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

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Abstract: Portions of the Th–N phase diagram were determined by X-ray, microscopic, chemical, and thermal analyses of phases equilibrated with N_2 (up to 3 atm) at temperatures up to 2820°. The Th–ThN portion of the phase diagram is a peritectoid–peritectic system wherein, upon heating, the face-centered-cubic (fcc) Th phase with a N:Th ratio 0.08 ± 0.02 decomposes peritectoidally at 1605 ± 20° to body-centered-cubic (bcc) Th and ThN. The bcc Th phase with a N:Th ratio 0.09 ± 0.02 decomposes peritectically at 1800 ± 25° to liquid Th and ThN. The Th-rich boundary of the ThN phase extends from the N:Th ratio 0.97 ± 0.03 at 1576° to 0.87 at 2000°, while the N-rich boundary extends from the N:Th ratio 1.03 ± 0.03 at 1615° to 1.08 at 2065°. The mononitride phase melts congruently at 2820 ± 30° with the N:Th ratio 0.995 ± 0.005. The Th-rich boundary of the rhombohedral Th_3N_4 phase changes with increasing temperature from the N:Th ratio 1.33 at 1600° to 1.29 ± 0.03 at 1960°.

The thorium nitride phases have been identified by various investigators. The Th_3N_4 phase was first reported[2] in the early part of this century and was later found to have a rhombohedral Al_4C_3-type crystal structure.[3] A phase with the hexagonal rare earth type crystal structure, presumed to be Th_2N_3, has been reported.[4] However, the reported crystal structure is identical with that recently found for the sesquioxide, Th_2N_2O.[3,5] The crystal structure of the ThN phase was reported by Rundle[6] and Chiotti[7] to be face-centered cubic (fcc).

The melting point of the ThN phase depends on composition and, therefore, on N_2 pressure and has been measured by Chiotti[7] who found that ThN melts under a He atmosphere at 2630° and by Olson and Mulford[8] who reported that stoichiometric ThN melts in N_2 at 2790°. The solubility of nitrogen in solid fcc Th (845 to 1490°) has been reported by Gerds and Mallett.[9] Knowledge of the phase boundary compositions is of fundamental importance in the studies of physical properties. We have therefore investigated Th–N phases equilibrated under different conditions. In what follows, the experimental results are reported and summarized in a phase diagram.

Experimental Section

Materials. The initial work was done with arc-melted Th (99.8% pure, Nuclear Division of Union Carbide Corp., Oak Ridge, Tenn.) but most of the final results were obtained with crystal-bar (iodine process) Th (Metal Hydrides Division of Ventron Corp., Beverly, Mass.). The arc-melted Th contained, as impurities, 0.2% oxygen and in parts per million 3 Be, 200 C, 30 Si, 30 Cr, and 100 Fe. The experimental results obtained with specimens prepared from crystal-bar Th were observed to differ appreciably from those of the same N:Th ratio prepared from arc-melted Th in two ways; *viz.* (1) the solid–solid transition of Th was sharper and occurred in a narrower temperature range, and (2) the melting points of ThN were higher. These differences are probably due to the greater amounts of impurities in the arc-melted Th and, in those cases where differences were observed, the results obtained with the crystal-bar Th are adopted. The gases used were "ultra pure" (Matheson Co., "impurities 10 ppm") H_2 and either "spectroscopically" pure (Linde Co.) or "purified" (Matheson Co., 99.999% pure) grade N_2.

Preparations. Th–N phases were prepared in powder form and either cold pressed or hot pressed into cylinders 6 mm in diameter

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(1) This work was done under the auspices of the U. S. Atomic Energy Commission.

(2) C. Matignon and M. Delepine, *Ann. Chim. Phys.*, **10**, 130 (1907).

(3) R. Benz and W. H. Zachariasen, *Acta Cryst.*, in press.

(4) W. H. Zachariasen, *ibid.*, **2**, 388 (1949).

(5) R. Benz, *J. Am. Chem. Soc.*, **89**, 197 (1967).

(6) R. E. Rundle, *Acta Cryst.*, **1**, 180 (1948).

(7) P. Chiotti, *J. Am. Ceram. Soc.*, **35**, 123 (1952).

(8) W. M. Olson and R. N. R. Mulford, *J. Phys. Chem.*, **69**, 1223 (1965).

(9) A. F. Gerds and M. W. Mallett, *J. Electrochem. Soc.*, **101**, 175 (1954).

and 12 mm long. The methods of preparation were: (1) for ratios N:Th < 1, Th hydride was formed at 180° and vacuum decomposed at 700°, and the product Th powder was allowed to react at 500 to 900° with a measured quantity of N_2 and cold pressed; (2) for the N:Th ratio 1.0, Th hydride was converted to Th_3N_4 in a stream of N_2 (200 to 900°) and decomposed to ThN in a graphite die as it was pressed *in vacuo* at 1500°. The powders were transferred in a He atmosphere, but the compacted cylinders were briefly exposed to air during the transfers.

Procedure. The specimens were heated *in vacuo* (10^{-6} torr or less) or in N_2 atmospheres with an eddy-current concentrator. Different experiments were made depending on the phase boundary to be established.

Experiment 1. The peritectoid and peritectic temperatures were determined by observing heating and cooling arrests in radiant emission from Th + ThN cylinders using the thermal analysis apparatus designed by Rupert.[10-12] The cylinders were sometimes supported on a tungsten rod and heated directly by induction with no radiation shield and sometimes heated in a tungsten crucible in order to improve temperature uniformity.

