Some Phase Equilibria in the Uranium–Nitrogen System[1]

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Abstract: Portions of the U–N phase diagram were determined by X-ray, metallographic, chemical, and thermal analyses of phases equilibrated with N_2 (up to 5 atm.) at temperatures up to 2850°. The U–UN portion of the diagram is a eutectic with the eutectic composition near pure U. The UN phase region has a U-rich boundary with an N:U ratio equal to or less than 0.96 ± 0.02 at 1500° and 0.92 ± 0.02 at 1800°. The N-rich boundary has an N:U ratio of 1.04 ± 0.02 at 1600°. The mononitride melts congruently with the N:U ratio 0.96 ± 0.03 at 2835 ± 30°. The body-centered-cubic $\rightleftarrows$ hexagonal transition of the sesquinitride was found to occur at 1120°, but the transition temperature may be dependent on composition. The composition of the hexagonal phase is $UN_{1.47 \pm 0.02}$ near the decomposition pressure at 1315°.

Rundle and co-workers[2] first characterized phases in the U–N system as NaCl-type face-centered-cubic (f.c.c.) UN, Mn_2O_3-type body-centered-cubic (b.c.c.) U_2N_3, and CaF_2-type f.c.c. UN_2. They found the U–UN and UN–U_2N_3 regions to be two phase over an unspecified temperature range. From variation of the UN_2 lattice parameter with composition, they concluded U_2N_3 and UN_2 form a continuous series of solid solutions in agreement with previously determined[3] N_2-pressure isotherms for the composition range $UN_{1.56}$–$UN_{1.65}$. Later, the hexagonal form of U_2N_3, isostructural with Th_2N_3,[4] was identified.[5,6] Recently, N_2-pressure dependence of the UN "apparent melting point"[7,8] and the temperature dependence of nitrogen solubility in liquid[9] were reported. In what follows, information on these phases is extended and summarized in a phase diagram.

Experimental Section

Materials. Ca-reduced U metal was 99.9 ± 0.01% pure. The particular metal used in determination of U melting point and solid–solid transition temperatures contained impurities, in parts per million: <0.2 B, 40 O, 1 Al, 40 C, 15 Si, <2 Ca, 20 Cr, 2 Mn, 15 Fe, <5 Co, 30 Ni, 6 Cu, <100 Zr, <25 Nb, <25 Mo, <1 Sn, <30 Ta, and <1 Pb. Gases used were "ultra pure" (Matheson Co., impurities <10 p.p.m.) H_2 and either "spectroscopically" pure N_2 or "purified"-grade (Matheson Co., 99.9996% pure) N_2.

Preparations. U–N phases were prepared in powder form and pressed into cylinders by one of two methods, depending on the N:U ratio.

(1) For N:U ratios less than 1, a standard volumetric gas apparatus was used. To begin preparation, a weighed amount of U metal was allowed to react with H_2 in a silica tube at 150° to yield UH_3. This was decomposed *in vacuo* at 400° to metal powder, and a measured amount of N_2 was introduced and allowed to react as the U powder was slowly heated from 300 to 800°. The product powder was cold pressed at 6000 kg./cm.^{2} into U + UN cylinders either 6- or 10-mm. diameter and 13 mm. long.

(2) For N:U ratios of 1 or greater, a standard gas train was used to treat U with H_2 at 150° and form UH_3 powder which was then converted to $UN_{1.7}$ powder in a stream of N_2 at 400°. The reaction was terminated by heating to 900° in N_2. Cylinders 10 mm. in diameter of composition $UN_{1.0}$ were formed by decomposition of the $UN_{1.7}$ powder in a graphite die at 1500° as it was pressed under a load of 200 kg. These were used in melting point runs to determine the UN solidus above 2600° and in anneals to determine the solidus between 1500 and 1800°.

Powders were transferred in He atmosphere, but compacted samples were briefly exposed to air during transfers.

Apparatus and Procedure. U solid–solid transition temperatures were determined as thermal arrests in samples evacuated and heated in a resistance-type furnace. Temperatures were measured with a Pt–Rh thermocouple connected to a potentiometer and located in a hole drilled into the sample.

All other experiments were conducted with a current concentrator to heat samples by induction *in vacuo* (10^{-6} torr) or N_2 atmospheres. Temperatures achieved by induction heating were determined with an optical pyrometer calibrated against another pyrometer recently certified by the U. S. Bureau of Standards. Samples of composition U to UN were provided with 6 mm. deep, 1.5-mm. diameter sight holes for temperature measurements and were supported on a 1.5-mm. diameter tungsten rod. The sesquinitrides were heated in a tungsten crucible. Temperature measurements were made by means of a sight hole in the lid. With induction heating, different experiments were made depending on the phase boundary to be established.

