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METALS AND CERAMICS DIVISION

THORIUM CERAMICS DATA MANUAL

Volume II – Nitrides

Revised

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Volume II. Nitrides

ABSTRACT

Physical, chemical, and mechanical properties of thorium nitrides, alone and in combination with other nitrides and other thorium compounds, are collected from the literature through January 1973 (51 references). The thorium-nitrogen phase equilibrium is reviewed. Although mechanical property data are still sparse, recent physical and chemical characterization of ThN has confirmed its high metallic conductivity, furnished detail on hydrolysis and oxidation, and expanded the knowledge of the (Th,U)N and Th(C,N) systems.

This volume will include the following divisions: system information, thorium mononitride systems, and Th_3N_4 systems. The carbonitrides that are substitution products of the mononitride will be covered with it. The oxynitride and other complex compounds are covered under Th_3N_4 systems.

SYSTEM INFORMATION

The thorium-nitrogen phase diagram, taken from Benz *et al.*,[1] is shown in Fig. 1. The only stable compounds shown are ThN and Th_3N_4. The reported[2,3] Th_2N_3 has been identified[4] as the oxynitride Th_2N_2O. This compound is formed from heating ThN and ThO_2 in nitrogen. The high-temperature homogeneity range of ThN is much less than indicated by Fig. 1. Reexamination of the phase boundaries at the same laboratory[5,6] has narrowed the range: the thorium-rich limit is at least 0.975, and the nitrogen-rich limit is stoichiometric. The nitrogen pressure in equilibrium with both liquid thorium and ThN is reported by Olson and Mulford[7] over the range 2416 to 2790°C to be

$$\log p\,(\mathrm{atm}) = 8.086 - 33{,}224/T + 0.958 \times 10^{-17} T^5 ,$$

or

$$\log p\,(\mathrm{N/m^2}) = 13.092 - 33{,}224/T + 0.958 \times 10^{-17} T^5 ,$$

where T is in °K. Oxygen contamination greatly increases this pressure. The equilibrium nitrogen pressure over ThN and Th_3N_4, measured by several investigators, is shown in Fig. 2. The disagreement is likely due to carbon contamination, as expected from dissolved carbon lowering the activity of ThN, shifting the equilibrium to higher nitrogen pressure in

$$Th_3N_4 \rightleftharpoons 3ThN + {}^{1}\!/_{2}N_2 .$$

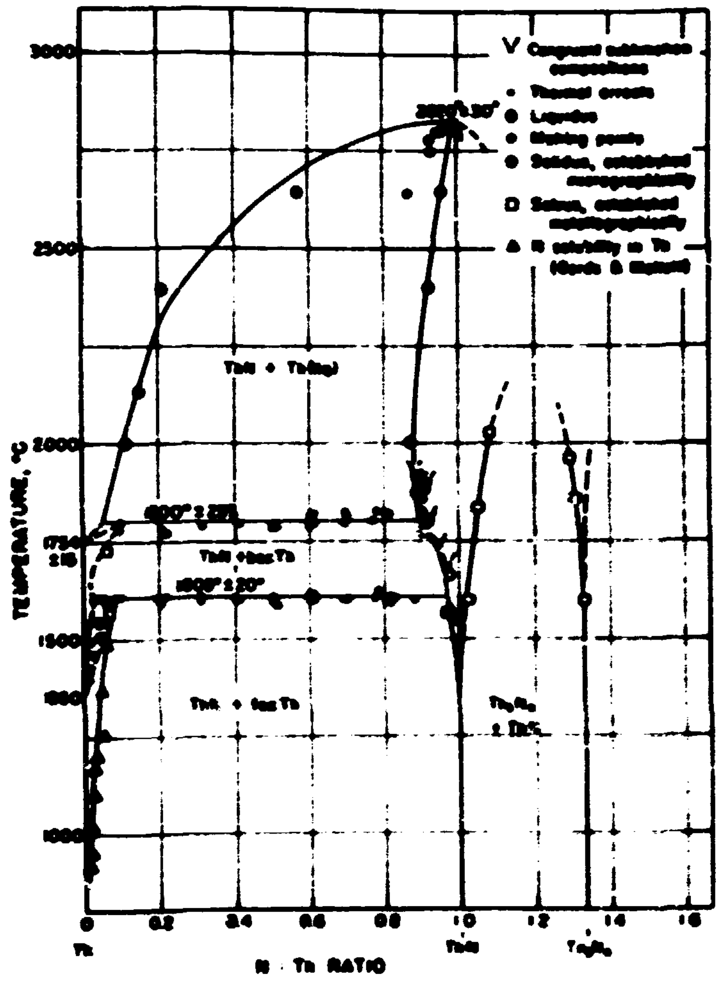

Fig. 1. The Thorium-Nitrogen Phase Diagram. From R. Benz, C. G. Hoffman, and G. N. Rupert.[1] Copyright by the American Chemical Society and reprinted with permission.

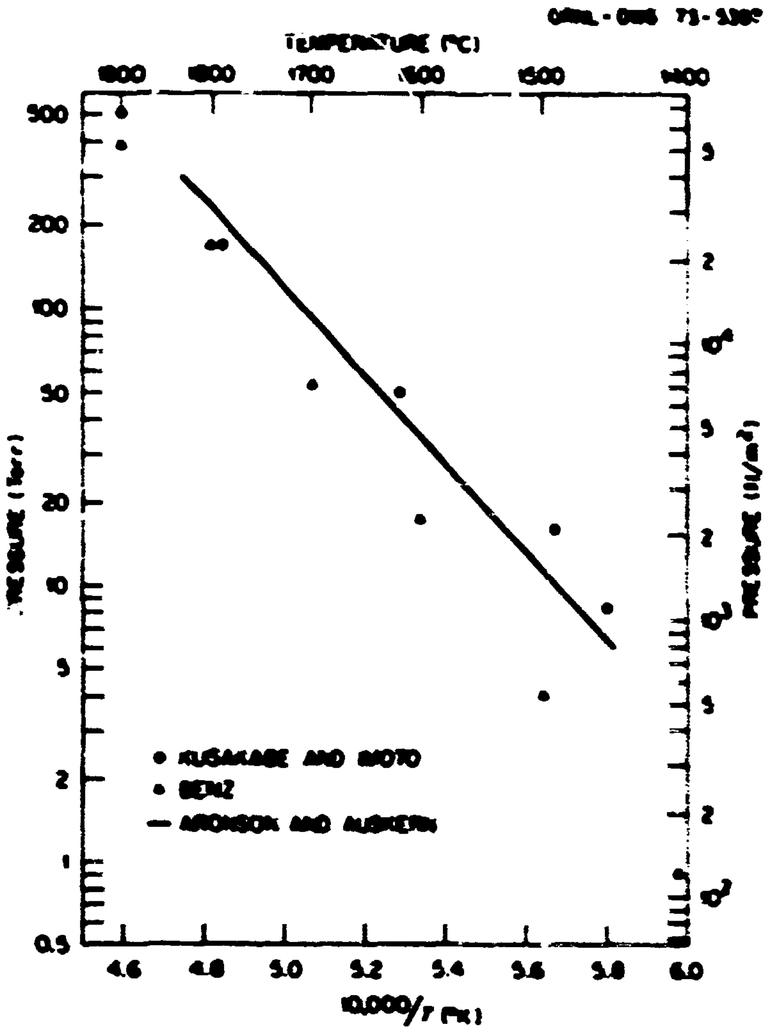

Fig. 2. Nitrogen Pressures over ThN-Th_3N_4, as measured by Aronson and Auskern,[8] Benz,[9] and Kusakabe and Imoto.[10]

The increase in dissociation pressure in the presence of carbon has been verified experimentally by Benz.[9]

THORIUM MONONITRIDE SYSTEMS

A. Thorium Mononitride

1. Composition

The thorium-rich boundary of the ThN phase was found by Benz[5] at a nitrogen-to-thorium atom ratio of 0.975 ± 0.01 at 2000 and 2100°C. Benz and Troxel[6] regard that ratio as a lower bound and indicate that the nitrogen-rich limit is the stoichiometric ratio.

2. Preparation

Thorium mononitride is generally made as powder from the hydride or metal (usually powdered by hydriding and dehydriding) by heating in nitrogen or from the hydride and ammonia. Synthesis below 1000°C gives Th_3N_4; this is decomposed to ThN at higher temperatures. Benz *et al.*[5] prepared specimens by cold and hot pressing. Olson and Mulford[7] induction melted thorium under 2 atm N_2 at 2000°C to get ThN ingots. Weaver[11] prepared dense ThN specimens by zone melting thorium rods in 1.3 atm N_2. He found the porosity was too great in pressed and sintered samples and too nonuniform in arc-cast samples for measurement of thermal and electrical conductivity.

3. Crystal Properties

Structure. Face-centered cubic NaCl type.

Lattice Parameter and Thermal Expansion. Values of the room-temperature lattice parameter of carefully prepared ThN range from 5.155 to 5.162 Å. Most investigators[5,7,12,13] report close to 5.159. The value most precisely reported is 5.16190 ± 0.00015 by Venard *et al.*[14] Measurements to 900°C by Street and Waters[12] are shown in Fig. 3; they derive a mean coefficient of expansion of (7.39 ± 0.042) × 10^{-6}/°C over the range measured. Aronson *et al.*[13] made x-ray diffraction measurements over the range 800 to 1300°C; Fig. 4 compares their expansion values for ThN and some other thorium compounds studied in the same work. The coefficient of expansion of ThN corresponding to these results is 8.2 × 10^{-6}/°C over the range 800 to 1300°C. The data of Aronson *et al.* and Street and Waters agree reasonably well in the region of overlap. Lattice parameters measured up to 2300°C in a study[15] of the Th-N-C system are presented with those of Th(C,N) in Section F3.