Experiment 2. The solubility of nitrogen in fcc Th at 1550° and in bcc Th at 1750° was obtained micrographically by measuring the areas of the phases in sections of Th + ThN specimens which had been equilibrated at temperature and cooled. The bulk N:Th ratios of the specimens were 0.05 and 0.10. The ThN particles segregated from the Th phase during cooling. They were observed microscopically to be finely dispersed. In order to agglomerate and to allow growth of the precipitated ThN particles prior to areal analyses, the specimens were annealed 16 hr starting at 1200° and the temperature was slowly decreased to 1000°. Using these analyses, the solubility expressed in N:Th ratios was obtained by adding 0.02 which represents the solubility of nitrogen in Th at 1000° as reported by Gerds and Mallett.[9]

Experiment 3. In order to determine the Th-rich ThN liquidus, Th + ThN cylinders were equilibrated at selected temperatures and cooled in a stream of He gas. The composition of the liquid was obtained from the proportion of dendritic ThN precipitate and Th found in the quenched specimens.

Experiment 4. An upper limit for the N:Th ratio of the Th-rich ThN phase boundary was set by determination of the steady-state sublimation compositions in the temperature range 1537 to 1930°. ThN and Th + ThN cylinders were centered in a tungsten susceptor and heated *in vacuo* for various periods of time at selected temperatures in order to effect an appreciable weight loss by vaporization (up to 10%). The final N:Th ratios were determined by ignition in air to ThO_2.

The principle of the method is as follows. The N:Th ratios in the specimens that had been sublimed for sufficiently long periods of time were observed to vary in a systematic and uniform way with temperature. The variation of pressure under the experimental conditions was small and negligible. Therefore, assuming equilibrium conditions were realized, the specimens were single phase (*viz.*, ThN in case under consideration) at temperature. Since these compositions lie in the ThN phase region, the corresponding N:Th ratios represent an upper limit to that of the Th-rich boundary.

Experiment 5. The Th-rich ThN boundary at various temperatures between 1576 and 2820° (congruent melting point) was obtained micrographically. Th + ThN cylinders were equilibrated at temperature (either *in vacuo* or in N_2 atmospheres), cooled in a stream of He, and annealed 16 hr at 1200 to 1450° in order to agglomerate the Th precipitate formed in ThN crystals. They were sectioned, polished, and analyzed micrographically. Under conditions such that it can form, liquid Th precipitated rapidly from ThN and was readily observed in quenched specimens. In contast, the precipitation of solid Th was appreciably slower. It was observed, microscopically, only after the specimens had been annealed as described above. The micrographic analyses give the difference in nitrogen solubility between the equilibration temperature and the anneal temperature. The solidus boundary was obtained by assuming negligible solubility at the temperature of anneal.

Experiment 6. In order to determine the composition of the N-rich ThN boundary and the Th-rich Th_3N_4 boundary in the temperature range 1600 to 2000°, Th + ThN cylinders with pycnometric density 11.5 ± 0.02 g/cc were equilibrated with N_2 at pressures just below and just above, respectively, the decomposition pressure of the Th_3N_4 phase. The cylinders were heated in tungsten crucibles. The compositions were determined both by ignition to ThO_2 and micrographically.

Lattice parameters were obtained from X-ray diffraction powder photographs taken with Ni-filtered Cu Kα radiation in a 115-mm diameter camera. Uncertainties of lattice parameters denote standard deviation in the measurement of distances on X-ray films. In order to determine compositions micrographically, the areas of different phases recorded on film were cut out and weighed. The Th content was determined by ignition in air to ThO_2 at 800°, and the nitrogen was computed by difference.

Results

The Peritectoid and Peritectic Temperatures and Nitrogen Solubility in Solid Th. Crystal-bar Th melted at 1754 ± 15°. The thermal arrest of the fcc–bcc transition initiated at 1370° on heating and 1365° on cooling. The transition lasted over a temperature range of 25° on heating and cooling at a 2°/sec rate of temperature change. The transition initiated at 1378° on heating and 1360° on cooling and extended over a slightly broader temperature range at a higher rate of temperature change (12°/sec). Thus, the value observed for the fcc–bcc transition in Th is 1365 ± 35° under our experimental conditions.

Th + ThN cylinders with various N:Th ratios up to 0.96 were subjected to thermal analysis. In the vicinity of the peritectoid temperature, three distinct thermal effects were observed. These consisted of one thermal arrest and two changes in cooling rates. The arrest is associated with the peritectoid reaction. It occurred at 1605 ± 20° (heating and cooling) with N:Th ratios 0.08 to 0.88 as shown in Figure 1. The arrest was not detected with the extreme N:Th ratios 0.01 and 0.96. The second thermal effect was most pronounced at about 1570° with N:Th ratios 0.1 to 0.88 but broadened continuously toward 1400° as the N:Th ratio was decreased from 0.1 to 0.01. This thermal effect is due to the dissolution of ThN into solid Th during heating and the reprecipitation of ThN during cooling. The third thermal effect was most pronounced at about 1645°. It extended over a temperature range of about 40°. It was strongest in Th-rich cylinders and was observed with N:Th ratios 0.06 to 0.2. It is due to the dissolution of ThN into bcc Th during heating and the reprecipitation of ThN from bcc Th during cooling. We did not obtain a reliable dependence on the N:Th ratio and conclude only that the boundary of the bcc Th phase (plus N in solid solution) at the peritectoid temperature does not exceed the N:Th ratio 0.06.