Experiment 1. For measurement of eutectic temperatures, arrests in optical emission from U + UN cylinders cooled through the eutectic were determined with the Rupert thermal analysis apparatus.[10]

Experiment 2. To determine the UN liquidus, U + UN cylinders were used to saturate liquid U with nitrogen at various temperatures and the composition of the liquid was determined from the proportion of dendritic UN precipitate found in quenched phases.

Experiment 3. In order to fix an upper limit to the N:U ratio in the U-rich UN phase boundary in the temperature region 1500 to 1800°, UN and U + UN cylinders were heated for various periods of time at selected temperatures and analyzed to yield congruent sublimation compositions. Cylinders which were heated and cooled *in vacuo* were supported on a tungsten rod and surrounded by a tungsten susceptor.

Experiment 4. To prepare metallographic samples, used for Figures 2 to 6, UN or U + UN cylinders were heated without a susceptor.

Experiment 5. To determine the composition of the N-rich UN boundary, either U + UN or UN cylinders of pycnometric density 13.9 ± 0.3 g./cc. were annealed in N_2 at pressures just below the decomposition pressure of the sesquinitride. Cylinders were heated without a susceptor.

Experiment 6. To determine the UN solidus above 2650° and the UN congruent melting point, UN cylinders were heated in N_2

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(1) This work was performed under the auspices of the United States Atomic Energy Commission.

(2) (a) R. E. Rundle, N. C. Baenziger, A. S. Wilson, and R. A. McDonald, *J. Am. Chem. Soc.*, 70, 99 (1948); (b) R. E. Rundle, N. C. Baenziger, A. S. Newton, A. H. Danne, T. A. Butler, I. B. Johns, W. Tucker, and P. Figard, "Chemistry of Uranium," J. J. Katz, Ed., Office of Technical Services, Department of Commerce, Washington 25, D. C., 1958, p. 53.

(3) Battelle Memorial Institute Report CT-2700, Feb. 1, 1945.

(4) W. F. Zachariasen, *Acta Cryst.*, **2**, 388 (1949).

(5) D. A. Vaughan, *Trans. AIME*, **206**, 78 (1956).

(6) W. Trzebiatowski, R. Troc, and J. Leciejewicz, *Bull. Acad. Polon. Sci., Ser. Sci. Chim.*, 10, 395 (1962).

(7) D. L. Keller, "Development of Uranium Mononitride," BMI-X-10006 (EURAEC-424), April–June 1962.

(8) W. M. Olson and R. N. R. Mulford, *J. Phys. Chem.*, **67**, 952 (1963).

(9) J. Bugl and A. A. Bauer, *J. Am. Ceram. Soc.*, 47, 425 (1964).

(10) G. N. Rupert, *Rev. Sci. Instr.*, **34**, 1183 (1963).