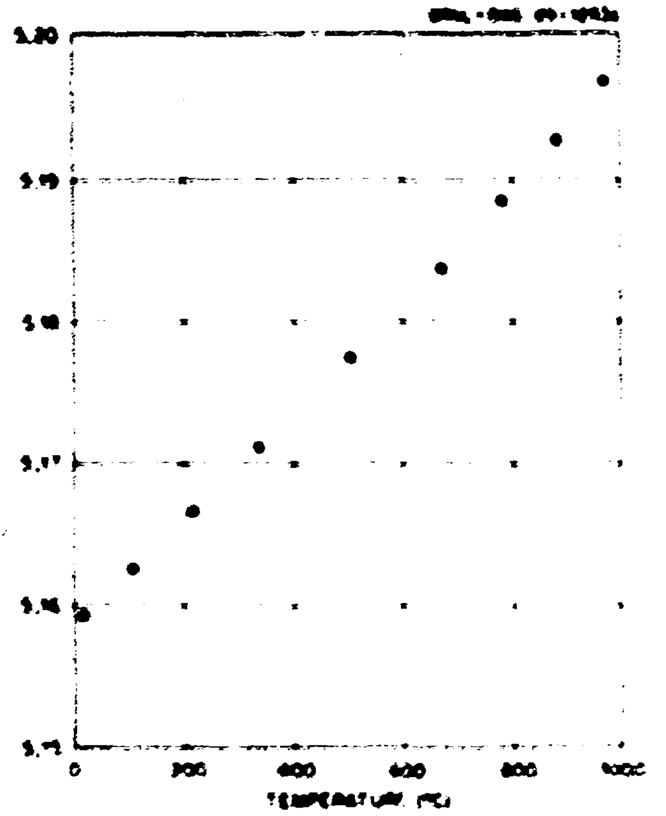

Fig. 3. Temperature Variation of the Lattice Parameter of ThN. Based on Street and Waters.[12]

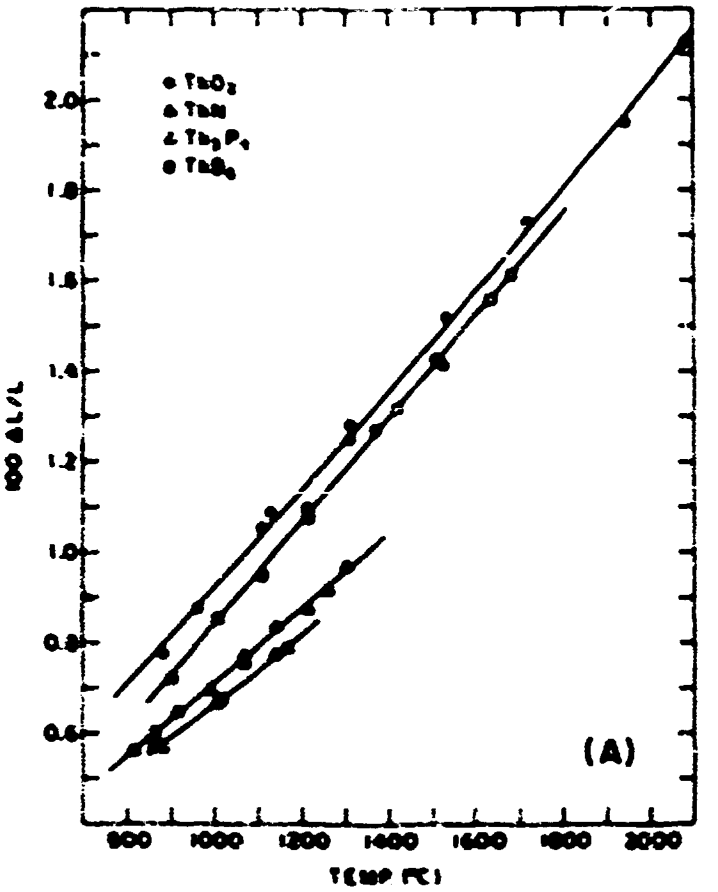

Fig. 4. Thermal Expansion of ThN. Copied from S. Aronson *et al.*[13] with permission of the American Ceramic Society. Similarly measured expansions of other thorium compounds are included for comparison.

Color. Golden yellow,[7] green-yellow.[16]

Density. The density corresponding to a_0 = 5.159 is 11.901 g/cm^3.

4. Thermodynamic Properties

The specific heat from 3 to 9°K was found by de Novion and Costa[17,18] to be given by

$$C_v/T = 3.12 + 0.0847T^2 \text{ mJ mole}^{-1} (°K)^{-2} .$$

Values by Danan *et al.*[19] to 300°K are given in Table 1. From these specific heat measurements Danan *et al.* calculated the following standard functions for ThN at 298.15°K.

$$S = 56.0 \pm 1.0 \text{ J mole}^{-1} (°K)^{-1}$$

$$= 13.4 \pm 0.2 \text{ cal mole}^{-1} (°K)^{-1} ;$$

$$H - H_0 = 8450 \pm 150 \text{ J/mole}$$

$$= 2040 \pm 35 \text{ cal/mole} ;$$

$$-(G - H_0) = 8250 \pm 150 \text{ J/mole}$$

$$= 1970 \pm 35 \text{ cal/mole} .$$

Table 1. Heat Capacity of Thorium Mononitride From Danan *et al.*[19]

Temperature (°K)	C_p, Heat Capacity (J mole^{-1} °K^{-1})	C_p, Heat Capacity (cal mole^{-1} °K^{-1})
10	0.138	0.033
15	0.488	0.117
20	1.38	0.330
25	2.79	0.667
30	4.60	1.10
40	8.25	1.97
50	11.5	2.75
60	14.35	3.43
70	16.95	4.05
80	19.4	4.64
90	21.7	5.19
100	23.9	5.72
120	27.8	6.65
140	31.2	7.46
160	34.1	8.15
180	36.6	8.75
200	38.7	9.25
220	40.5	9.68
240	42.0	10.03
260	43.2	10.32
280	44.75	10.58
300	45.1	10.78

From their measurements of the decomposition pressure of Th_3N_4, Aronson and Auskern[5] and Kusakabe and Imoto[10] have derived the following functions of formation at 298.15°K:

	A and A[5]	K and I[10]
ΔH_f°, kJ/mole	379	390
kcal/mole	90.6	93.1
ΔS_f°, J mole^{-1} (°K)$^{-1}$	98.3	105
cal mole^{-1} (°K)$^{-1}$	23.5	25.1

Gingerich[20] estimates the heat of sublimation as 203.1 ± 10 kcal/mole, or 849 ± 42 kJ/mole. Venard and Spruiell[21] estimate the standard free energy of formation to be −51.1 kcal/mole, or −214 kJ/mole, at 1000°C.

5. Change of State

Thorium mononitride melts congruently under sufficient nitrogen pressure. Reported melting points are 2820 ± 30°C under 2 atm (2 × 10^5 N/m^2)N_2 by Benz *et al.*,[1] 2820 ± 35 under 2.6 atm N_2 by Benz,[5] and 2790 ± 30°C at slightly under 1 atm N_2 by Olson and Mulford.[7] The melting point is lowered by impurities, particularly oxide,[1,7] which is almost always present in

ThN. Blum and Guinet[22] demonstrated eutectic formation between ThN and ThO_2, and Benz[23] showed that under at least 100 torr N_2 the eutectic occurs at 19 mole % ThO_2 and 2660°C. Also, melting under too little nitrogen lowers the melting point with loss of nitrogen.[1] Chiotti[3] found melting at 2630°C under helium.

Solid-gas equilibria are given under "System Information."

6. Electrical and Magnetic Properties

Auskern and Aronson[16] measured several electrical properties of ThN specimens pressed in vacuum at 5000 psi (35 MN/m^2) and 1275°C and then annealed in vacuum 13 hr at 1800°C to a density of 9.95 g/cm^3. The results are shown in Fig. 5. The second Hall effect specimen was annealed only 4 hr at 1800°C but reached a density of 10.6 g/cm^3.

Weaver[11] reports two sets of electrical resistivity measurements on a specimen of zone-melted ThN. Figure 6 shows his low-temperature results. His high-temperature results over the range 300 to 1300°K are fitted by $0.347 + 0.058144T$ μΩ-cm. In the range of overlap these results are about 10% below those in Fig. 5. Weaver[11] also measured the absolute thermoelectric power of both arc-cast and zone-melted ThN from 80 to 400°K. The variation about zero was slight, less than 1μV/°K, over the range measured.

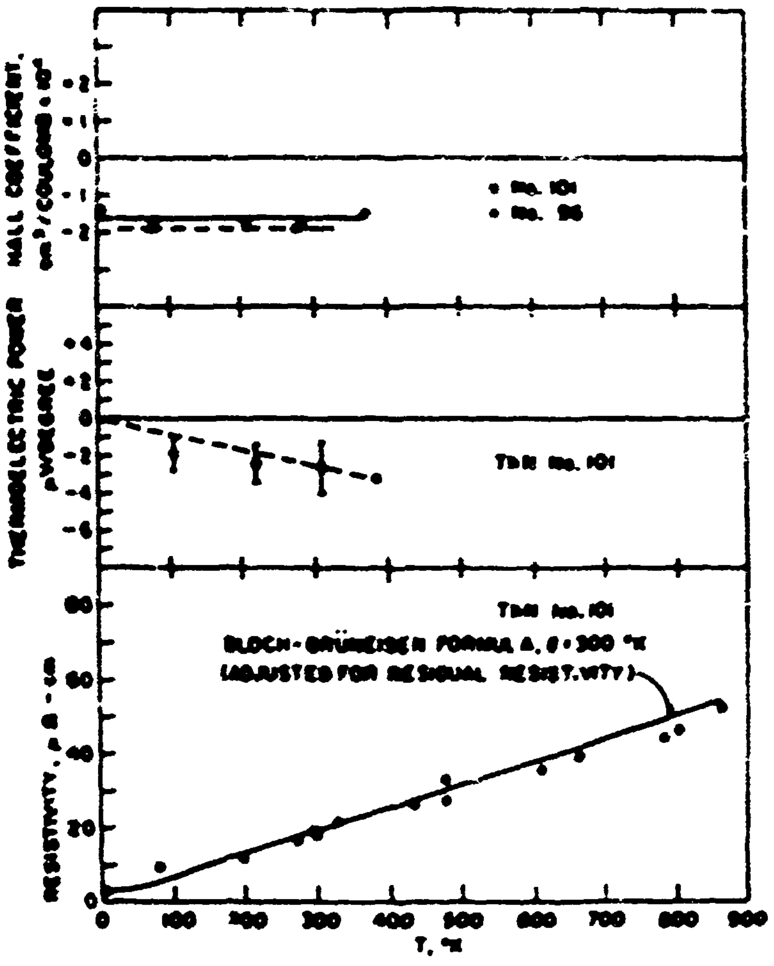

Fig. 5. Hall Coefficient, Thermoelectric Power, and Electrical Resistivity of ThN as Functions of Temperature. Reprinted with permission from A. B. Auskern and S. Aronson,[16] copyright by Pergamon.