The peritectic arrests were observed to occur at 1800 ± 25° (heating and cooling) with N:Th ratios 0.40 to 0.82. With these compositions, a change in cooling rate near the Th melting point was also detected. No peritectic arrest was detected with N:Th ratios 0.88 and 0.96. With N:Th ratios up to 0.31, cylinders could not be supported at the peritectic temperature and, therefore, the arrests with these compositions were not obtained; cylinders with N:Th ratios up to 0.1 formed liquid and collapsed at the Th melting point while cylinders with N:Th ratios 0.19 and 0.31 col-

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

(11) G. N. Rupert, *ibid.*, **36**, 1629 (1965).

(12) G. N. Rupert, "Versatile High Temperature Thermal Analysis Apparatus," paper presented at the First International Conference on Thermal Analysis," Aberdeen, Scotland, Sept 6–9, 1965; see, also "Thermal Analysis," J. P. Redfern, Ed., Macmillan and Co., Ltd., London, 1965.

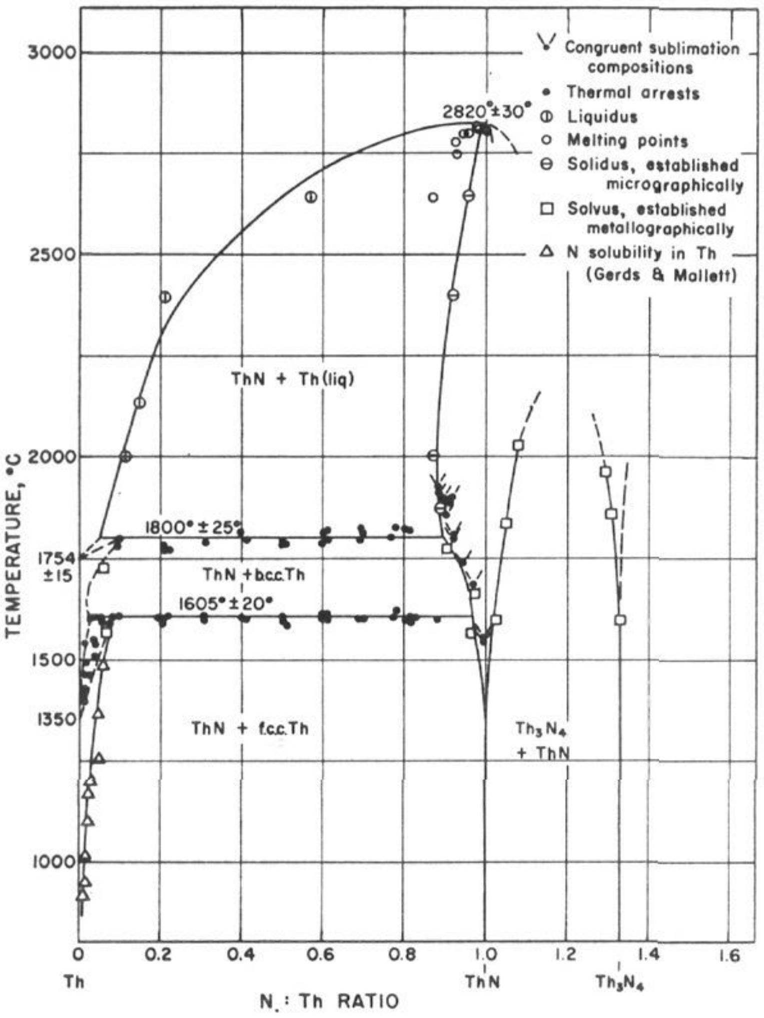

Figure 1. The Th–Th_3N_4 phase diagram.

lapsed at 1790°. The results of thermal analyses are plotted in Figure 1.

The N:Th ratio in the N-rich boundary of Th was deduced from areal analyses of polished sections. The resulting N:Th ratios are 0.08 for fcc Th at 1550° and 0.08 for bcc Th at 1750°. The solvus curves for solid Th in Figure 1 are based upon these and the above-mentioned thermal analysis data. The lattice parameter of fcc Th in the quenched phases was found to be 5.090 ± 0.009 A, and no systematic dependence on the quench temperature or nitrogen content was observed. This is in agreement with the general observation that the bulk of the nitrogen precipitated rapidly from solid Th. Figure 2 is a photomicrograph showing the parent Th phase containing particles of ThN that had formed by precipitation.

ThN Liquidus. Liquid Th was saturated with nitrogen at 2000, 2139, and 2400° by heating Th + ThN cylinders *in vacuo*. It was saturated at 2644° by heating a Th + ThN cylinder in 15 torr of N_2 which is a pressure slightly below the decomposition pressure of the ThN phase. The N:Th ratios of the liquidus was found micrographically to be 0.12 at 2000°, 0.14 at 2139°, 0.21 at 2400°, and 0.53 at 2644°. These results are plotted in Figure 1 and used to draw the liquidus connecting the ThN congruent melting point (see below) and the peritectic tie line. Figure 3 is a photomicrograph of the liquidus composition which had been equilibrated at 2000° and cooled in a stream of He gas.