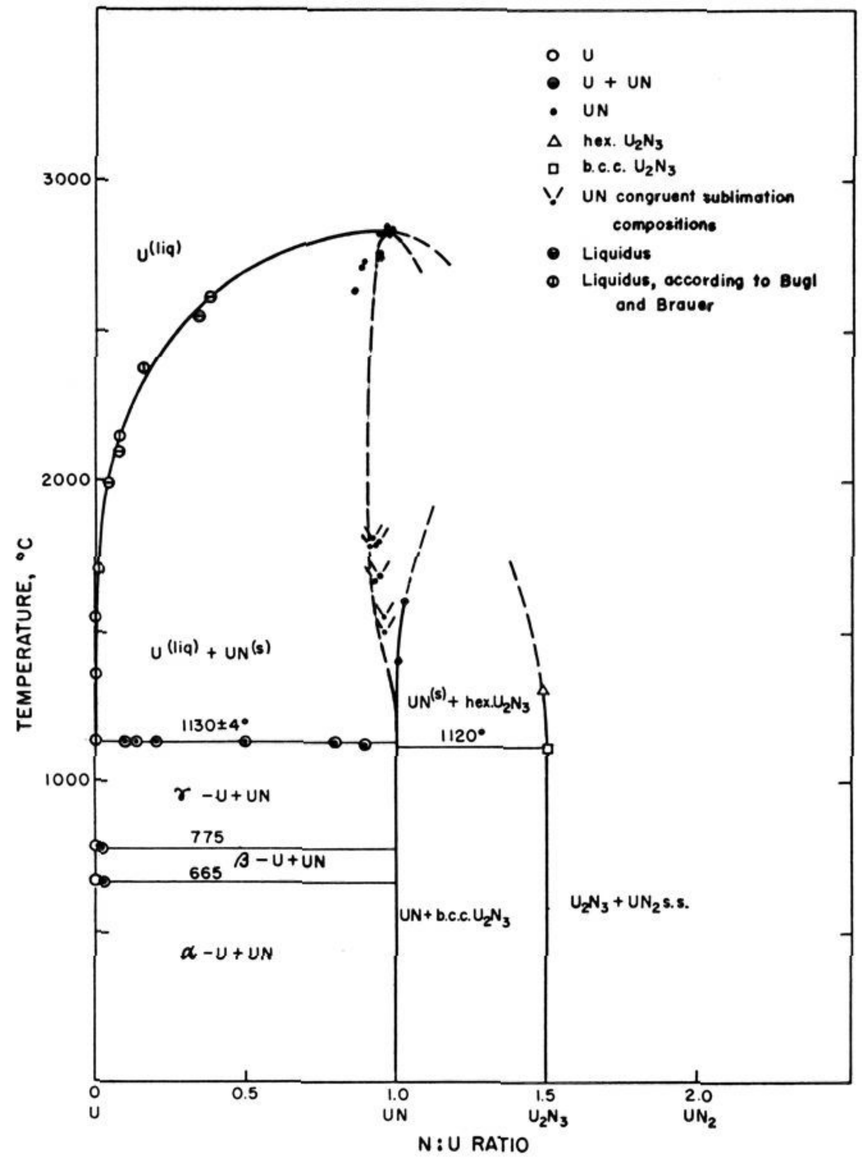

Figure 1. U–N partial phase diagram.

at various pressures, and, after equilibration just below the melting point, the temperature was slowly increased until liquid appeared. UN cylinders were usually heated with a tungsten susceptor in order to improve temperature uniformity, but some were heated without the susceptor.

Experiment 7. Sesquinitrides were formed by reaction of UN with N_2 at various pressures and temperatures.

Quenched phases were identified from X-ray powder photographs taken with Cu Kα radiation in a 115-mm. diameter camera. Lattice parameters were computed with use of an extrapolation described by Vogel and Kempter.[11] Uncertainties given for lattice parameters denote standard deviation in measurement of distances on X-ray films.

U was determined, in most cases, by ignition in air to U_3O_8 at 800°, and, after correction for oxygen impurity as UO_2, N was computed by difference. U and N in some samples were determined by the Analytical Group in this laboratory using titration methods. The latter chemical analyses give N:U ratios to within 0.02. The Analytical Group determined oxygen by ignition to CO which was analyzed gas volumetrically as CO_2. They determined tungsten colorimetrically in randomly selected samples.

Results

Solid–Solid Transitions of U. Initiation temperatures for thermal arrests on heating and cooling cylinders of the composition $UN_{0.02}$ are given in Table I. Because of possible mechanical and impurity effects introduced in preparation of $UN_{0.02}$, thermal arrests are compared with those obtained with U before and after subjection to the same treatment except for the N_2 addition, *i.e.*, arrests obtained with the original U button and arrests obtained with U metal after it has been hydrided, dehydrided, and cold pressed.

U–UN Eutectic. The melting point of U was found to be 1132 ± 4° in agreement with Dahl and Cleaves.[12]

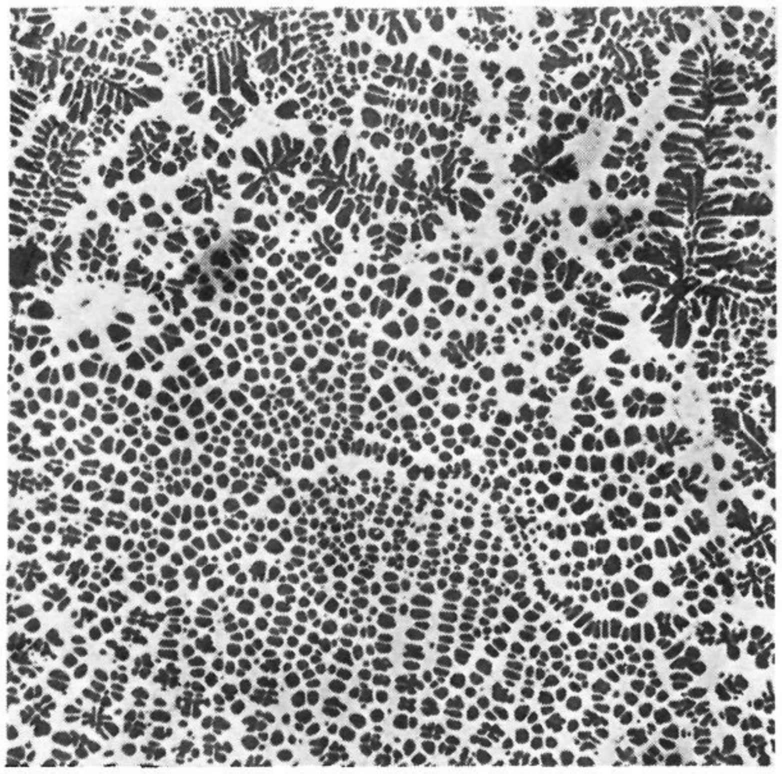

Figure 2. UN liquidus, bulk N:U ratio 0.34, after quenching from 2550° (×100).