Aronson and Auskern[24] measured the magnetic susceptibility of three ThN specimens at 190, 76, and 22°C; values ranged from 1.65 to 1.84 X 10^{-6} emu/g, and the decrease with increasing temperature was less than the difference among specimens. Raphael and de Novion[25] found a susceptibility of 1.42 X 10^{-7} emu/g, constant over the range 4 to 300°K. However, Didchenko and Gortsema[26] found ThN diamagnetic.

Measuring the nuclear magnetic resonance of ^{14}N in ThN, Kuznietz[27] found a positive Knight shift of (10.7 ± 1.5) x 10^{-4}. Giorgi *et al.*[28] found ThN superconducting up to 3.2°K.

7. Heat and Mass Transport

Diffusion. Benz[9] has interpreted the growth rate of ThN scales on liquid thorium in nitrogen in terms of an average interdiffusion coefficient in the ThN phase. His coefficients average 2.3 X 10^{-8} cm^2/sec at 1900°C, 1.7 X 10^{-7} cm^2/sec at 2100°C, and 1.83 X 10^{-6} cm^2/sec at 2400°C. The temperature dependence corresponds to an activation energy of 99.4 ± 30 kcal/mole, or 416 ± 125 kJ/mole.

Thermal Conductivity. Measurements by Weaver[11] on zone-melted specimens are shown in Fig. 7. From these data, electrical resistivity data, and a separation of thermal conductivity into lattice and electronic components, Weaver extrapolated his results to obtain the high-temperature estimate given in Fig. 8.

Emissivity. Kusakabe and Imoto[10] report the following values for emissivity at the wavelength 0.65 μm.

T(°C)	ε_{ThN}
1508	0.900
1566	0.865
1625	0.814
1680	0.790
1740	0.756
1915	0.699

8. Mechanical Properties

No information is available yet.

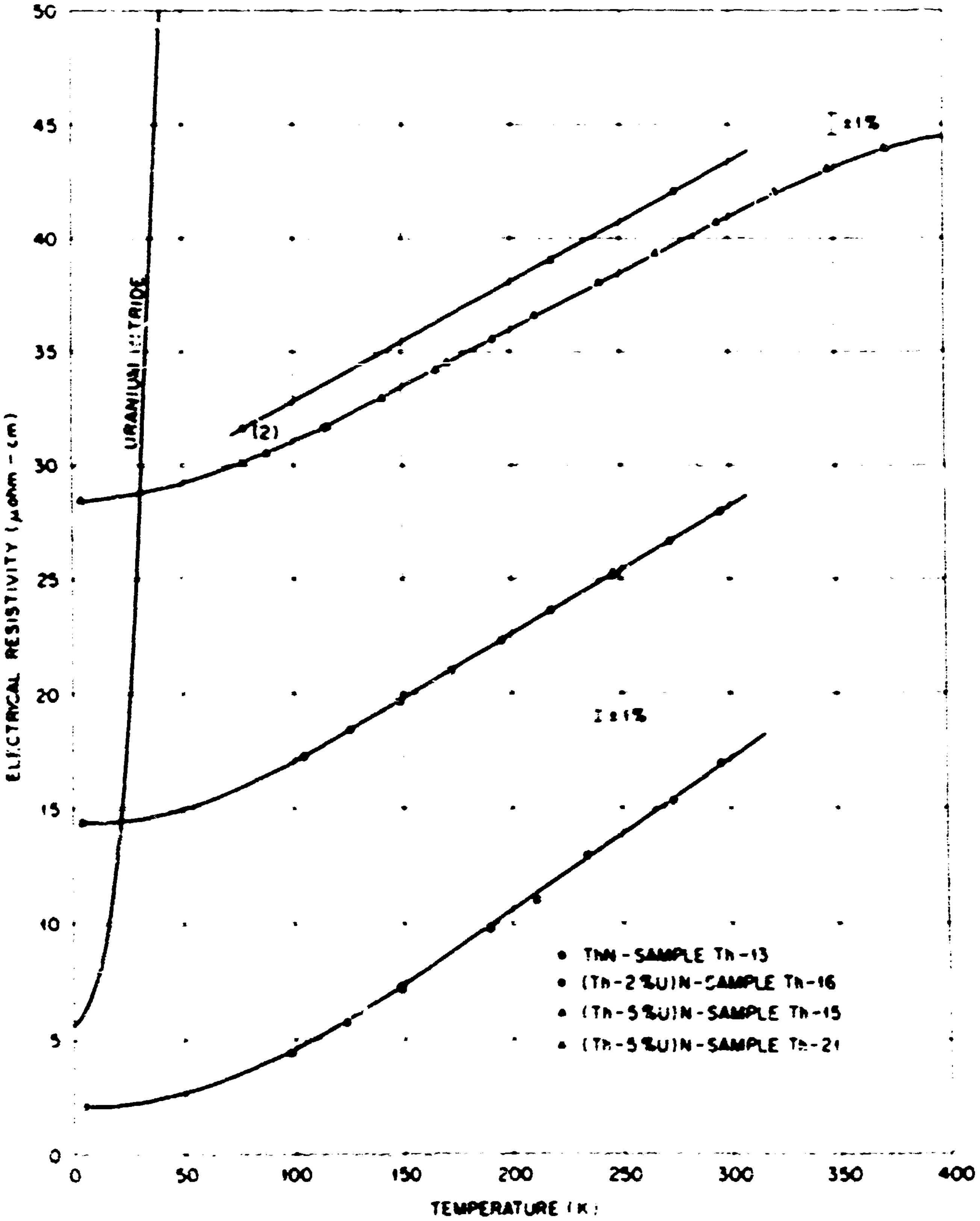

Fig. 8. Electrical Resistivity of ThN, (Th,U)N, and UN. From Weaver.[11]

9. Chemical Properties

Olson and Mulford[7] report that ThN ingots exposed to air acquire a black film within minutes and that the powder reacts readily with air to form ThO_2. Chiotti[3] reports that the powder can be readily handled in air but disintegrates in a short time in moist air and burns vigorously when ignited. Also, ThN reacts with water and is readily attacked by nitric acid.[3] Aronson *et al.*[13] found that above 1300°C, ThN reacted with the residual vapors in a vacuum system at 5×10^{-4} torr (0.07 N/m^2), apparently with gradual substitution of carbon to form ThC and ultimately ThC_2.

Sugihara and Imoto[29] measured the hydrolysis of ThN powder. Their reaction curves shown in Fig. 9 can be fitted by first-order kinetics with an activation

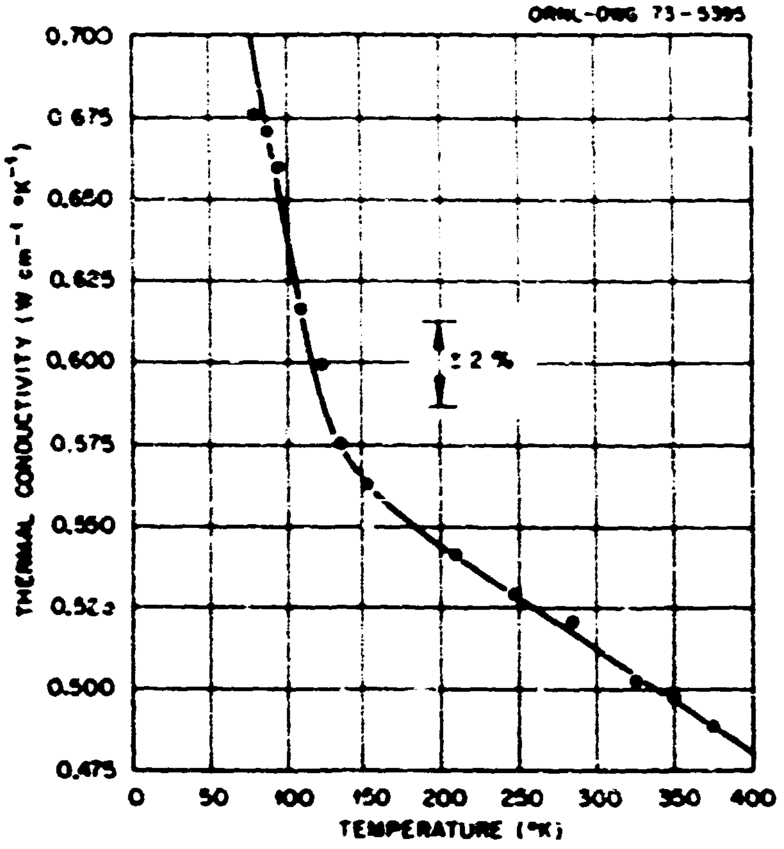

Fig. 7. Thermal Conductivity of ThN. From Weaver.[11]

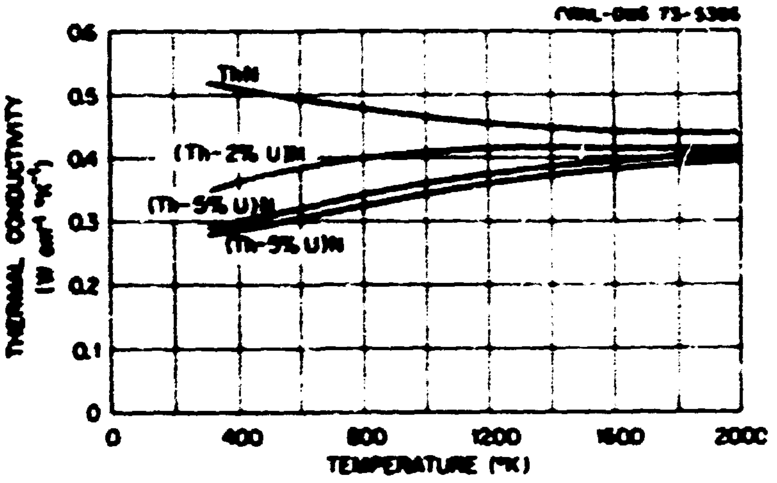

Fig. 8. Thermal Conductivity of ThN and (Th,U)N Extrapolated to High Temperatures. From Weaver.[11]

energy of 15 kcal/mole (63 kJ/mole). The products are hydrogen gas, dissolved ammonia, and ThO_2. When ThN was exposed to water vapor at a heating rate of 5°C/min, ammonia and hydrogen were evolved as shown in Fig. 10.