Th-Rich ThN Phase Boundary in the Temperature Range 1537 to 2650°. The final N:Th ratios of specimens that were heated for different periods of time at selected temperatures in the range 1537 to 1930° are listed in column 4 of Table I. Oxygen analyses of samples are listed in column 5 of Table I. The tungsten

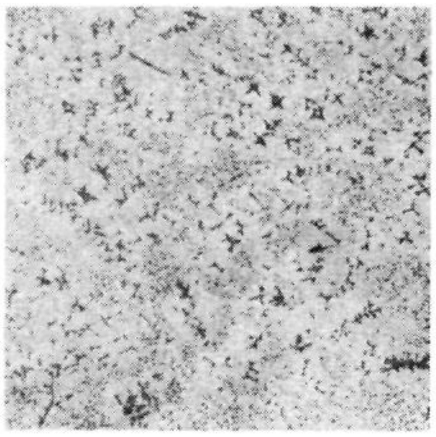

Figure 2. Photomicrograph of a $ThN_{0.05}$ specimen which was annealed 0.5 hr at 1761° and cooled. Particles of ThN precipitate appear as dark islands in Th (×250).

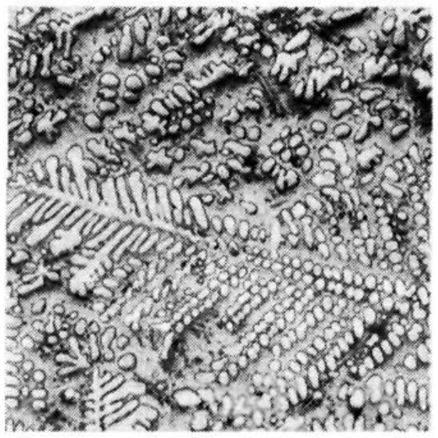

Figure 3. Photomicrograph of Th-rich ThN liquidus which was equilibrated at 2000° and cooled. Dendritic ThN appears in a matrix of Th (×250).

content of samples was less than 0.1% by analysis. X-Ray diffraction powder patterns of samples contained lines corresponding to the fcc ThN phase. In some cases, faint lines corresponding to the ThO_2 phase were visible. The values of the ThN lattice parameters are listed in the last column of Table I.

Table I. Analyses of the ThN Steady-State Sublimation Compositions

Sublimation conditions			Product analyses		
Temp, °C (±25°)	Time, hr	Initial N:Th ratio	N:Th ratio (±0.04)	O, %	a_0, A (±0.001)
1930	68	0.97	0.88	0.39	5.160
1913	16	0.84	0.88	0.42	5.156
1901	19	1.0	0.91	0.35	5.162
1900	12	1.0	0.89	...	5.161
1895	23	0.84	0.90	0.38	5.162
1894	13	1.0	0.91	...	5.160
1871	21	0.90	0.88	0.11	5.159
1856	10	0.80	0.90	...	5.157
1805	70	1.0	0.92	0.31	5.160
1795	38	0.95	0.92	0.29	5.158
1733	96	0.92	0.94	0.34	5.156
1657	78	0.88	0.91	0.26	5.155
1628	48	0.92	0.93	...	5.156
1558	60	1.0	0.99	...	5.159
1537	94	0.97	0.99	0.27	5.158

The values range from 5.155 to 5.162 A. This may be due to variations in the levels of impurities such as oxygen or possibly carbon (from pump oils) that can accumulate during the long periods of vaporization. The values of the lattice parameters tend to be higher in those specimens heated at higher temperatures;

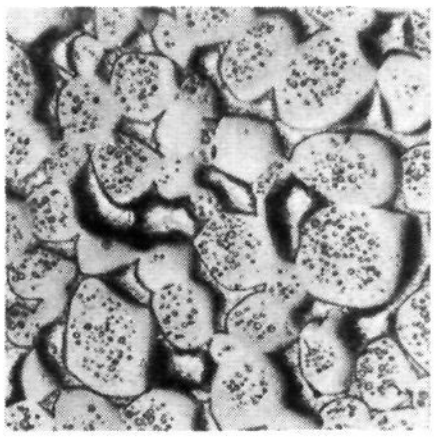

Figure 4. Photomicrograph of a specimen with the bulk N:Th ratio 0.6 that was equilibrated at 1833°, cooled, and annealed 16 hr at 1450°. The large grains are ThN. These are surrounded by excess Th at grain boundaries. The particles in the ThN grains were formed by precipitation of Th (×250).

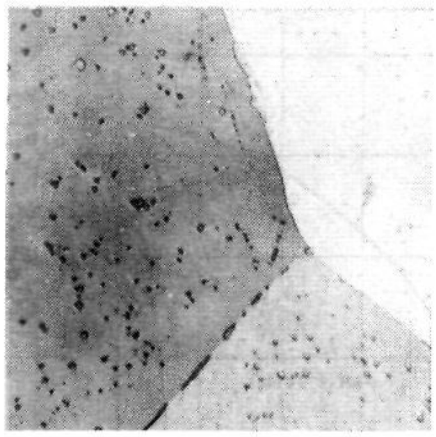

Figure 5. Photomicrograph of a specimen with the bulk N:Th ratio 1.06. The specimen was prepared by equilibrating a dense ThN specimen in 130 torr N_2 at 1833°. The three large grains are ThN with different shades of contrast that developed from air etching. The small dark islands are Th_3N_4 particles that formed by *precipitation* (×250).

however, no general correlation with N:Th ratio or with thermal history was realized. The products were porous with pycnometric densities 10.4 to 11.4 g/cm^3.

