KERNFORSCHUNGSZENTRUM

KARLSRUHE

Juli 1969 KFK 1011

Institut für Material- und Festkörperforschung

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Ternary Uranium-Transition Metal-Nitrides [+)]

by

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Ternary Uranium-Transition Metal-Nitrides

Because of the importance that UN has attained as a potential nuclear fuel the reaction behaviour of this compound with transition elements or their nitrides is of special interest. Two questions led us to the investigation of uranium-nitride bearing systems. On the one side the fission product behaviour and compatibility problems are important, on the other the general interest in the constitution itself is of interest since very little is as yet known about such systems.

We know from the systems with transition metals that the nitrides often show a behaviour similar to the corresponding carbides. I will therefore compare in some cases results in carbide systems with the results in nitride systems, and point out some characteristic features. The ternary uranium-transition metal-nitrides, which occur partly as mixed phases of binary nitrides, partly as new ternary complex nitrides are prepared mainly by arc melting under 3 - 5 atm nitrogen with subsequent homogenization. Without going into details of the preparation techniques [1], I will only mention that it is very difficult to prepare well defined nitride-samples containing three or more components, being in an equilibrium state. The ternary nitrides have been investigated by x-ray diffraction, metallographically and with microprobe analyser.

The fig.1 shows the ternary uranium-transition metal nitrides we have found. The only result known was the complete miscibility between UN and the actinide nitrides ThN and PuN. Our investigations show that UN and the isotype mononitrides of the rare earths Y, La, Ce, Pr and Nd form homogenous mixed phases over the whole concentration range [2][3]. One can assume, because of the similarity in the chemical behaviour of the lanthanides and because of the complete miscibility in the quasibinary system UN-LaN, which is the system with the greatest difference in lattice parameter, that all lanthanide nitrides and UN are completly miscible. Regarding the corresponding carbide systems we must note that presently no monocarbides or defectmonocarbides of La, Ce, Pr and Nd are known to exist. The behaviour of the nitrides and carbides is similar in systems containing the IV A transition metals Ti, Zr and Hf; we have a very limited solubility of UN with TiN and complete solubility of UN with ZrN and HfN [4]. The same is true for the carbides.

While the monocarbides of the V A transition metals Nb and Ta are more stable than UC and completly miscible with UC, the mononitrides NbN and especially TaN are so unstable that at 2000°C and 300 Torr N_2

they do not exist as cubic mononitrides. But they can be stabilized by solution in UN. This is possible for Nb at 2000°C up to a composition $(U_{0,5}Nb_{0,5})N_{1-x}$, for Ta at the same conditions up to a composition of approximatly $(U_{0,9}Ta_{0,1})N_{1-x}$. In these systems with the V A transition metals ternary isotype complex nitrides occur. Whereas the Ta-containing phase is stable at 2000°C we have observed the V- and Nb-containing phases at 1800°C. In fig.2 one can see micrographs of ternary alloys in the system U-V-N, namely of a specimen arc melted (1), arc-melted and homogenized at 2000°C (2), and arc-melted and homogenized at 1800°C (3). In case (1) and (2) UN is in equilibrium with VN_{1-x}, in the specimen (3) one can see the complex nitride as the reaction zone between UN and VN_{1-x}. In this specimen the composition was found by microprobe analysis to be UVN_{2-x}. We could not determine exactly the nitrogen content. The corresponding compositions were also found for the Nb- and Ta containing phases.

The nitrides of the sixth group transition metals are so unstable, that UN is in equlibrium with these metals. This is of technical importance in view of Cr-alloys as cladding materials for fuels. But as soon as one has excess nitrogen or oxygen an uranium-chromium complex nitride will be formed. Fig.3 shows a photomicrograph of an arc-melted specimen homogenized at 1300°C in nitrogen. Although Cr_2N should be found at these conditions, here we have UN, the complex-nitride as the reaction zone and pure chromium. This is due to the incomplete reaction. The composition of this complex nitride was found by microprobe analysis to be about $U_{1,9}Cr_{1,1}N_{2+x}$. We are trying to find out this composition more exactly.

The platinum metals form no nitrides. Because of the stable uranium-platinum metal phases, the platinum metals react at high temperatures with UN forming these metallic phases and free nitrogen. For instance

$$UN + 3Ru = URu_3 + \frac{1}{2}N_2$$

Preliminary EMF-measurements in our laboratory have shown a free energy of formation of URu_3 of $G^o_{1000} \sim -50$ kcal/mole. [5] This very high value for a metallic phase explains the observed reaction.