Ozaki *et al.*[30] found little difference in the oxidation of ThN powder in 0.2 and 1.0 atm O_2. The reaction was about 15% complete in 4 hr at 395°C and 75% at 480°C. The conversion ratio C followed the expression $1 - (1 - C)^{1/3} = kt$ with an activation energy ranging from 16 to 20 kcal/mole (65 to 80 kJ/mole). The powder ignited at 520°C.

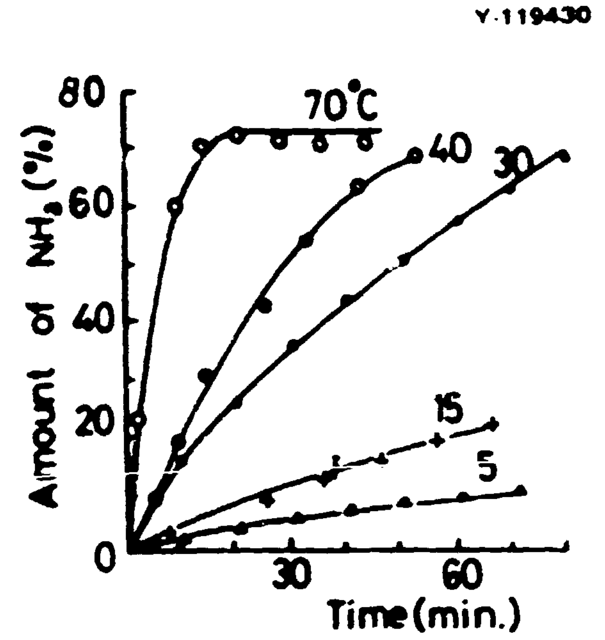

Fig. 9. Hydrolysis of ThN at Various Temperatures. From Sugihara and Imoto.[29]

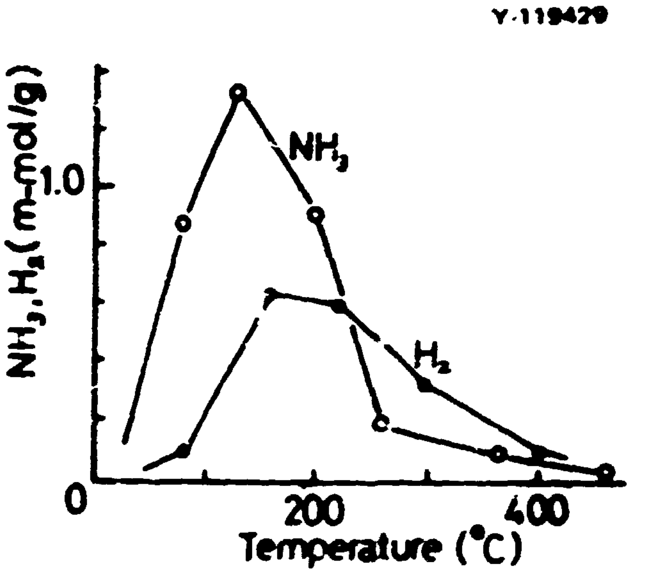

Fig. 10. Gas Evolution during Heating ThN in Water Vapor. From Sugihara and Imoto.[29]

10. Surface Properties

No information is available.

B. Thorium-Uranium Mononitrides

1. Composition

Thorium and uranium mononitrides form a continuous series of solid solutions. Equilibria between the mixed nitride phase and the component metals at 1000°C were determined by Venard and Spruiell.[21]

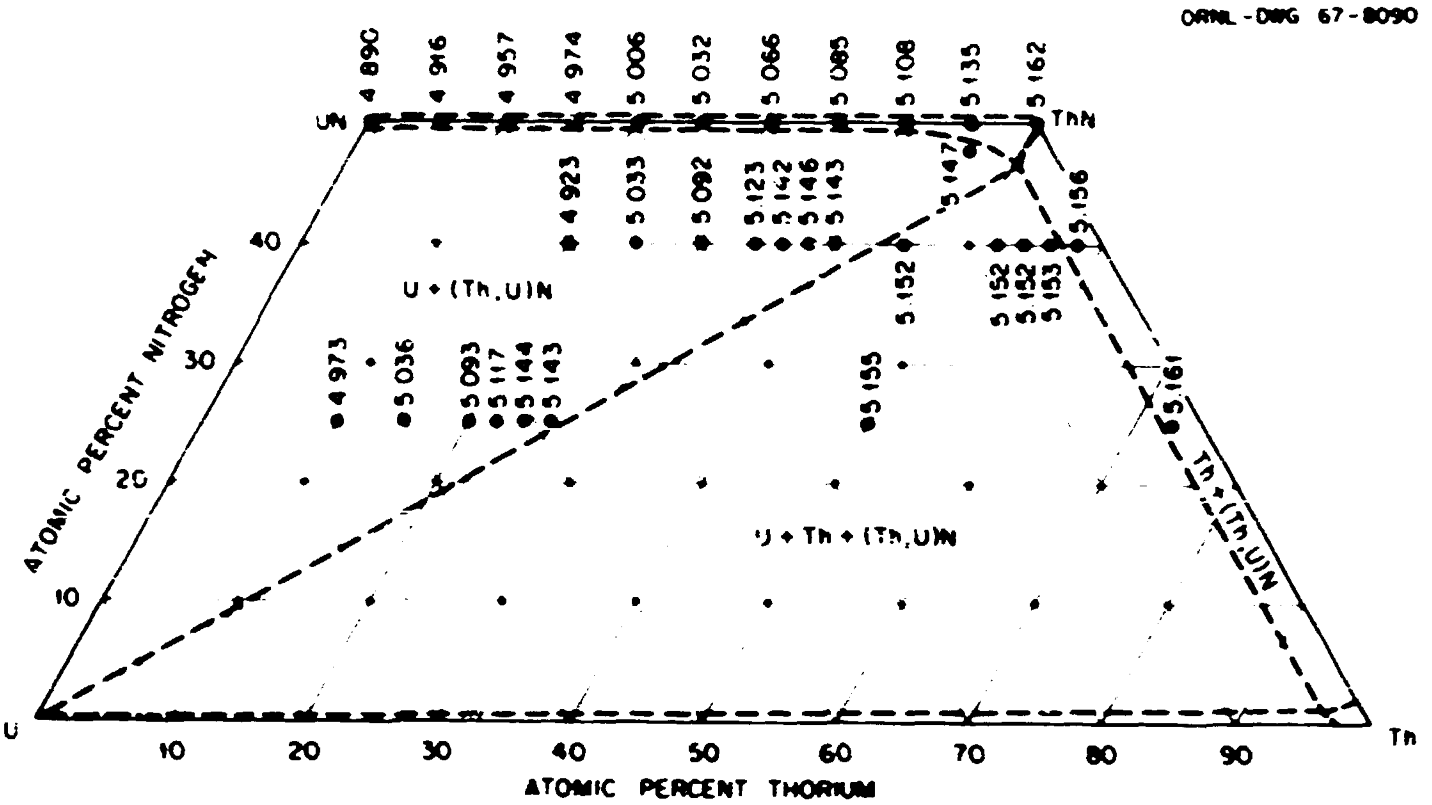

Fig. 11. *Phase Equilibria in the Th-U-N System at 1000°C.* From Venard and Spruiell.[21] Copyright by North-Holland Publishing Company and reproduced with permission. Lattice parameters are shown for (Th,U)N for several overall compositions. Compiler's note: The parameters for the two highest uranium contents at 40 at. % N are quite low for the (Th,U)N compositions that would have to be in equilibrium with metallic uranium to give the overall composition indicated. Very likely these values reflect incomplete equilibration.

Their equilibrium diagram is Fig. 11. The greatest hypostoichiometry was for the composition $Th_{0.944}U_{0.056}N_{0.866}$, which exists at 1000°C in equilibrium with both metals. No information was obtained on the nitrogen-rich composition limits.

2. Preparation

Coarse (Th,U)N powders were prepared from arc-melted thorium-uranium alloys by two hydride-dehydride cycles, reaction with flowing nitrogen at 400 to 800°C, and decomposition to (Th,U)N at 1450 to 1500°C under vacuum.[21] To avoid the heterogeneous thorium-uranium alloys as starting materials, de Novion[17] pressed and sintered mixed 10-μm ThN and UN powders. Despite three cycles of crushing, pressing, and sintering at 1600°C, the specimens were not homogeneous as determined by x-ray diffraction.

Weaver[11] prepared ThN specimens containing up to 5% UN by zone melting thorium-uranium alloys under 1.3 atm N_2. Uranium-rich specimens were difficult to obtain this way because of their lower melting points and concomitant slower diffusion. Material prepared by arc melting the metallic alloys under nitrogen contained porosity that was too great and too irregular to permit transport property measurements that could be corrected for porosity.

3. Crystal Properties

Lattice parameters for (Th,U)N were determined by Venard *et al.*[15] and are shown in Table 2. "Agreement with Vegard's law is quite good."[15]

Table 2. Lattice Parameters of (Th,U)N

From Venard *et al.*[15]

Mole % ThN	Lattice Parameter (Å)
0	4.89034 ± 0.00025
10.24	4.91561 ± 0.00015
20.40	4.95712 ± 0.00086
30.54	4.97434 ± 0.00079
40.60	5.00608 ± 0.00105
50.00	5.03219 ± 0.00043
60.64	5.06339 ± 0.00115
70.56	5.08531 ± 0.00080
80.38	5.10826 ± 0.00019
90.24	5.13461 ± 0.00046
100.00	5.16190 ± 0.00015

4. Thermodynamic Properties

No information is available.

Table 3. Smoothed Values of Absolute Thermoelectric Power of (Th,U)N
From Weaver[11]

Temperature (°K)	Thermoelectric Power (μV/°K)			
	Arc Melted		Zone Melted	
	(Th-1% U)N	(Th-5% U)N	(Th-2% U)N	(Th-5% U)N
80			3.8	5.3
90	1.4	5.9	4.2	5.6
100	1.5	6.0	4.6	5.8
110	1.6	6.3	4.9	6.1
120	1.8	6.6	5.3	6.5
130	1.9	7.0	5.6	6.8
140	2.0	7.4	6.0	7.2
150	2.1	7.9	6.3	7.5
160	2.2	8.5	6.6	7.9
170	2.3	8.9	6.9	8.3
180	2.4	9.4	7.2	8.8
190	2.5	9.8	7.5	9.2
200	2.6	10.2	7.7	9.6
210	2.7	10.5	7.9	9.9
220	2.7	10.8	8.2	10.2
230	2.8	11.1	8.4	10.5
240	2.8	11.3	8.5	10.6
250	2.8	11.4	8.6	10.8
260	2.7	11.5	8.7	10.9
270	2.7	11.6	8.7	11.0
280	2.5	11.5	8.7	10.9
290	2.3	11.4	8.6	10.8
300	1.9	11.1	8.5	10.6
310	1.7	11.1	8.4	10.5
320	1.7	11.4	8.5	10.7
330	1.8	11.7	8.8	10.9
340	2.1	11.9	9.1	11.1
350	2.4	12.0	9.4	11.2
360	2.6	12.1	9.7	11.3
370	2.7	12.2	9.9	11.4
380	2.8	12.3	10.1	11.4
390	2.8	12.4	10.3	11.4
400	2.7	12.4	10.6	11.4

5. Change of State

No information is available.

