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Preparation and Crystal Structure of β-Ta_2N

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Samples of the tantalum nitride β-Ta_2N were obtained from the elements by the sintering of tantalum in nitrogen at 2000°C. In the zone melting of tantalum in nitrogen, samples with a lamella structure of β-Ta_2N and ε-TaN were formed. The crystal structure of β-Ta_2N was refined from a neutron diffraction powder pattern using the profile analysis method and the trigonal space group $P\bar{3}1m$ (No. 162). Unit cell parameters are $a = 5.285$ (5) Å, $c = 4.919(3)$ Å, with $Z = 3$. The composition of the sample investigated was $TaN_{0.43(1)}$.

Introduction

The phase diagram for the system tantalum–nitrogen indicates the existence of three tantalum nitrides (*1*). The crystal data for these three phases are listed in Table I. According to the phase diagram β-Ta_2N and δ-TaN have broad composition ranges and ε-TaN a rather narrow composition range. A structure for β-Ta_2N has been proposed with tantalum atoms in a hexagonal close packing and the nitrogen atoms randomly distributed in the octahedral holes of the packing (*2*). Another model has an ordered arrangement of the nitrogen atoms (*3*). A structure for ε-TaN of the CoSn type has been proposed (*4*). In this structure the tantalum atoms are in a hexagonal packing and the nitrogen atoms are placed in some of the holes in the structure. δ-TaN is a high temperature phase with the sodium chloride structure (*1*).

In a high temperature crystal growth program it was found that single crystals of

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TABLE I

CRYSTAL DATA FOR β-Ta_2N, ε-TaN AND δ-TaN

Phase	Crystal structure	Lattice parameters (Å[a])		Composition	Reference
		a	*c*		
β-Ta_2N	Hexagonal	3.042	4.905	$TaN_{0.41}$	(*2*)
		3.042	4.909	$TaN_{0.50}$	(*2*)
		5.283	4.928	$TaN_{0.50}$	(*3*)
	Trigonal	5.285(5)	4.919(3)	$TaN_{0.43(1)}$	This work
ε-TaN	Hexagonal	5.185	2.908		(*3*)
		5.196(4)	2.911(2)		This work
δ-TaN	Cubic	4.331		$Ta_{0.52}N_{0.48}$	(*1*)
		4.345		$Ta_{0.58}N_{0.42}$	(*1*)

[a] The unit cell parameters in Ref. (*2*) are given in *kX*.

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TiN and ZrN could be made by zone melting or zone annealing of titanium and zirconium in pure nitrogen (*5*) and well-characterized specimens of β-Nb_2N and γ-NbN could be obtained using these preparative techniques (*6*). The purpose of this investigation was to study the crystal growth and preparation of specimens of the tantalum nitrides and to study the crystal structure of the compounds. In the following the formula β-Ta_2N will be used for the nonstoichiometric specimen investigated.

Experimental

Sample preparation and X-ray technique. Attempts have been made to prepare single crystals of β-Ta_2N and ε-TaN by zone melting or zone annealing techniques. The starting materials were powders of Ta and nitrogen gas of the nominal purity 99.99%. The metal powder was placed in rubber molds which were sealed, evacuated, and pressed at an isostatic pressure of 500 MPa to produce rods. The rods were either sintered in pure nitrogen to produce rods of tantalum nitride or were zone melted in pure helium (99.99% He) to produce solid bars of tantalum. Samples of β-Ta_2N were obtained by annealing solid bars of Ta in pure nitrogen at 2000°C, 1.4 MPa for 20 hr. Samples of tantalum nitride containing ε-TaN and β-Ta_2N could be obtained in different ways. (I) A rod of isostatically pressed tantalum was heated with an R.F. coil in 1.7 MPa of nitrogen. At approximately 800°C a violent exothermic reaction between tantalum and nitrogen started. The temperature jumped to at least 1700°C measured by a disappearing filament optical pyrometer. After approximately 30 sec the reaction was completed and the temperature of the specimen dropped to that determined by the power level of the heating element. (II) An isostatically pressed rod of tantalum was treated as described in (I) followed by annealing in pure nitrogen at 1250°C, 1.3 MPa for 4 hr. (III) Zone melting of bars of tantalum in pure nitrogen always resulted in specimens showing a lamella structure of β-Ta_2N and ε-TaN within primary formed grains (of δ-TaN). This is in agreement with the eutectoid point (δ-TaN $\rightarrow$ β-Ta_2N + ε-TaN) in the phase diagram. The specimens were annealed or zone melted in an ADL MP crystal growth furnace with a 30-kW R.F. power supply (*5*).