I will briefly now discuss the four complex nitrides, we have found. Fig.4 shows the structure data of these compounds. Lattice parameters of the orthorhombic complexnitrides with the metals of the 5th group, V, Nb, and Ta and the intensities of x-ray patterns lead us to conclude, that these compounds are isotype with the complex carbides of the sixth group transition metals Cr, Mo, W, namely $UCrC_2$, $UMoC_2$ and UWC_2 [6][7]. The ratio a to b with 1,73 corresponds nearly to a hexagonal symmetry, especially in the case of Nb and Ta. The same is true for the complex carbides $UMoC_2$ and UWC_2. The volume of one mole - this is the volume of one fourth of the elementary cell - corresponds to the volume which would take the same mole in a hypotetical cubic face centred mononitride arrangement (values in parenthesis in fig.4).

The Cr-containing complex nitride shows a structural relation to complex carbides with platinum metals, which we have found recently [8]. For instance:

	a	c
U_2RuC_2	3,44 Å	12,56 Å
U_2OsC_2	3,46 Å	12,58 Å

The latter phase is quasitetragonal at the exact composition U_2OsC_2 but is orthorhombically distorted at compositions higher in carbon. We found in the three phase field U_2C_3 + C + U_2OsC_2 parameters of

a = 3,52 Å   b = 3,46 Å   c = 12,63 Å

It seems that there is a close relation between these

U-Pt-metal complex carbides and the U-Cr-complex nitride (a = 3,74 Å, b = 3,31 Å, c = 12,37 Å). Their exact structure is as yet unknown.

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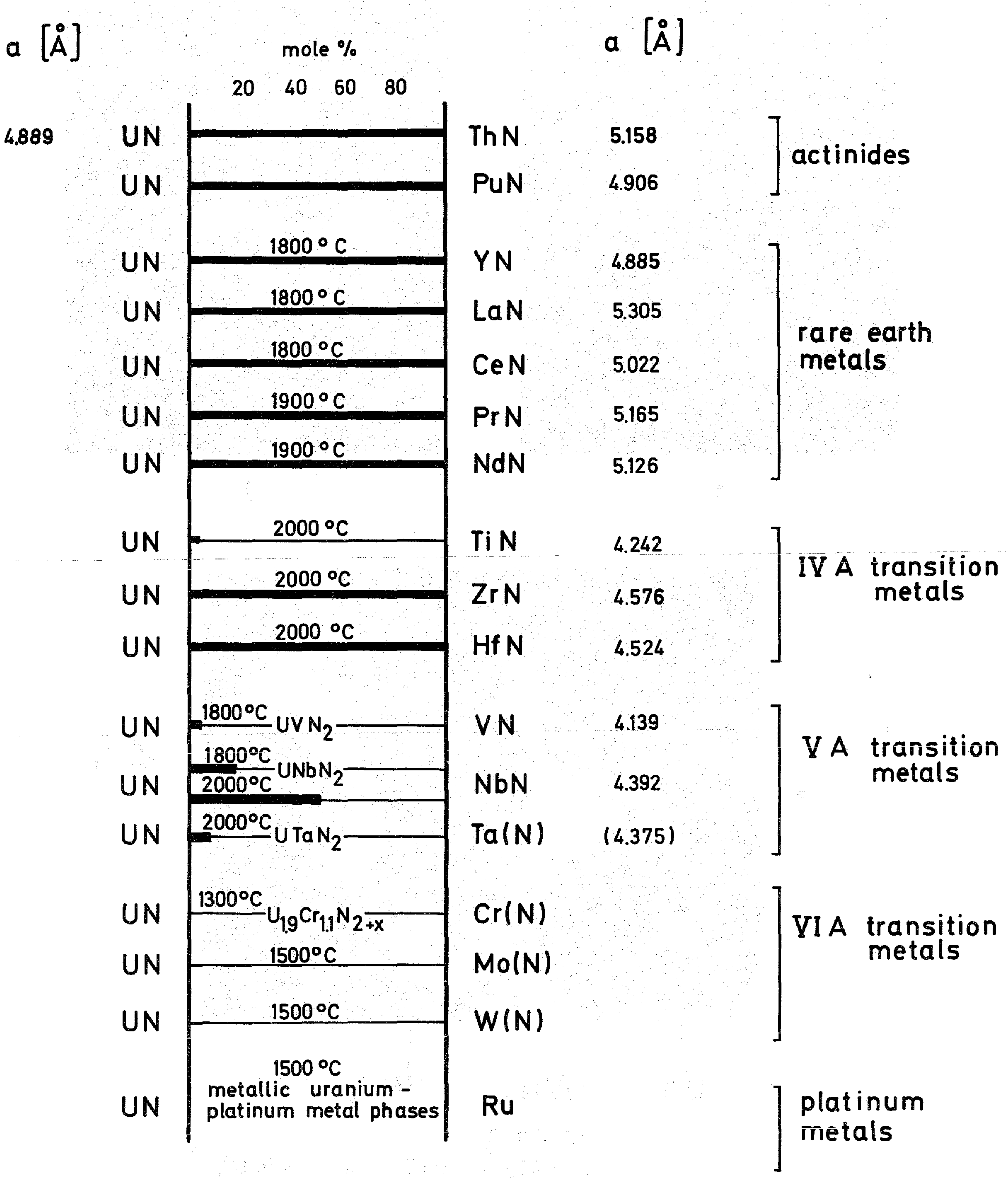
Figures:

Fig.1 Ternary nitrides occuring in uranium-transition metal-nitrogen systems.