The final N:Th ratios were obtained both with specimens that were initially nitrogen rich, *i.e.*, had higher N:Th ratios, and with specimens that were initially Th rich, *i.e.*, had appreciably lower N:Th ratios. The specimens that were initially rich in nitrogen evolved N_2 rapidly upon being heated and probably attained the final N:Th ratio in only a fraction of the time at temperature. In contrast, Th distilled only slowly at temperature, and it was not feasible to obtain the steady sublimation compositions by starting with specimens containing a large excess of Th. The slow vaporization of Th is illustrated by the results of the two experiments listed in the lines which are fourth and third from the bottom of Table I. In these two experiments, the specimens were initially Th rich with the respective N:Th ratios 0.88 and 0.92. At the end of the experiments, the N:Th ratios were found to be higher, *viz.*, 0.91 and 0.93, respectively, corresponding to preferential vaporization of Th. However, the final values are significantly lower than those obtained in the other experiments and evidently the final compositions in these two experiments do not represent that of equilibrium. The values of the N:Th ratios of the other products listed in Table I decrease from 0.99 at 1537° to 0.88 at 1930°. These results are plotted in Figure 1 with V-shaped symbols. The data represent compositions that lie within the boundaries of the ThN phase.

Cylinders that were heated in the above-described manner at temperatures above 1930° resulted in more dense products (densities 11.1 to 11.6 g/cc), more or less rapid reaction with the tungsten support, and formation of liquid Th.

The Th-rich boundary was also determined micrographically by areal analyses of a series of Th + ThN cylinders. The cylinders were equilibrated *in vacuo* at selected temperatures, cooled in a stream of He, and annealed. The N:Th ratios computed from the relative proportion of Th precipitate found within ThN grains are 0.97 at 1576°, 0.96 at 1665°, 0.91 at 1775°, 0.89 at 1870°, 0.87 at 2000°, 0.92 at 2400°, and 0.96 at 2645°. These results are plotted in Figure 1 and used to draw the solvus and solidus at the Th-rich ThN phase boundary. Figure 4 is a photomicrograph showing Th precipitate in ThN grains.

The N:Th ratio in the N-rich phase boundary at 1615, 1835, and 2065° was determined from the composition of dense ThN cylinders which had been equilibrated, respectively, 7 days in 14 torr of N_2, 4 days in 119 torr of N_2, and 3 days in 600 torr of N_2. The N_2 pressures were selected in order to be slightly below the decomposition pressure of Th_3N_4. The N:Th ratios of the products were found to be 1.03 ± 0.03 at 1615°, 1.05 at 1835, and 1.08 at 2065°. The respective products contained 0.35, 0.22, and 0.30% oxygen. X-Ray diffraction powder patterns of samples contained strong lines corresponding to the ThN phase and faint lines corresponding to the Th_3N_4 phase, presumably, precipitate. The porportions of Th_3N_4 precipitate in the ThN grains were also determined micrographically in the same specimens. The results agree, respectively, with those determined by ignition as given above. Thus, virtually all of the excess nitrogen precipitated from the ThN phase as it cooled. Figure 5 is a photomicrograph showing Th_3N_4 precipitate in ThN.

ThN Congruent Melting Point. First, the melting points were determined with ThN prepared from arc-melted Th. Cylinders of ThN were supported on a tungsten rod, surrounded by a tungsten susceptor to improve temperature uniformity, and heated in N_2 atmospheres. Upon observing incipient melting, the power was turned off and the N_2 was displaced with a stream of He as the specimen cooled. With increasing N_2 pressure, the melting points were observed to increase from 2640° at 0.03 atm of N_2 to 2770° at 1 atm of N_2, and the N:Th ratios in the cooled products ranged, respectively, from 0.85 to 0.98. Microscopically, the products consisted of ThN with Th in grain boundaries. The melting points in 2 to 5 atm of N_2 ranged from 2750 to 2790°, and the product N:Th ratios ranged from 1.00 to 1.04. Microscopically these products consisted of ThN with up to 20% of (O + N)-rich grain boundary phases. The latter phases were identified from X-ray diffraction powder patterns to be Th_3N_4 and Th_2N_2O. A typical result is listed in line 1 of Table II, and a photomicrograph of the product is shown in Figure 6. All the melted products that originated from arc-melted Th contained an appreciable quantity of oxygen (0.3 to 1.5%) and tungsten (up to 5%). In order to test for the influence of these impurities on the ThN melting points, a cylinder was prepared

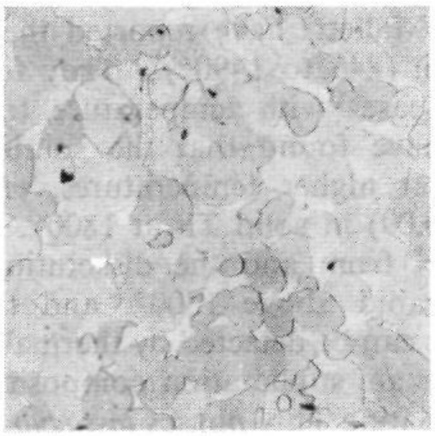

Figure 6. Photomicrograph of ThN which melted incongruently in 3 atm of N_2 at 2760°. The specimen was prepared from arc-melted Th. The bulk N:Th ratio is 1.03 as determined by ignition. The dark spheroidal grains are ThN. The light regions are a mixture of Th_3N_4 and Th_2N_2O phases (×250).

from ThN powder mixed with 5 mole % ThO_2, and one was prepared containing 5 mole % tungsten. Both melted 50° lower in 2 atm of N_2 than did cylinders of ThN with no additions; therefore, the above-described experiments were repeated using ThN specimens prepared from crystal-bar Th, and the cylinders were heated by induction with no tungsten susceptor.