Guinier powder patterns were obtained of all products using a Guinier de Wolff camera with Co$K\alpha_1$, $\lambda = 1.78892$ Å, and germanium, $a_{Ge} = 5.6576$ Å, as an internal standard. Optical metallography has also been used to characterize the specimens.

Neutron diffraction powder patterns of a sample of pure β-Ta_2N and of samples containing ε-TaN and β-Ta_2N were measured at room temperature at the DR3 reactor at Risø, using 1.688 Å neutrons. The samples were housed in 10-mm diameter containers of aluminium.

Crystal Data and Structure Refinement

β-Ta_2N. The diffraction pattern measured in the 2-θ interval 10.0 to 88.9 in steps of 0.1° could be indexed with a hexagonal cell with $a_H = \sqrt{3}\ a$, and $c_H = c$ where a and c are comparable with the unit cell parameters for β-Ta_2N from Ref. (*2*) Table I. This indicates a structure for β-Ta_2N similar to that of β-Nb_2N (*6*). This model for the structure was refined using the profile analysis least-squares program F418 (*7*). The results of the refinements are listed in Tables II and III. The two nitrogen sites are only partly occupied corresponding to the composition $TaN_{0.43(1)}$ for the sample of β-Ta_2N. In the refinements of the structure the atomic scattering lengths for Ta and N were 0.691 and 0.940 ($\times 10^{-12}$ cm), respectively (*9*).

Conclusion

The investigation shows that single crystals of δ-TaN cannot be obtained using the zone melting technique. Single crystals of β-Ta_2N can be made by annealing of Ta in nitrogen at 2000°C and 1.4 MPa. Samples containing ε-TaN and β-Ta_2N are obtained in an exothermic reaction between the elements and in zone melting of tantalum in pure nitrogen. The neutron diffraction patterns show that the zone melted samples only contain ε-TaN

TABLE II

RESULTS OF THE REFINEMENT OF THE STRUCTURE OF β-Ta_2N[a]

Atom	Atom site	x	y	z	Multiplicity	
					Theoretical	Calculated
Ta	$6k$	$\frac{1}{3}$	0	$\frac{1}{4}$	0.5	0.5
N1	$2d$	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{2}$	0.16667	0.133(5)
N2	$1a$	0	0	0	0.08333	0.081(1)

[a] Scale factor = 0.0819. $R = 5.6\%$, $R(F^2) = 6.7\%$. For definition of R (profile) and $R(F^2)$ (nuclear) see Ref. (*8*). Overall temperature factor = 0.23(17) Å.^{2}

TABLE III

OBSERVED AND CALCULATED INTENSITIES FOR β-Ta_2N

h k l	I_{obs}	I_{calc}
0 0 1	295	273
1 0 0	174	54
1 0 1	6121	6157
1 1 0	391	83
0 0 2	813	607
1 1 1	19482	19248
2 0 0	38	14
1 0 2	67	25
2 0 1	2535	2465
1 1 2	14807	13813
2 1 0	58	17
2 0 2	82	16
0 0 3	41	34
2 1 1	3570	3205
1 0 3	1386	1455
3 0 0	10620	11110
3 0 1	405	166
1 2 2	126	24

and β-Ta_2N, and that the specimen obtained in the fast exothermic reaction mainly consists of the same two phases. The neutron diffraction investigation shows that β-Ta_2N has the same structure as β-Nb_2N (see Fig. 1).

Terao (*3*) has investigated the structure of β-Ta_2N using electron diffraction techniques and has described the structure in space group $P312$ (No. 149). However, if the origin is shifted to $(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$, the space group for the structure is $P\bar{3}1m$ (No. 162), and the atomic coordinates have the values listed in Table II. The two methods, electron and neutron diffraction thus give the same structure for

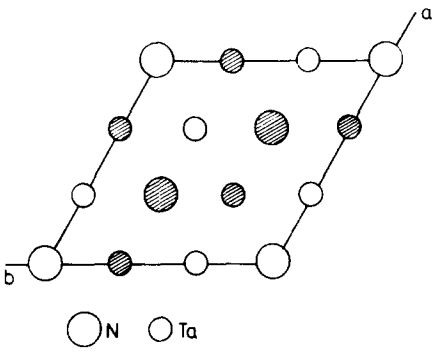

FIG. 1. Projection of the structure of β-Ta_2N along the [001] direction. Nitrogen atoms with $z = 0.5$ and tantalum atoms with $z = 0.75$ are hatched.

β-Ta_2N. In addition, the neutron diffraction investigation gives the composition $TaN_{0.43(1)}$ of the sample. This composition is within the composition range given in the phase diagram (*1*) for Ta_2N.

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