Eutectic arrests for various N:U ratios up to 0.76 occurred at 1130 ± 1° while the arrest for the N:U ratio 0.90 was at 1125°. The lower value obtained for the latter composition, which has the weakest arrest, is probably due to experimental error. Results are shown in Figure 1. The eutectic temperature 1130° is assigned an uncertainty of 4° based upon the reproducibility of the first named samples and uncertainty in the pyrometer calibration.

Table I. Solid–Solid Transition Temperatures of U and $UN_{0.02}$

Material	Phase change	Transformation temp., °C. Heating	Cooling	Rate, °C./min.
As-reduced U button	α–β	670 ± 2	660 ± 2 (supercooled)	3
	β–γ	776	774	
Cold-pressed U powder	α–β	670	651	3
	β–γ	774	774	
Cold-pressed $UN_{0.02}$	α–β	670	651	3
	β–γ	778	774	3

UN Liquidus. Liquid U was saturated with N_2 at 2000 and 2100° by heating U + UN cylinders under vacuum. Liquid U was saturated with N_2 at 2550 and 2612° by heating U + UN cylinders in N_2 at 20 and 40 torr, respectively, a pressure slightly below the decomposition pressure of the UN phase. The compositions of the liquid, in mole per cent UN, were determined from relative areas of U and UN phases in polished sections to be 4 at 2000°, 8.3 at 2100°, 34 at 2550°, and 37 at 2612°. Results plotted in Figure 1 were used to draw the liquidus connecting the UN congruent melting point and the eutectic point. A photomicrograph of N_2-saturated U quenched from 2550° is shown in Figure 2.

UN Solidus at Temperatures 1500 to 1812°. First, a series of U + UN cylinders with N:U ratios 0.7

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[11] R. E. Vogel and C. P. Kempter, *Acta Cryst.*, **14**, 1130 (1961).

[12] A. I. Dahl and H. E. Cleaves, *J. Res. Natl. Bur. Std.*, **43**, 513 (1949).

Table II. Analyses of U–N Cylinders Used in Determination of the UN Solidus at 1500 to 1800°

Annealing conditions			Product analyses			
Temp., °C.	Time, hr.	Initial N:U	N:U by ignition	N:U by titration	O, %	W, %
1812	10	0.86	0.92	...	...	...
1800	96	0.87	0.93	...	0.27	<0.1
1797	49	0.87	0.91	...	...	...
1797	48	1.0	0.92	...	0.3	...
1687	67	1.0	0.95	...	0.28	<0.1
1670	28	1.0	0.93	...	0.35	<0.1
1550	24	1.0	...	0.96	0.12	...
1500	120	1.0	0.96	...	0.55	...

to 0.95 were heated under vacuum by radiation from a tungsten susceptor at selected temperatures in the range 1400 to 2100° and cooled. Products, according to metallographic examination, were in all cases two-phase, *viz.*, U + UN. Products, according to X-ray diffracted powder patterns, consisted of UN with U detectable only in those cases where N:U ratios were less than 0.85. Failure to detect U metal by X-ray diffraction in the N:U ratios 0.85 to 0.95 is probably due to the low sensitivity of this method of analysis. UN lattice parameters were the same in all cases, *viz.*, 4.889 ± 0.001 Å. It is apparent from these results that if a U excess existed in the UN phase, it was not retained when cooled under the described conditions. Evidence for a U-rich UN phase is given below. It will become apparent that failure to quench in the U-rich UN phase is due to rapid precipitation of liquid U.