Table II. The Variation of the ThN Melting Points with Composition in the Vicinity of the Congruent Melting Point

		Product analyses	
Mp, °C (± 30°)	N_2 pressure, atm	N:Th ratio (±0.02)	O, %
2770	3.00	1.03	0.37
2810	3.00	1.00	...
2820	2.00	0.99	...
2823	2.00	0.98	0.10
2811	2.00	0.98	0.14
2810	1.00	0.99	...
2801	1.00	0.96	...
2800	1.00	0.95	0.04
2780	0.263	0.93	...
2748	0.193	0.93	...
2643	0.026	0.87	0.05

The melting points of ThN and the product N:Th ratios are listed in lines 2 to 11 of Table II and plotted in Figure 1. The specimens which were melted in less than 1 atm of N_2 contained an appreciable quantity of Th formed by decomposition. Sections of typical products are shown in Figures 7 and 8. The maximum or congruent melting point occurred at 2820 ± 30° in 2 atm of N_2, in agreement with the value 2790 ± 30° reported by Olson and Mulford.[8] The N:Th ratio in the product was found to be 0.99 ± 0.02 by ignition. Microscopically, the product appeared to be single phased, but a sample that was subsequently annealed 12 hr at 1430° contained particles of Th precipitate corresponding to a N:Th ratio 0.995 ± 0.005. Figure 9 shows a section of the melted product after it was annealed. The fcc ThN lattice parameters were essentially the same in all the melted products, *viz.*, 5.157 ± 0.001 A, and annealing had no significant effect on the value.

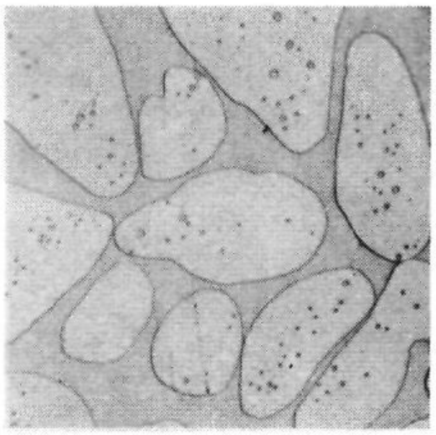

Figure 7. Photomicrograph of a ThN specimen that was melted incongruently at 2643° in 20 torr of N_2 and annealed under vacuum 13 hr at 1400°. The bulk N:Th ratio is 0.87. The spheroidal grains are ThN. These are surrounded by Th that formed by decomposition upon melting. The ThN grains contain small islands of Th metal precipitate that were agglomerated by annealing (×1000).

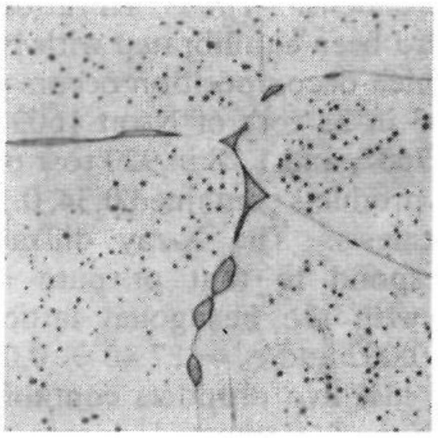

Figure 8. Photomicrograph of ThN melted incongruently at 2800° in 1 atm of N_2 and annealed under vacuum 13 hr at 1400°. The bulk N:Th ratio is 0.95. The phases present are the same as that in Figure 7, but less Th is present (×1000).

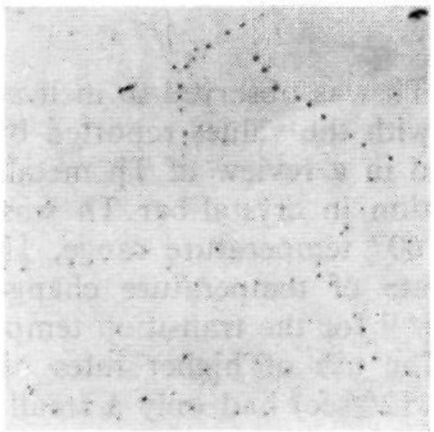

Figure 9. Photomicrograph of ThN melted congruently at 2820° in 2 atm of N_2 and annealed under vacuum 12 hr at 1430°. The bulk N:Th ratio is 0.995. The specimen consists of large ThN grains which contain tiny islands of Th metal precipitate (×1000).

Th_3N_4. The powder was formed either by reaction of Th powder with N_2 at temperatures 500 to 1000° or by heating Th hydride powder in a stream of N_2 at temperatures 300 to 1000°. More dense Th_3N_4 was formed by equilibration of dense ThN with N_2 at temperatures 1200 to 2000°.