6. Electrical and Magnetic Properties

Electrical resistivity measurements by Weaver[11] on zone-melted specimens are given in Fig. 6. His absolute thermoelectric power measurements are listed in Table 3. De Novion[17] measured the magnetic susceptibility from a few degrees Kelvin to room temperature for imperfectly homogenized (Th,U)N. The susceptibility increases regularly with uranium content, except uranium-rich specimens show magnetic ordering at low temperatures. A transformation was observed in $Th_{0.2}U_{0.8}N$ at 32°K; none was observed at 60 mole % UN or less.

7. Heat and Mass Transport

Thermal conductivity measured by Weaver[11] is shown in Fig. 12. His extrapolated values for higher temperatures are shown in Fig. 8.

8. Mechanical Properties

No information is available.

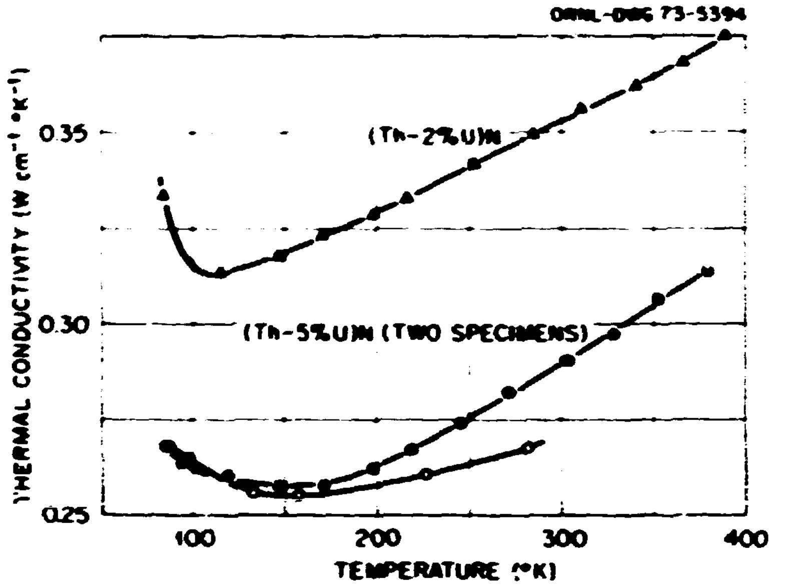

Fig. 12. Thermal Conductivity of (Th,U)N. Measured by Weaver.[11]

9. Chemical Properties

Weaver[11] found that samples of porous arc-cast (Th,U)N left exposed to the air were completely converted to oxide in about two days.

10. Surface Properties

No information is available.

C. Thorium Plutonium Mononitrides

Pardue *et al.*[31] prepared a mononitride from Pu–20% Th, isostatically pressed it at 1540°C and 10,000 psi (70 MN/m^2), and heated it 48 hr in flowing nitrogen at 1720°C. Its lattice parameter was 4.980 ± 0.001 Å, and its evaporation loss was 0.0296 g/cm^2 in 5 hr at 1550°C.

D. Binary Systems with Nonfuel Nitrides

Benz and Zachariasen[32] prepared and determined the crystal structure of the orthorhombic compounds Th_2MnN_3 and Th_2CrN_3. They have respective decomposition pressures of 11 torr N_2 at 1300°C and 1 torr at 1600°C.

E. Ternary and More Complex Systems with Other Nitrides

No information is available.

F. Thorium Carbonitrides

1. Composition

Street and Waters[33] found complete solid solubility between ThC and ThN. As carbon is substituted for nitrogen in ThN, the tolerance of nonmetal vacancies by the lattice increases, permitting an increasing range of hypostoichiometric compositions. This is shown in the ternary phase diagrams of Fig. 13, taken from Benz and Troxel.[6] The lowest temperature of these diagrams (1500°C) is in the range of complete miscibility of ThC and α-thorium, but a small nitrogen content produces a miscibility gap. Also Fig. 13 shows that inclusion of carbon at very high temperatures permits hyperstoichiometry as the range of miscibility of ThC and γ-ThC_2 is approached.

2. Preparation

Carbonitrides have been made by heating cold-pressed pellets of the mixed carbide and nitride at 1600°C (ref. 33) or 2000°C (ref. 5). Hypostoichiometric solid solutions have been made[24,34] by heating mixtures of ThN, thorium, and carbon in vacuum at 1700 to 1800°C. Samples for electrical measurements[34] were hot pressed at 1300°C and 5000 psi (35 MN/m^2) in vacuum and then annealed in vacuum at 1800°C for 5 to 17 hr. Sugihara and Imoto[29] prepared Th(C,N) samples by cold pressing a mixture of ThN and carbon powders and then heating 4 hr in vacuum at 1700 to 1750°C. Benz and Troxel[6] reported that mixtures of ThC and ThN were not completely homogenized in 0.5 hr at 2200°C. Benz and Balog[15] homogenized in vacuum for 1 min at 2100°C, but to achieve uniformity they crushed, pressed, and homogenized three times.

3. Crystal Properties

Street and Waters[33] found linear variation of the lattice parameter with composition from 5.338 Å for ThC to 5.158 Å for ThN. Benz[5] found parameters in agreement with those of Street and Waters; both worked with material close to stoichiometric. For hypostoichiometric materials Auskern and Aronson[34] found agreement with measured parameters and linear interpolation between values for ThN and ThC_x, with *x* chosen to fit the composition. Their values are:

$ThC_{0.778}N_{0.108}$	5.320 Å
$ThC_{0.625}N_{0.275}$	5.288 Å
$ThC_{0.537}N_{0.389}$	5.266 Å
$ThC_{0.461}N_{0.489}$	5.246 Å
$ThC_{0.203}N_{0.738}$	5.197 Å
$ThC_{0.029}N_{0.937}$	5.165 Å

High-temperature lattice parameters for ThC-ThN compositions reported by Benz and Balog[15] are shown

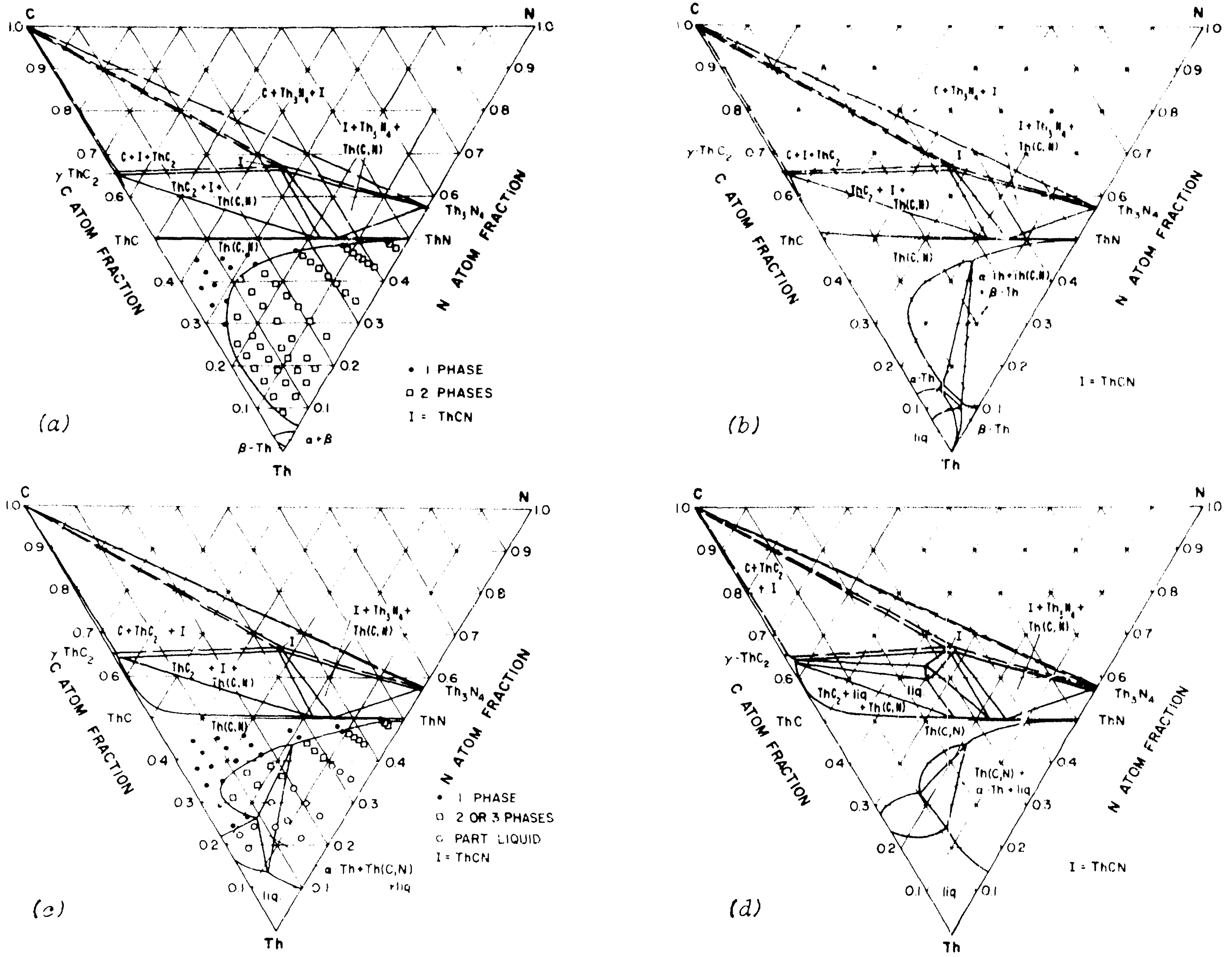

Fig. 13. The Thorium-Carbon-Nitrogen System. (*a*) 1500°C. (*b*) 1715°C. (*c*) 2000°C. (*d*) 2200°C. From Benz and Troxel.[6] Copyright by Academic Press, Inc., and reprinted with permission.