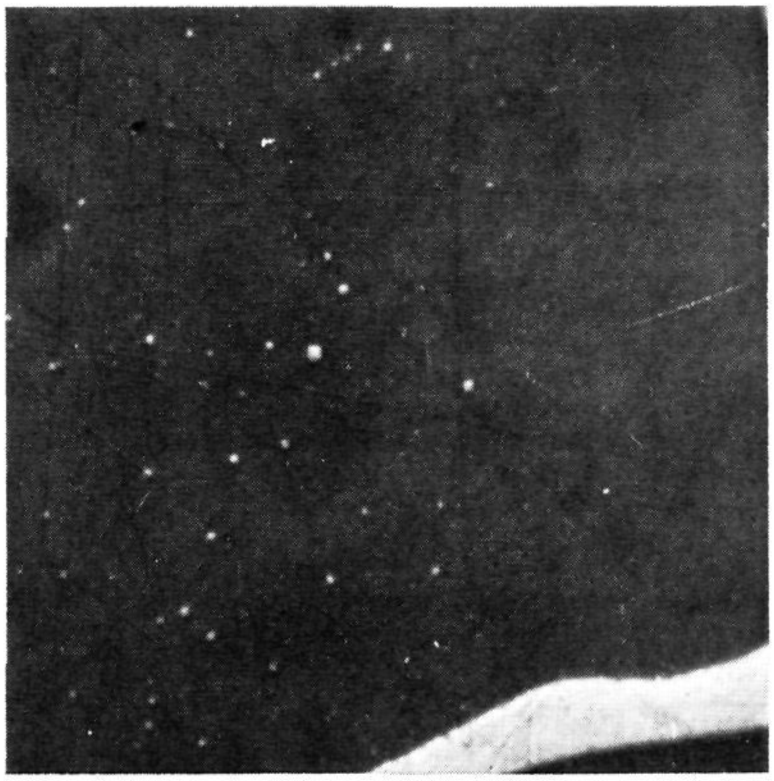

Figure 3. U + UN mixture, bulk N:U ratio 0.92, annealed 24 hr. at 1600° and quenched. U which has precipitated as liquid appears as islands in UN grains (×1500).

Next, the variation of congruent sublimation composition of UN with temperatures in the range 1500 to 1812° was determined. UN and U + UN cylinders surrounded by a tungsten susceptor *in vacuo* were heated until the composition no longer varied with time at the selected temperature. Results are given in Table II. Products, according to X-ray diffraction powder patterns, were UN with the lattice parameter 4.889 ± 0.001 Å. Cylinders heated in this manner in the temperature range 1850 to 2100° resulted in liquid formation and more or less rapid reaction with the tungsten support. Below 1800°, pure solid UN can be vaporized *in vacuo* indefinitely without appearance of liquid. From these and previously discussed results (see also Discussion), the solidus below 1800° was drawn as a broken line in Figure 1. A photomicrograph of U precipitated from U-rich UN of bulk composition $UN_{0.92}$ quenched from 1600° is shown in Figure 3. Obtained by the most rapid quenching achieved with our apparatus, U precipitate appears partly as islands within the UN grains.

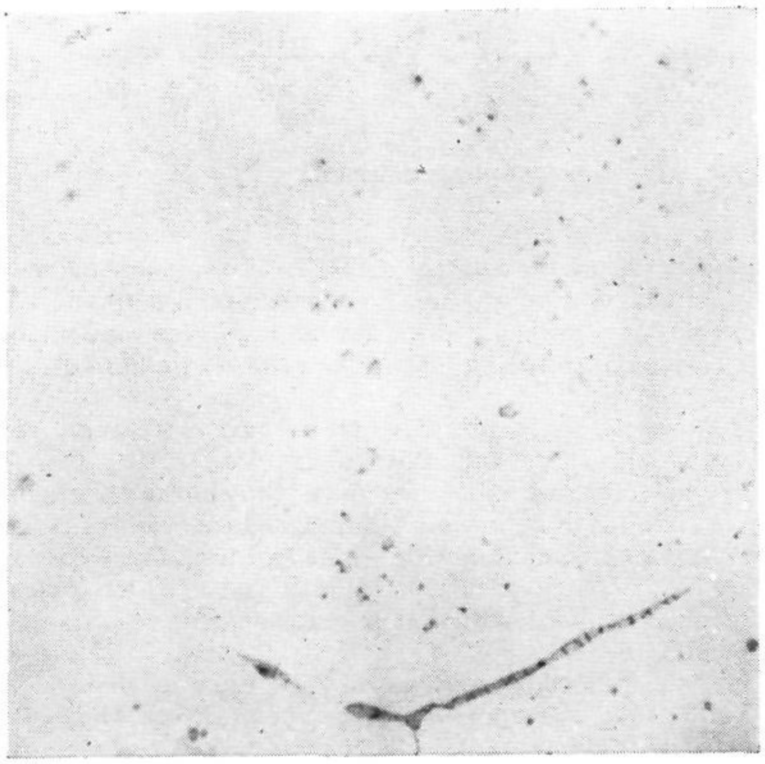

Figure 4. UN reacted 5 days at 1600° with 2 atm. of N_2 which is a pressure just below that for the formation of U_2N_3. The product, bulk N:U ratio 1.04, contains U_2N_3 solid precipitate which appears as dark island within UN grains (×1000).