Various N:Th ratios 1.02 to 1.28 were prepared by equilibration of measured amounts of Th powder and N_2 at 1000°. X-Ray diffraction powder patterns of samples contained lines corresponding to a mixture of ThN and Th_3N_4. When Th powder was equilibrated at 1000° with an excess of N_2 at selected pressures, 0.004 to 2 atm, the final N:Th ratios were found to be 1.33 ± 0.02. X-Ray diffraction powder patterns of samples contained only the lines corresponding to pure Th_3N_4. Thus, no significant deviation from stoichiometric composition was detected for the Th_3N_4 phase at 1000°.

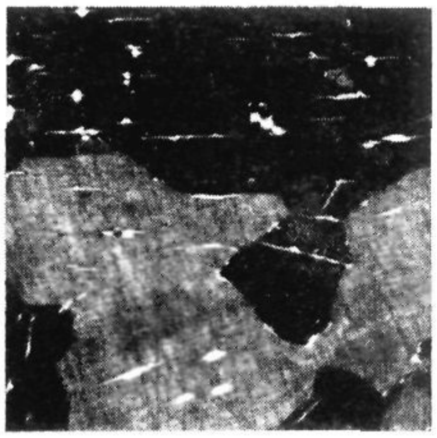

Figure 10. Photomicrograph of Th-rich Th_3N_4. The bulk N:Th ratio 1.28 was prepared by equilibration of dense ThN 20 hr at 1950° in 920 torr of N_2. The light elongated sections are probably ThN which segregated upon cooling (air etched ×300).

At higher temperatures, the composition range of the Th_3N_4 phase broadens. The N:Th ratios of the Th_3N_4 phase which had been equilibrated with N_2 at pressures near that at which decomposition occurs were found to be 1.33 ± 0.03 in 33 torr of N_2 at 1603°, 1.31 in 255 torr of N_2 at 1760°, and 1.28 in 920 torr of N_2 at 1960°. The respective products contained 0.34, 0.18, and 0.46% oxygen by analysis. The X-ray diffraction powder patterns correspond to that of pure rhombohedral Th_3N_4 phase with the hexagonal lattice parameters $a_0 = 3.869 \pm 0.002$ and $c_0 = 27.40 \pm 0.02$ A. Microscopically, the last two products contained 1 to 3 vol. % ThN which had segregated during cooling. The Th-rich Th_3N_4 phase boundary shown in Figure 1 is based upon these results. A photomicrograph of a typical Th-rich Th_3N_4 specimen, after it was cooled from 1960°, is shown in Figure 10.

Discussion

Crystal-bar Th was observed to melt at 1754 ± 15° in agreement with the values reported by Chiotti and Adams, quoted in a review of Th metallurgy.[13] The fcc–bcc transition in crystal-bar Th was observed to occur over a 60° temperature range, 1335 to 1395°, at a 2°/sec rate of temperature change. The published values[13–17] for the transition temperature fall in this range. The use of higher rates of temperature change (up to 12°/sec) had only a small effect on the range of temperatures over which the transition occurred. Therefore, it seems probable that temperature gradients are not the major cause for the observed temperature range. Hysteresis and/or impurities may have contributed significantly to the observed temperature range of transition. Because the transition did not occur isothermally under our experimental conditions and because nitrogen is a likely contaminant which could raise the observed temperature of transition, the value for the polymorphic transition in pure Th is suggested to lie in the lower part of the stated temperature range.

Gerds and Mallett[9] have reported the solubility of nitrogen in Th (845 to 1490°). They found that the solubility increases with temperature to 6 at. % at 1490°. We have found that the solubility becomes even greater at higher temperatures, *viz.*, 8 at. % (N:Th ratio 0.09) in solid Th at 1800°. The precipitation of ThN from and the dissolution of ThN in solid Th is rapid above 1300°, and the associated thermal effects can be detected by thermal analysis.

The steady-state sublimation compositions were determined by heating ThN phases *in vacuo* (less than 10^{-6} torr) with continuous pumping for extended periods of time with up to 10% weight loss by vaporization. The final compositions were found to vary from the N:Th ratio 0.99 at 1537° to 0.88 at 1930°. The observed rate of sublimation was relatively slow and, under these conditions, it is not easy to demonstrate unambiguously that a steady-state sublimation was achieved. The principal difficulty of ensuring a steady-state stems from the imperfect vacuum (imposed by the limitations of the pumping system) in which the specimens were vaporized. Because of the low but finite pressure of gases prevailing in the vacuum chamber, the heated specimens were constantly exposed to (1) a source of contamination, particularly oxygen pickup, and to (2) a finite N_2 pressure. The solubility of oxygen in ThN is not known. Thus, oxygen contamination introduces an uncertainty because it may dissolve in the ThN phase and thereby alter the final N:Th ratio, whereas the N:Th ratios listed in Table I are calculated by assuming all the oxygen was present as a second phase, *viz.*, ThO_2. The variation of the ThN lattice parameters given in Table I suggests that some oxygen dissolution may have indeed occurred, but X-ray diffraction powder patterns showed that at least part of the oxygen in the quenched phases was present as the second-phase ThO_2. The presence of N_2 could affect the composition of the ThN phase by virtue of mass action. The gas present in the heating chamber as the ThN specimens were sublimed was probably predominantly N_2 at a pressure approximately equal to that indicated by the vacuum gauge, 1×10^{-6} torr or less. At a given temperature, if the N_2 pressure is allowed to exceed that characteristic of the congruently subliming ThN phase, one may expect the N:Th ratio of the condensed phase to shift to higher values. For our experimental conditions, the shift in the N:Th ratio is estimated to be significant at temperatures up to 1650°.