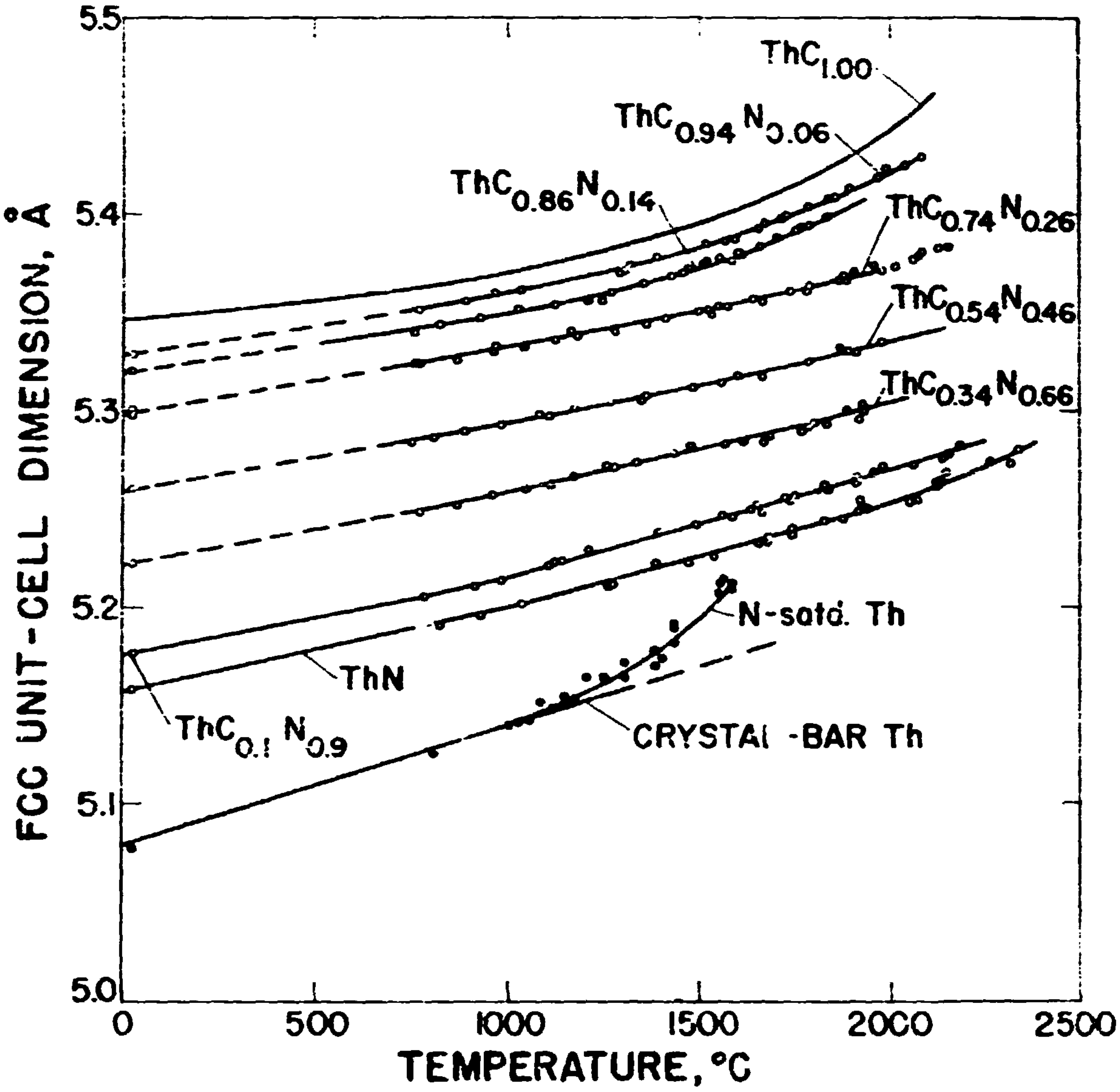

Fig. 14. Lattice Constants of Th(C,N) Compositions. From Benz and Balog.[16] Copyright by Academic Press and reproduced with permission.

in Fig. 14. Their results show agreement with Vegard's law at 1800°C.

4. Thermodynamic Properties

Benz[5] gives the following for the relative internal free energies of mixing of ThC and ThN in the solid and liquid states:

$$\Delta G^{M(s)} = 7.2[X^{(s)}_{\mathrm{ThN}}(T-3090) + X^{(s)}_{\mathrm{ThC}}(T-2770)] + RT[X^{(s)}_{\mathrm{ThN}} \ln X^{(s)}_{\mathrm{ThN}} + X^{(s)}_{\mathrm{ThC}} \ln X^{(s)}_{\mathrm{ThC}}] - (13{,}000 \pm 7{,}000)X^{(s)}_{\mathrm{ThN}}X^{(s)}_{\mathrm{ThC}} \text{ cal/mole}$$

$$= 30[X^{(s)}_{\mathrm{ThN}}(T-3090) + X^{(s)}_{\mathrm{ThC}}(T-2770)] + RT[X^{(s)}_{\mathrm{ThN}} \ln X^{(s)}_{\mathrm{ThN}} + X^{(s)}_{\mathrm{ThC}} \ln X^{(s)}_{\mathrm{ThC}}] - (54{,}000 \pm 29{,}000)X^{(s)}_{\mathrm{ThN}}X^{(s)}_{\mathrm{ThC}} \text{ J/mole;}$$

$$\Delta G^{M(l)} = RT[X^{(l)}_{\mathrm{ThN}} \ln X^{(l)}_{\mathrm{ThN}} + X^{(l)}_{\mathrm{ThC}} \ln X^{(l)}_{\mathrm{ThC}})] - (6{,}600 \pm 7{,}000)X^{(l)}_{\mathrm{ThN}}X^{(l)}_{\mathrm{ThC}} \text{ cal/mole}$$

$$= RT[X^{(l)}_{\mathrm{ThN}} \ln X^{(l)}_{\mathrm{ThN}} + X^{(l)}_{\mathrm{ThC}} \ln X^{(l)}_{\mathrm{ThC}})] - (28{,}000 \pm 29{,}000)X^{(l)}_{\mathrm{ThN}}X^{(l)}_{\mathrm{ThC}} \text{ J/mole ;}$$

the X's are mole fractions.

5. Change of Stat

Melting points and equilibrium nitrogen pressures given by Benz[5] for carbonitride solid solutions are listed in Table 4. Note the maximum.

Table 4. Melting Points of Th(C,N) Solid Solutions From Benz[5]

Composition	Lattice Parameter (Å)[a]	Melting Point (°C)[b]	Nitrogen Pressure (atm)	Nitrogen Pressure (N/m²)
				× 10⁵
$ThC_{0.97}$	5.346	2500		
$ThC_{0.80}N_{0.21}$	5.310	2670	0.01 ± 0.005	0.01
$ThC_{0.70}N_{0.29}$	5.305	2720	0.05 ± 0.01	0.05
$ThC_{0.57}N_{0.39}$	5.276	2810	0.18 ± 0.03	0.18
$ThC_{0.48}N_{0.49}$	5.262	2850	0.30 ± 0.04	0.30
$ThC_{0.47}N_{0.47}$	5.241	2910	(1.5)[c]	(1.5)[c]
$ThC_{0.34}N_{0.56}$	5.225	2910	(2.0)[c]	(2.0)[c]
$ThC_{0.28}N_{0.63}$	5.220	2920	(2.0)[c]	(2.0)[c]
$ThC_{0.1}N_{0.9}$[d]	5.188	2875		
$ThN_{1.00}$	5.158	2820	2.6 ± 0.6	2.6

[a] ±0.001 Å.

[b] ±35°C.

[c] Probably below true equilibrium pressure, since the composition, measured after melting, shows loss of nitrogen.

[d] Nominal.

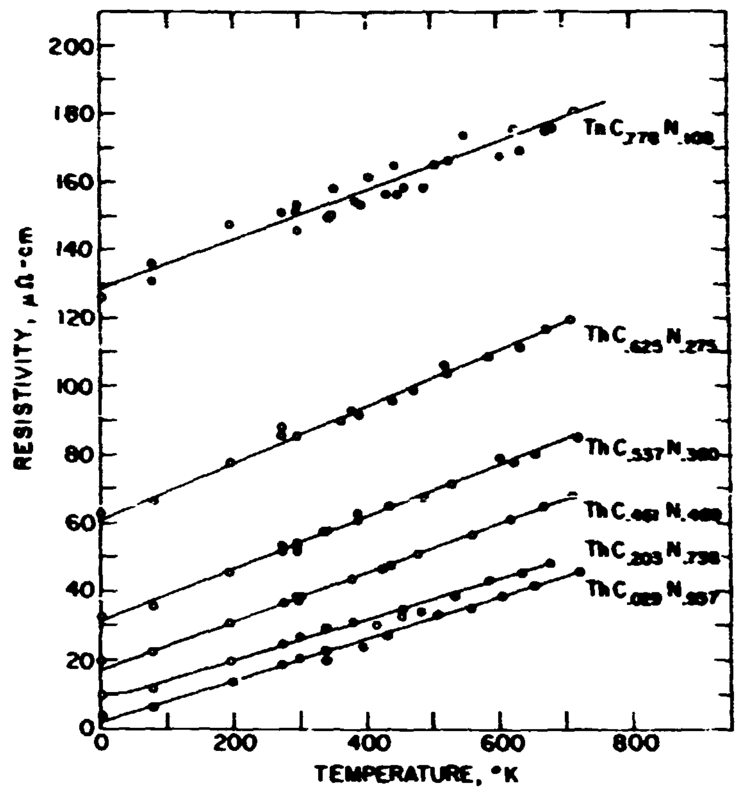

Fig. 15. Electrical Resistivity of Thorium Carbonitrides. Values have been corrected to zero porosity by multiplying by (1 − P)/(1 + P/2), where P is the pore fraction. Copied from A. B. Auskern and S. Aronson[34] with permission; copyright by American Institute of Physics.