The N:U ratio in the N-rich UN phase boundary at 1600° was determined from a sample annealed 5 days in 2 atm. of N_2, a pressure slightly lower than the decomposition pressure of the sesquinitride. In order to reduce reaction with N_2 during cooling, a U + UN cylinder with pycnometric density 14.0 was used. The anneal was terminated by cooling the sample in N_2. The final composition, which represents that of the N-rich UN boundary at 1600°, was found to be $UN_{1.04\pm0.02}$. In a similar experiment, it was found that the boundary composition is $UN_{1.02\pm0.02}$ at 1400°. The products, according to X-ray diffraction powder patterns, were predominantly UN with a lattice parameter 4.889 ± 0.001 Å. plus a minor proportion of b.c.c. U_2N_3 and a

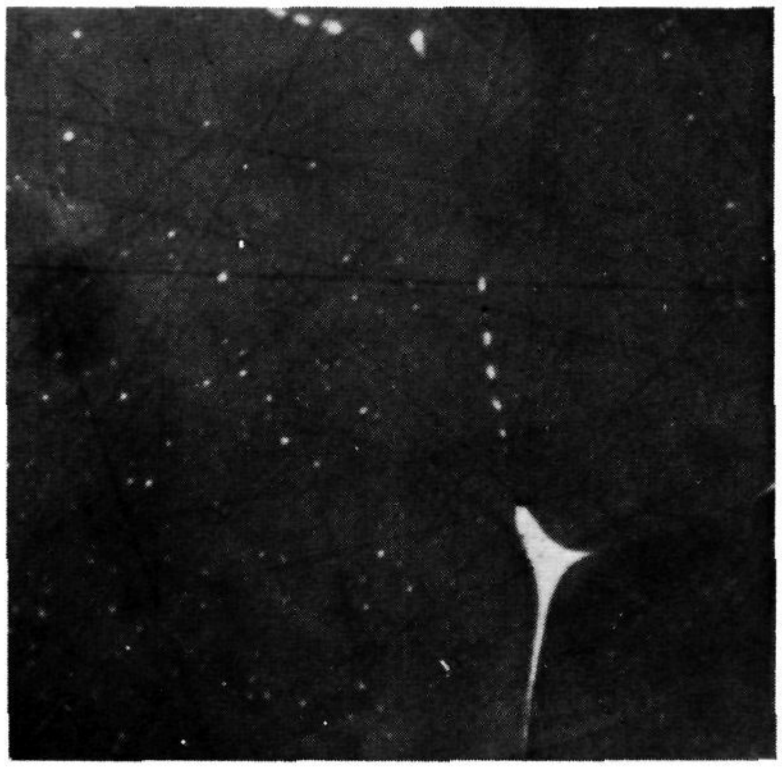

Figure 5. Congruently melted UN, bulk N:U ratio 0.97, after being melted at 2840° in 2 atm. of N_2 and quenched. U precipitated as liquid has, in part, formed fine islands and, in part, migrated to grain boundaries of UN (×1500).