Two necessary conditions for equilibrium were realized: (1) after a sufficiently long time the compositions of specimens sublimed at a fixed temperature for different periods of time were the same, and (2) the final compositions at a fixed temperature were assumed by specimens that were initially richer in nitrogen and by specimens that were initially richer in Th. Thus, it is concluded that the final compositions correspond to that of an equilibrium state and, as shown in Figure 1, represent points within the boundaries of the ThN phase.

The steady-state sublimation compositions fall in the ThN phase region (1537 to 1930°) very near the Th-rich phase boundary in a fashion similar to that of the UN congruent sublimation compositions.[18] When

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U-rich UN was cooled from the retrograde region, liquid U precipitated rapidly and only a portion was retained within UN grains. Similarly, when Th-rich ThN was quenched from temperatures 1870 to 2000°, liquid Th precipitated rapidly, but precipitation of solid Th was slower and it could be resolved optically only after the specimens were annealed at temperatures 1200 to 1450°. Therefore, in contrast to the experimental results obtained with the UN phase, quantitative microscopic data could be obtained for the Th-rich ThN phase boundary. The microscopic and the congruent sublimation results are consistent as shown in Figure 1.

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Ranges of Composition of the Th_2N_2O and ThO_2 Phases Equilibrated with Different Nitrogen (Plus Oxygen) Atmospheres[1]

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Abstract: The Th_3N_4, Th_2N_2O, and ThO_2 phases were equilibrated with N_2 at different pressures and selected temperatures between 1600 and 2000°. An appreciable homogeneity range in the Th_2N_2O and ThO_2 phases was revealed by microscopic examination of the cooled products. The compositions of all the phases and phase mixtures were found to be describable by the single formula $ThN_{4/3-(2z/3)}O_z$, where z is the composition variable ranging in value from 0 to 2. Accordingly, the elements in these phases exhibit valences identical with those of the ions Th^{4+}, N^{3-}, and O^{2-}.

Measurements of the electrical conductivity of ThO_2[2] and emf measurements with ThO_2[3] as an electrolyte indicate that ThO_2 is substantially ionic. When ThO_2 crystals are doped with lower valent cations, *e.g.*, La^{3+}, anion vacancies are formed accompanied by a diminished crystal density[4] and an enhanced electrical conductivity.[2,5] In principle, anion vacancies may also be formed by incorporating higher valent anions such as N^{3-} into the ThO_2 anion sublattice. In what follows, some conditions are described under which the oxygen atoms in the ThO_2 phase are replaced by nitrogen atoms. As the N:O ratio is increased, the hexagonal Th_2N_2O and, ultimately, the rhombohedral Th_3N_4 phases are formed.[6] The existence of an appreciable composition range in the Th_2N_2O and ThO_2 phases is established microscopically. Under the experimental conditions, the compositions of the Th_3N_4, Th_2N_2O, and ThO_2 phases and phase mixtures equilibrated under a variety of conditions fall on a plane in the Th–N–O phase diagram, and these compositions conform to those required for ionic valences.

Experimental Section

Procedure. Various mixtures of Th + ThN + ThO_2 (3 to 50 mole % Th as ThO_2) were made by adding weighed quantities of ThO_2 to known amounts of Th + ThN powders that had been prepared by a method previously described.[7] Each mixture was pressed into a 3-g cylinder 6 mm in diameter, sintered *in vacuo*, and allowed to react with N_2 at selected pressures (up to 2 atm) and temperatures (800 to 2000°) in a tungsten crucible.

The products were analyzed for Th by ignition of samples to ThO_2 in air at 800°. For specimens that contained 25 mole % ThO_2 or less, the O:Th ratio of the product was taken to be the same as that of the original mixture; nitrogen was computed by difference. The N:Th ratios obtained in this way were reproducible within ±0.03. Specimens that were prepared from mixtures with more than 25 mole % ThO_2 suffered an appreciable loss of oxygen when heated to 2000°. This was evident because of the erosion of the tungsten crucible. Thus, the difference method described above is not a dependable method for computing the oxygen and nitrogen contents of the products with more than 25 mole % ThO_2. Additional information on the compositions of products was inferred from microscopic examinations as described below. Lattice parameters were determined from high-angle lines in photographs of X-ray diffraction powder patterns taken with Ni-filtered Cu Kα radiation in a camera 115 mm in diameter.

Results

The mixtures that were heated in the temperature range 800 to 1200° did not equilibrate, and X-ray diffraction powder patterns of samples revealed the presence of complex mixtures of Th_3N_4, ThO_2, and Th_2N_2O phases in the products. The mixtures that were heated in the temperature range 1550 to 2000° reached equilibrium in the N_2 atmosphere within 1 day. Of the equilibrated mixtures, those containing 25 ± 2 mole % ThO_2 exhibited powder diffraction patterns of only the hexagonal Th_2N_2O phase with $a_0 = 3.883 \pm 0.001$ and $c_0 = 6.187 \pm 0.002$ A, in agreement with that reported

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