6. Electrical and Magnetic Properties

Several electrical properties of hypostoichiometric carbonitrides were measured by Auskern and Aronson.[34] The resistivity, Hall coefficient, and thermoelectric power are given in Figs. 15–17 respectively. The same authors' magnetic susceptibility values[24] are listed in Table 5.

Giorgi et al.[28] found thorium carbonitrides superconducting, with the transition temperature a maximum of 5.8°K at 78% ThC, dropping off sharply with increasing carbide content, and dropping off gradually to about 3°K at 50% ThC.

7. Heat and Mass Transport

Benz[9] has interpreted the growth rates of (Th,U)N scales on thorium-carbon alloys in nitrogen in terms of a composition-average interdiffusion coefficient in the ThN phase. His coefficients average 5.6 × 10^{-11} cm²/sec at 1400°C, 1.0 × 10^{-10} cm²/sec at 1500°C, 6.7 × 10^{-10} cm²/sec at 1600°C, 2.9 × 10^{-9} cm²/sec at 1700°C, 4.9 × 10^{-9} cm²/sec at 1750°C, and 6.9 × 10^{-9} cm²/sec at 1800°C. These values are fitted quite well by an Arrhenius extrapolation of the higher temperature values for ThN cited from the same work in Section A7.

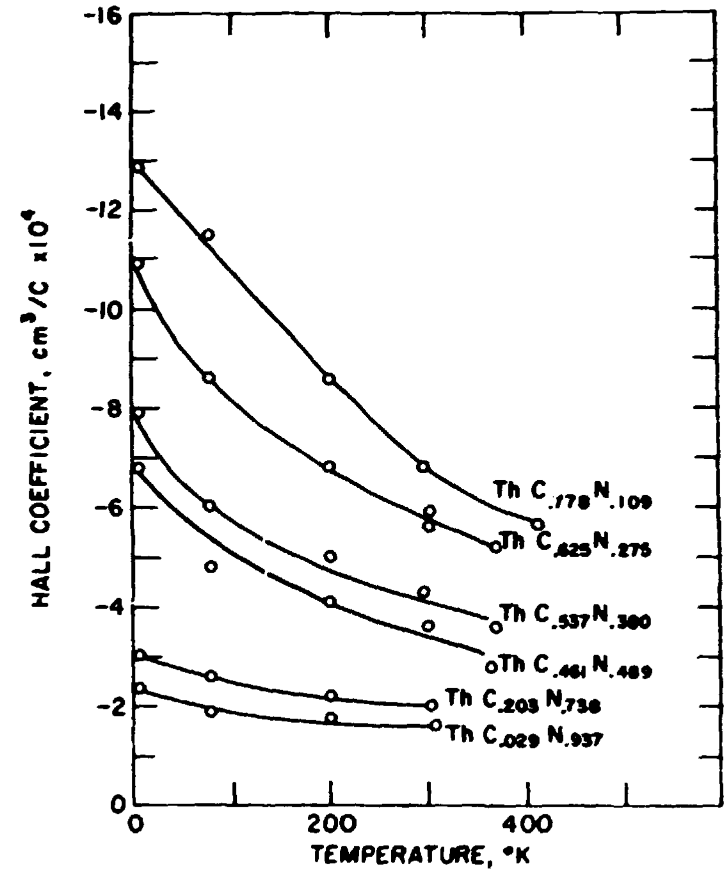

Fig. 16. Hall Coefficient of Thorium Carbontrides. Values have been corrected to zero porosity by multiplying by 1 − P, where P is the pore fraction. Copied from A. B. Auskern and S. Aronson[34] with permission; copyright by American Institute of Physics.

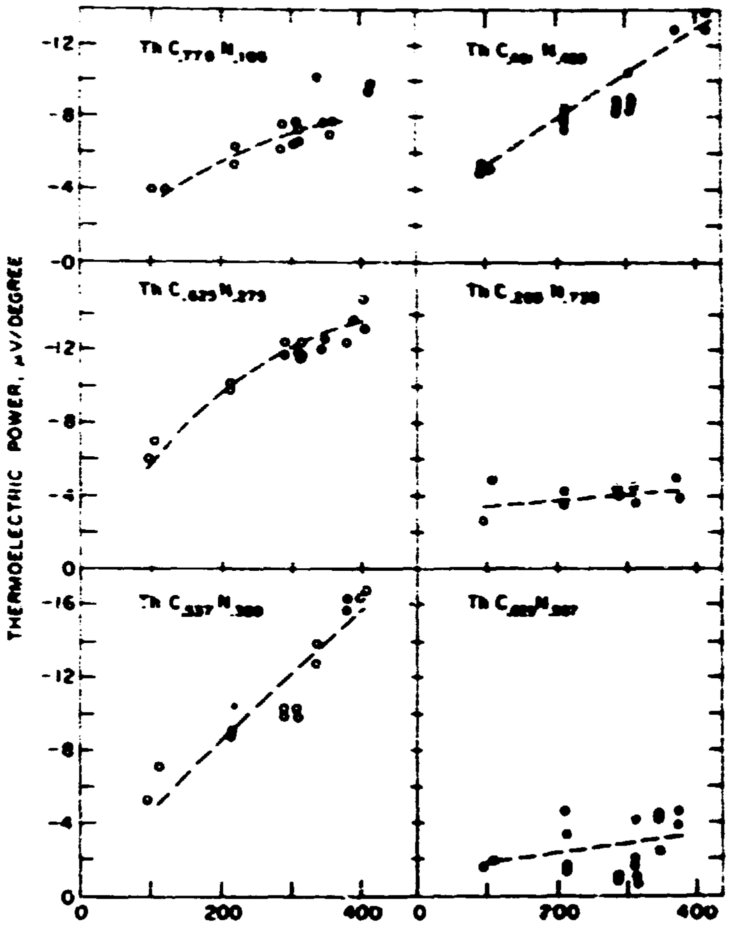

Fig. 17. Absolute Thermoelectric Power of Thorium Carbonitrides. Copied from A. B. Auskern and S. Aronson[34] with permission; copyright by American Institute of Physics.

Table 5. Magnetic Susceptibilities of Thorium Carbonitrides From Aronson and Auskern[24]

Composition	Lattice Parameter (Å)	Susceptibility (emu/g) at –		
		22°C	–76°C	–190°C
		$\times 10^{-8}$	$\times 10^{-8}$	$\times 10^{-8}$
$ThC_{0.775}N_{0.113}$	5.320	14.6	14.6	15.2
$ThC_{0.625}N_{0.275}$	5.288	13.5	13.6	13.9
$ThC_{0.459}N_{0.489}$	5.246	14.2	14.2	14.5
$ThC_{0.202}N_{0.734}$	5.197	15.6	15.9	16.0
$ThC_{0.206}N_{0.749}$	5.199	14.6	14.7	14.8
$ThC_{0.251}N_{0.936}$[a]	5.164	18.3	18.6	18.8

[a] Compiler's note: This composition appears to be in error; a carbon subscript of 0.03 to 0.06 would be more consistent with other information in the paper.

8. Mechanical Properties

No information is available.

9. Chemical Properties

Benz[5] melted carbon-rich carbonitrides on tantalum and other carbonitrides on tungsten without evidence of interaction. Auskern and Aronson[34] found no interaction with molybdenum dies during hot pressing with 30 min contact at 1300°C.

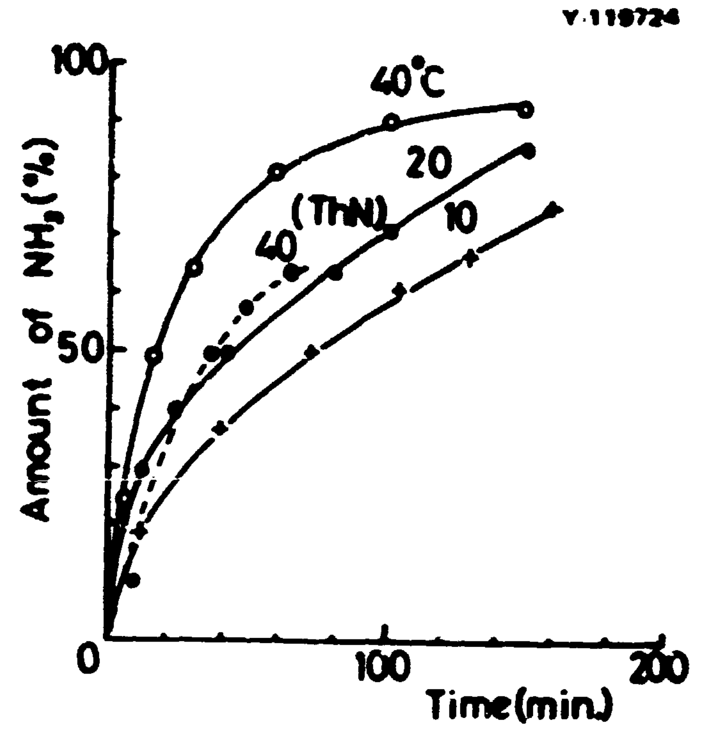

Fig. 18. Rate of Hydrolysis of $ThC_{0.62}N_{0.38}$. Copied from Sugihara and Imoto.[29]

Rate curves reported by Sugihara and Imoto[29] for the hydrolysis of $ThC_{0.62}N_{0.38}$ are given in Fig. 18. One curve for ThN is included to show the accelerating effect of carbon. The reaction products were dissolved ammonia and gaseous H_2, CH_4, and C_2H_6. Heating carbonitrides with a range of compositions in water vapor gave principally ammonia, methane, and hydrogen, with small amounts of ethane and methylamine and a carbonaceous residue.

10. Surface Properties

No information is available.

G. ThN-Oxide System

Two investigations have sought the limiting composition $ThN_{1-x}O_x$ by measuring the simultaneous solubility of thorium and ThO_2 in ThN, with conflicting results. Benz[23] found the limiting x in the formula to be 0.04 at 1600°C, increasing to 0.12 at 2100°C and then decreasing to zero at 2600°C. Kusakabe and Imoto[35] report a limiting x of about 0.2 at 1600°C and 0.3 at 1800°C. Benz[23] also found that the solubility of ThN in ThO_2 becomes detectable (about 0.5 mole %) at 2550°C and increases to 10 mole % under 100 torr N_2 at the eutectic temperature of 2660°C. The ThO_2-ThN eutectic is described in Section A5. Selected equilibrium diagrams given by Benz[23] for the Th-N-O system are shown in Fig. 19.