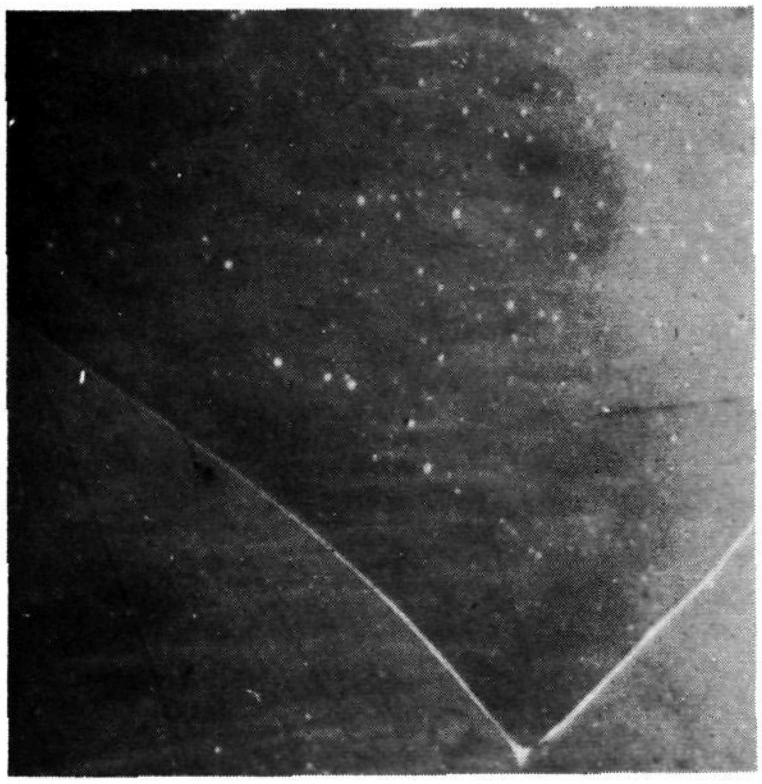

Figure 6. Solid UN with N:U ration 0.99 annealed at 2770° in 2 atm. of N_2 and quenched. The N:U ratio is greater than that of congruently melted UN and the character of the U precipitate is similar to that in Figure 5, showing that liquid U can migrate rapidly to grain boundaries even at the lowest temperature of segregation (×1500).

possible trace of UN_2. A photomicrograph of U_2N_3 precipitated from N-rich UN is shown in Figure 4. The sample which had a bulk composition $UN_{1.04}$ was annealed at 1600° and cooled. A minor dark phase associated with most of the light gray U_2N_3 precipitate may be UN_2 or UO_2.

UN Solidus at Temperatures 2650 to 2850°. Compositions of the UN, after being melted in various N_2 atmospheres and quenched, are listed in Table III.

Table III. UN Liquid Formation

Temp., °C.	N_2 pressure, atm.	Product analysis N:U	O, %	W, %
2830 ± 30	5.0	0.98 ± 0.02	0.18	3
2825	4.0	0.97	0.17	0.16
2820	4.0	0.98	0.25	<0.2
2819	3.0	0.97	0.53	...
2853	2.0	0.97	...	...
2840	2.0	0.98	...	...
2836	1.9	0.96	0.22	...
2835	2.0	0.95	0.20	...
2751	1.0	0.95	0.39	...
2725	0.10	0.89	0.23	<0.2
2719	0.10	0.88	0.36	...
2659	0.062	0.87	0.29	...

A tungsten susceptor was used to heat all samples except the fifth and sixth. To ensure equilibrium between solid UN and N_2, samples were held at a temperature within 50° below the liquification temperature for 3 min., then slowly heated until liquid appeared. Upon observing incipient melting, power was turned off and a stream of He was introduced to displace the N_2. Products showed only a minor surface darkening as evidence for possible N_2 reaction during cooling. Product samples contained only the UN phase, according to X-ray diffraction powder patterns, with lattice parameters 4.891 ± 0.002 Å., but metallographic examination revealed both U and UN. From the data in Table III, the solidus in the temperature range 2650 to 2835° was drawn as shown in Figure 1. This is extended to the lower segment of the solidus by a broken line. The congruent melting point occurs at 2835 ± 30° and the composition $UN_{0.96\pm0.03}$. Uncertainty in the temperature is based on an estimated uncertainty in the pyrometer calibration. The relatively low value of the melting point of the fourth sample listed in Table III is probably due to the larger oxygen impurity. Low values of the N:U ratio (relative to the solidus) in samples melted in N_2 at pressures below 1 atm. are due to partial decomposition to liquidus compositions. A photomicrograph of typical U precipitate formed from U-rich UN of bulk composition $UN_{0.97}$, cooled from the congruent melting point in N_2, is shown in Figure 5. The photomicrograph in Figure 6 shows U precipitation in a cylinder of bulk composition $UN_{0.99}$, a N:U ratio even greater than that of the congruent melting point, after being annealed in 2 atm. of N_2 at 2770° and cooled. The sample was cooled to 1100° in *ca.* 7 sec., and Figure 6 shows that during this time U precipitated and migrated to grain boundaries as a liquid. These fine grain boundaries disintegrate and form spheroidal islands of U if annealed 5 min. at 1150°.

Sesquinitrides. The b.c.c.–hexagonal transition is slow, and therefore thermal arrests are not detectable. Furthermore, bracketing the transformation temperature by analysis of annealed and quenched phases is complicated because nondense samples with large surface areas, when cooled, tend to react with the N_2 atmosphere, and dense samples equilibrate slowly. Hexagonal U_2N_3 was found to transform predominantly to b.c.c. U_2N_3 after being annealed 1 or more days at 1000 to 1120°, followed by cooling in a stream of He. Conversely, b.c.c. U_2N_3 powder transformed predominantly to hexagonal U_2N_3 in 2 days at 1156°. Body-centered-cubic U_2N_3 remained unchanged after 21 days at 1100°. Body-centered-cubic and hexagonal sesquinitrides, pure according to X-ray diffraction powder patterns, were prepared as follows: b.c.c. sesquinitride was formed by equilibration of UN powder for 48 hr. with 0.158 atm. of N_2 at 1120°, and hexagonal sesquinitride was obtained by reaction of dense (pyncnometric density 13.7 g./cc.) UN for 4 days in 0.41 atm. of N_2 at 1315°. The product N:U ratio of the b.c.c. phase was 1.50 ± 0.02 and the lattice parameter was 10.706 ± 0.002 Å. The product N:U ratio of the hexagonal phase was 1.47 ± 0.02 and the lattice parameters were a_0 = 3.7000 ± 0.0002 and c_0 = 5.847 ± 0.002 Å.