Fig.2 Micrographs of uranium-vanadium-nitrogen alloys.

Fig.3 Micrograph of an arc melted UN-Cr specimen homogenized in nitrogen.

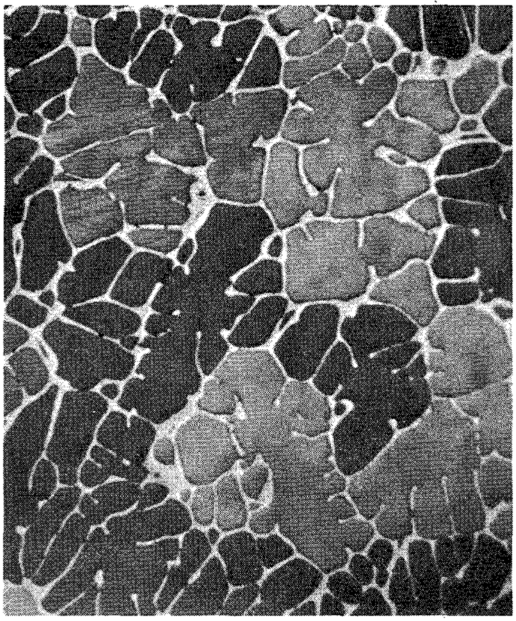
Fig.4 Structure data of the orthorhombic uranium-transition metal complex nitrides.



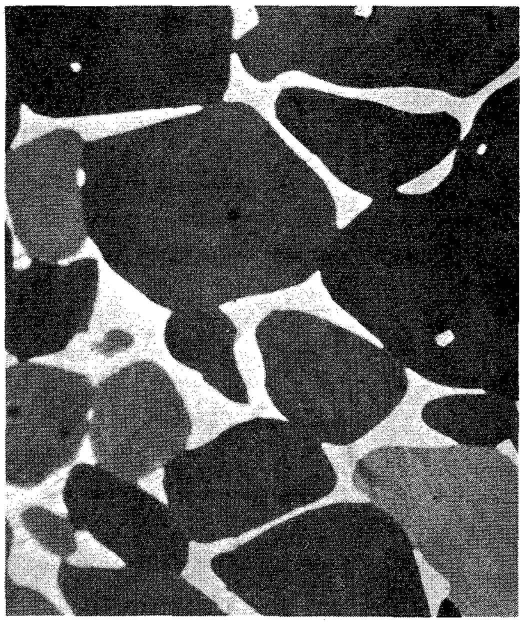
Ternary nitrides occuring in uranium - transition metal - nitrogen systems (300 Torr N_2)

▬ mixed phase — coexistant phases

Fig. 1

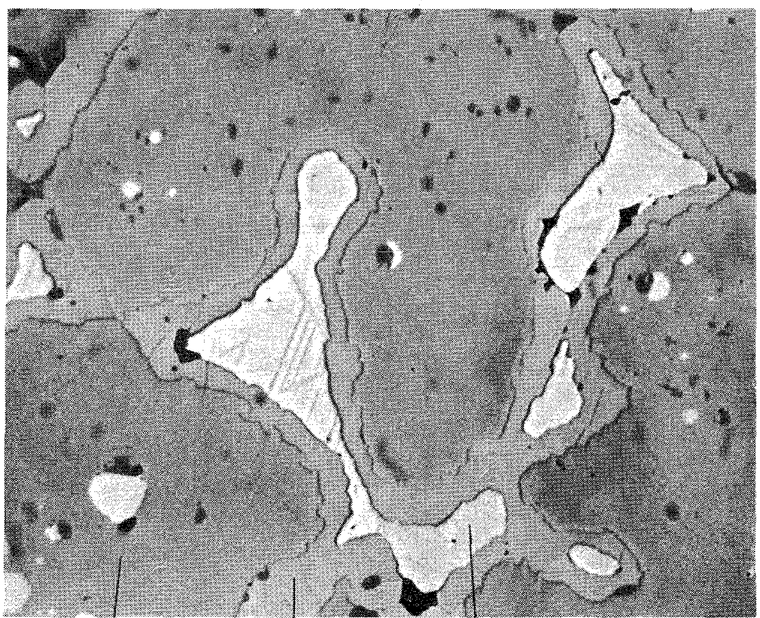


1



2

3



20 μ

UN UVN$_{2-x}$ VN$_{1-x}$

orthorh.

