Stockholm 99.6 %) respectively in a constant stream of dry ammonia up to 800 °C for a few hours. The temperature was then lowered at a constant rate down to 300° C over a period of four weeks. The nitrogen content was determined by the Kjeldahl method, and was found to be 49.6 atom-% of N in the molybdenum sample and 41.7 atom-% of N in the tungsten sample. For the X-ray analysis a Guinier-type camera constructed at this Institute was used, with a ground and bent quartz crystal monochromator.

MoN (δ phase)

The diffraction pattern of this molybdenum nitride contained strong lines corresponding to a simple hexagonal sublattice, and a series of comparatively weak superlattice reflections. The latter reflections were generally stronger for large deviation angles than for small angles. An ordered distribution of the nitrogen atoms in the interstices of a "perfect" sublattice should give extra reflections hardly visible in the powder photograph, so in this case it seems necessary to assume a displacement of the metal atoms from the normal positions of the sublattice.

If both the a axis and the c axis of the sublattice are doubled, all the reflections can be interpreted. The unit cell dimensions will then be $a = 5.725$ Å, $c = 5.608$ Å; $c/a = 0.980$ ($V = 159.2$ Å^3). The Kjeldahl determination of nitrogen (49.6 atom-%) makes the ideal formula MoN very probable. The unit cell then contains eight formula units. The calculated density is 9.18, and the observed value was 8.60.

Only hkl reflections with $l \neq 2n$ were found to be absent in the diffraction pattern of the δ phase. This, together with space considerations, makes the space-groups D_{3h}^4, C_{6v}^4, D_6^6, and D_{6h}^4 the most probable ones. As the displacement of the metal atoms from the positions of the hexagonal sublattice is obviously very small, the only possible positions of the eight molybdenum atoms are:

in D_{3h}^4: $2(b)$ $00\frac{1}{4} + 6(h)$ x y $\frac{1}{4}$;
in C_{6v}^4: $2(a)$ $00z + 6(c)$ x $2z$ z;
in D_6^6 : $2(b)$ $00\frac{1}{4} + 6(h)$ x $2x$ $\frac{1}{4}$;
in D_{6h}^4: $2(b)$ $00\frac{1}{4} + 6(h)$ x $2x$ $\frac{1}{4}$;

The space-group D_{6h}^4 is chosen as it possesses the maximum symmetry common to the four space-groups.

The parameter x must then have a value close to $\frac{1}{2}$. It was therefore systematically varied between the values 0.480 and 0.500 in steps of 0.002. It is obvious from Table 1 that the agreement between calculated and observed intensities for the reflections are good if the value $x = 0.489$ is chosen.

Intermetallic distances are listed in Table 2.

The positions of the nitrogen atoms in molybdenum nitrides cannot be determined from X-ray data. However, space considerations suggest, that the nonmetal atoms in the δ phase are situated at the centres of trigonal prisms of metal atoms, as previously indicated by Hägg [1].

Table 1. Observed and calculated intensities for MoN.

h k l	Intensities Calculated	Observed	h k l	Intensities Calculated	Observed
100	0	0	224	32	25
101	4	5	500	0	0
110	0	0	314	0	0
002	65	75	501	4	5
200	121	125	323	5	5
102	0	0	215	1	2
201	2	2	330	0	0
112	0	0	420	30	25
210	0	0	413	3	2
202	125	125	502	0	0
211	4	5	006	6	5
103	1	2	404	32	25
300	0	0	305	2	2
301	4	5	421	0	0
212	0	0	106	0	0
203	1	2	332	0	0
220	35	45	510	0	0
302	0	0	422	56	45
004	13	15	116	0	0
310	0	0	324	0	0
104	0	0	511	1	0
311	1	2	503	4	5
213	3	5	206	34	25
222	65	75	315	0	0
114	0	0	414	0	0
400	26	25	512	1	0
303	3	2	423	0	0
312	0	0	216	0	0
204	54	45	405	0	0
401	0	0	600	13	15
320	0	0	601	0	0
402	41	45	430	2	2
214	0	0	306	0	0
321	7	5	504	0	0
313	0	0	431	9	10
105	0	0	513	1	0
410	0	0	325	7	10
304	0	0	520	4	5
411	3	5	602	43	45
322	0	0	107	0	0
403	0	0	334	1	0
205	0	0	521	17	25
412	0	0			

WN (δ phase)

The X-ray photograph of the tungsten sample containing 41.6 atom-% of N besides W_2N(β phase) indicated the presence of a phase not previously known (δ phase). The metal atoms are arranged in a simple hexagonal lattice with the lattice constants $a = 2.893$ Å, $c = 2.826$ Å; $c/a = 0.977$ ($V = 20.48$ Å^3). The composition of this nitride is not known, because it was not possible to prepare it in a pure state; the nitrogen content may be somewhat lower than

Table 2. Intermetallic distances in MoN.

Molybdenum atom in	Surrounding atom	Interatomic distance, Å	
2(*b*)	2 Mo in 2(*b*)	2.804	2.845
	6 Mo in 6(*h*)	2.865	
6(*h*)	2 Mo in 2(*b*)	2.865	2.851
	2 Mo in 6(*h*)	2.674	
	2 Mo in 6(*h*)	2.813	
	2 Mo in 6(*h*)	3.052	

Table 3. Interatomic distances in WN.

Atom	Surrounding atoms	Interatomic distance, Å
W	2 W	2.826
	6 W	2.893
	6 N	2.188
N	6 W	2.188

50 atom-%. If the nitrogen atom is situated at the centre of a trigonal prism of tungsten atoms, the space-group will be D_{3h}^1—$P\bar{6}m2$ with 1 W in 1(*a*) 000 and 1 N in 1 (*d*) 1/3 2/3 1/2 or (*f*) 2/3 1/3 1/2.

The decomposition of WN in vacuum at 600° C according to the reaction $2\,WN \rightarrow W_2N + \frac{1}{2}\,N_2$ was found to occur at a much faster rate than the corresponding decomposition of MoN (*δ*). This indicates a lower stability for the tungsten nitrides than for the molybdenum nitrides.

Interatomic distances for WN (*δ*) are listed in Table 3.

SUMMARY

The previously known simple hexagonal lattice of MoN (*δ*) exhibits a hexagonal superstructure formed by doubling the axes of the substructure. The new unit cell contains eight units MoN. The space-group is D_{6h}^4—$P6_3/mmc$ and the atomic coordinates are 2 Mo in 2(*b*) $00\frac{1}{4}$ and 6 Mo in 6(*h*) x, $2x$, $\frac{1}{4}$ with $x = 0.489$.

In the tungsten-nitrogen system a new phase (*δ*) has been found which has a composition close to the formula WN. It is isomorphous with the tungsten carbide WC. It is more unstable than MoN at high temperatures.

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