Discussion

Thermal arrests at the α–β and the β–γ solid–solid transitions of 99.9% pure U with increasing temperature were found to differ from that with decreasing temperature which is in agreement with Grogan,[13] Blumenthal,[14] and others. Thermal arrests obtained with the composition $UN_{0.02}$ and cold-pressed U powder are essentially the same as that of the As-reduced U except for the $\beta \rightarrow \alpha$ transition which is lower by 9°. As indicated in Figure 1, there is no effect on the polymorphic transitions of U which could be attributed to nitrogen.

The eutectic composition in Figure 1 is shown to be near pure U in accordance with the observed monotonic increase in the duration of thermal arrests with decrease in N:U ratio and in agreement with Blumenthal[15] who reported low solubility of nitrogen in liquid U near the melting point as determined by analysis of quenched phases. At the other end of the U + UN two-phase region, the eutectic line extends to near-stoichiometric UN at 1130°. This agrees with observed eutectic arrests and agrees with Rundle and coworkers,[2] who concluded all N:U ratios less than 1 are two-phase, *viz.*, U + UN, based upon X-ray analysis of quenched samples.

The UN liquidus as determined from the proportion of UN precipitate in quenched U–N melts confirms the liquidus as determined in the same way by Bugl and Bauer.[9]

From described results, the congruent sublimation composition is $UN_{0.92}$ at 1800° where it meets the U-rich UN boundary and crosses over to the liquid solution of nitrogen in U. The congruent composition is near stoichiometric UN at 1130°. At intermediate temperatures, the congruent sublimation compositions vary uniformly as shown in Table II and by v-shaped symbols in Figure 1. Along a curve (not shown in Figure 1) representing the congruent compositions, there is only one component variable. Consequently, neglecting effects of pressure, the region must be single-phase UN. From these considerations, congruent sublimation compositions represent an upper limit to N:U ratios in the U-rich phase boundary.

Data in Table III show that a slight decrease in melting temperature may occur with increase in N_2 pressure between 2 and 5 atm., but the variation is less than the uncertainty in temperature measurements. The N_2-pressure dependence of melting points is in agreement with that of Olson and Mulford.[8]

The hexagonal–b.c.c. transition temperature, 1120°, represents the temperature above which b.c.c.-to-hexagonal conversion and below which hexagonal-to-b.c.c. conversion was observed. In contrast, Mallett and Gerds[16] found hexagonal U_2N_3 among products of the U reaction with N_2 at 1 atm. pressure and at temperatures below 1000°. We observed that hexagonal phase decomposes to b.c.c. U_2N_3 below 1120°, and it is probable that the hexagonal phase is also unstable under the conditions investigated by Mallett and Gerds below 1000° in 1 atm. of N_2. We found U metal reacts with 5 torr of N_2 at 1000° to form UN and b.c.c. U_2N_3 with no hexagonal U_2N_3 detectable by X-ray diffraction analysis. An explanation for these observations may be that the decomposition pressure of the b.c.c. phase is below 5 torr at 1000°, while that of the hexagonal phase is above 5 torr. Then, with favorable diffusion–kinetic factors, or "epitaxy growth" as discussed by Evans,[17] the hexagonal phase may form below 1000° as a metastable layer on UN in 1 atm. of N_2. Lattice parameters of hexagonal U_2N_3 are in agreement with that obtained from mixtures with b.c.c. U_2N_3 by Vaughan[5] and Trzebiatowski, Troc, and Leciejewicz.[6]

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(13) J. D. Grogan, *J. Inst. Metals*, 77, 57 (1950).

(14) B. Blumenthal, *J. Nucl. Mater.*, 2, 23 (1960).

(15) B. Blumenthal, ANL-5349, Argonne National Laboratory, Lemont, Ill., 1955.

(16) M. W. Mallett and A. F. Gerds, *J. Electrochem. Soc.*, **102**, 292 (1955).

(17) P. E. Evans, *J. Am. Ceram. Soc.*, **45**, 305 (1962).