$a = 5.45_6$ Å $b = 3.18_4$ Å $c = 10.67_1$ Å

UN / VN 75/25

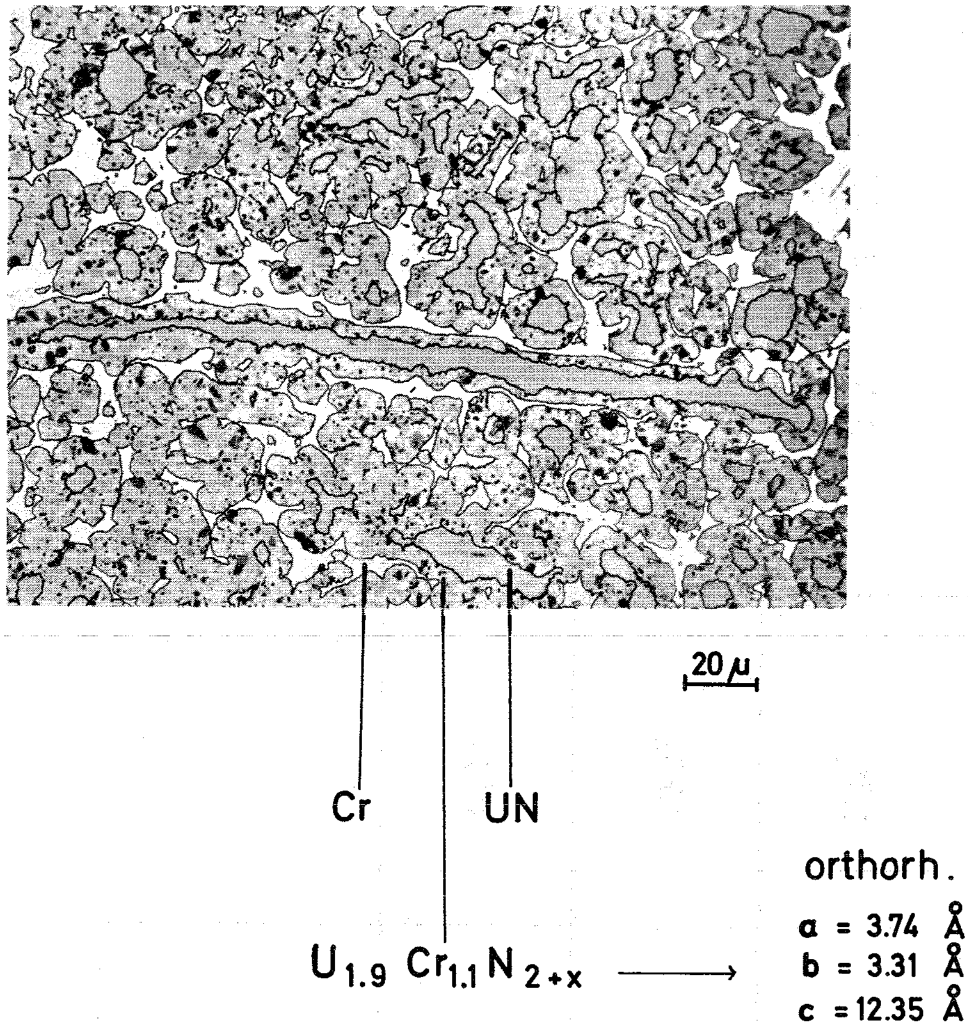
(1) arc melted (3 atm N_2)

(2) " " + 24h 2000°C 300 Torr N_2

(3) " " + 18 h 1800°C 300 Torr N_2

(Phase identification by microprobe analysis)

Fig. 2



Phase identification by microprobe analysis of an arc melted (3 atm N_2) and homogenized (63 h, 1300°C, 300 Torr N_2) UN - Cr specimen

Fig. 3

phase	lattice parameter	a / b	V $[10^{-24} cm^3]$
$UVN_{2(-x)}$	a = 5.45_6 Å b = 3.18_4 Å c = 10.67_1 Å	1.71_4	46.6 (46.3 - 47.1)
$UNbN_{2(-x)}$	a = 5.66_8 Å b = 3.26_6 Å c = 10.95_9 Å	1.73_5	50.4 (50.3 - 50.5)
$UTaN_{2(-x)}$	a = 5.64_5 Å b = 3.24_9 Å c = 10.93_7 Å	1.73_7	50.2 (49.5 - 50.3)
$U_{1.9}Cr_{1.1}N_{2+x}$ $(x<1)$	a = 3.74 Å b = 3.31 Å c = 12.37 Å		

Structure data of the orthorhombic uranium-transition metal complex nitrides

Fig. 4