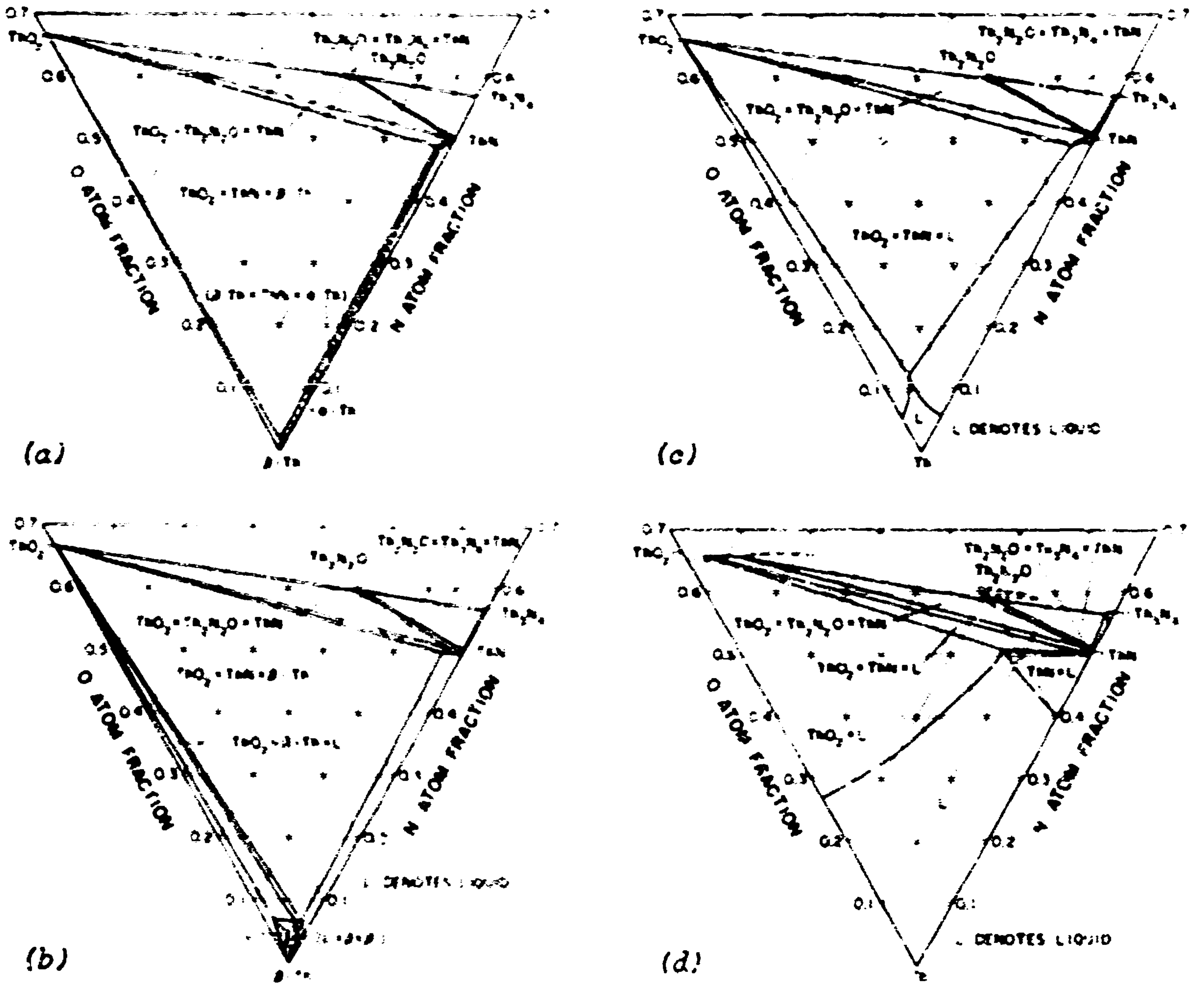

Fig. 19. The Th-N-O System. (a) 1580°C. (b) 1735°C. (c) 1850°C. (d) 2740°C. From Benz.[23] Copyright by North-Holland Publishing Company and reprinted with permission

Th_3N_4 SYSTEMS

Systems with other nitrides (parts B through E) have not been studied, except that Palisaar and Juza[36] have prepared and crystallographically characterized the compounds Li_2ThN_2 and $BeThN_2$. Compounds between Th_3N_4 and other thorium compounds are briefly described in parts F, G, H, and I.

A. Th_3N_4

1. Composition

Below 1000°C Benz *et al.*[1] report Th_3N_4 stoichiometric; at higher temperatures they found the following metal-rich limits on the nitrogen-to-thorium atom ratio:

1603°C	1.33 ± 0.03 under 33 torr N_2 (4400 N/m^2)
1760°C	1.31 under 255 torr N_2 (34,000 N/m^2)
1960°C	1.28 under 920 torr N_2 (123,000 N/m^2).

2. Preparation

The first Th_3N_4 characterized[37,38] was synthesized from the elements, and this is still the usual method.[8,16] Conditions can vary widely. Benz *et al.*[1] obtained Th_3N_4 from the hydride and nitrogen at 200 to 900°C. Benz and Zachariasen[4] reacted ThN with 0.13 atm (1.3 × 10^4 N/m^2) N_2 at 1320°C. Düsing and Huniger[39] precipitated Th_3N_4 from thorium vapor and nitrogen. Specimens for electrical measurements[16] have been hot pressed at 1340 to 1400°C in 1 atm (1 × 10^5 N/m^2) N_2.

3. Crystal Properties

Benz and Zachariasen[4] find for Th_3N_4 a rhombohedral structure, space group $R\bar{3}m$, with parameters a_0 = 9.398 A and α = 23.78°, with the corresponding

Table 6. High-Temperature Hexagonal Lattice Parameters of Th_3N_4, Measured by Benz and Balog[15]

Temperature (°C)	N_2 Pressure (torr)	N_2 Pressure (kN/m²)	a_0 (A)	c_0 (A)
25	vac.		3.87_4	27.39_2
760	vac.		3.89_1	27.5_5
1016	10	1.3	3.90_7	27.7_1
1236	10	1.3	3.91_7	27.8_3
1446	30	4	3.92_4	27.9_2
1512	570	76	3.91_8	28.0_0
1555	570	76	3.92_5	28.0_0
1680	570	76	3.92_6	28.0_3
1765	570	76	3.92_7	28.1_1
1905	600	80	3.92_6	28.1_4

hexagonal cell having a_0 = 3871 Å, c_0 = 27.385 Å. Using neutron diffraction to permit location of the nitrogen atoms, Bowman and Arnold[40] confirmed this structure and gave hexagonal parameters a_0 = 3.875 Å, c_0 = 27.39 Å. High-temperature hexagonal parameters reported by Benz and Balog[15] are given in Table 6. A metastable monoclinic form is reported by Juza and Gerke[41] with a_0 = 6.95, b_0 = 3.83, c_0 = 6.20 Å, and β = 90.7°.

The color of Th_3N_4 has been described as yellow-maroon,[37,38] maroon,[5] dark maroon,[16] dark brown, almost black,[42] and black.[39] Chiotti[3] describes his higher nitride as reddish brown, but he called it Th_2N_3 and may have had Th_2N_2O

4. Thermodynamic Properties

Heat of Formation. – By direct measurement Neumann *et al.*[42] obtained ΔH°_{292} = –308.4 kcal/mole = –1290 kJ/mole. From a heat of combustion of 564.8 kcal/mole (2363 J/mole) Neumann *et al.*[43] found ΔH°_{292} = –312.4 kcal/mole = –1307 kJ/mole. Brewer *et al.*[44] give ΔH°_{298} = –310.4 kcal/mole = –1299 kJ/mole.

Free Energy of Formation. – Brewer *et al.* give ΔG°_{298} = –283.6 kcal/mole = –1187 kJ/mole.

Entropy of Formation. – Brewer *et al.* give ΔS°_{298} = –89.6 cal mole⁻¹ (°K)⁻¹ = –375 J mole⁻¹ (°K)⁻¹.

Heat Capacity. – Sato[45] gives for 0 to 503°C

$$c_p = 0.04895 + 4.436 \times 10^{-5} t - 1.1384 \times 10^{-8} t^2 \text{ cal g}^{-1} (^\circ\text{C})^{-1}$$

$$= 0.2048 + 1.856 \times 10^{-4} t - 4.763 \times 10^{-8} t^2 \text{ J g}^{-1} (^\circ\text{C})^{-1}.$$

Free Energy Function. – From a Russian compilation, Voitovich[46] calculates the following values for $(G - H^\circ_{298})/T$:

Temperature, °C	298	500	1000	1500	2000
Function, cal mole⁻¹ (°K)⁻¹	43.2	45.8	59.5	71.7	82.5
Function, J mole⁻¹ (°K)⁻¹	180.7	191.6	248.9	300.0	345.2

5. Change of State

Decomposition pressure data are given under "System Information."

6. Electrical and Magnetic Properties

Auskern and Aronson[16] found the resistivity of Th_3N_4 to be very sensitive to heat treatment and to range from 10^5 to 10^8 ohm-cm at room temperature. Aronson and Auskern[24] found values of the magnetic susceptibility ranging from 0.3 to 0.6 × 10^{-8} emu/g over the range –190 to 22°C.

7. Heat and Mass Transport

No information is available yet.

8. Mechanical Properties

No information is available yet.

9. Chemical Properties

Early investigations[37,38] showed that Th_3N_4 hydrolyzes slowly in cold water and immediately on boiling and that it burns in oxygen, less luminously than thorium. Quantitative measurements of the hydrolysis by Sugihara and Imoto[29] are shown in Fig. 20. The products are ThO_2 and dissolved ammonia. Ozaki *et al.*[30] found that the reaction of Th_3N_4 powder with 0.2 atm O_2 was roughly fitted by $1 - (1 - C)^{1/3} = kt$, where C is the conversion ratio. The reaction was 25% complete in 7 hr at 340°C and 0.5 hr at 480°C. The activation energy over this range was 15.2 ± 1.7 kcal/mole (64 kJ/mole). Over the temperature range 1400 to 1800°C, the nitrogen decomposition pressure of Th_3N_4 in the presence of ThCN and Th(C,N) as measured by Benz[9] can be fitted by

$$\log p\ (\text{atm}) = 7.95 \quad 1.69 \times 10^4/T\ ,$$

$$\log p\ (\text{N/m}^2) = 12.96 \quad 1.69 \times 10^4/T\ .$$

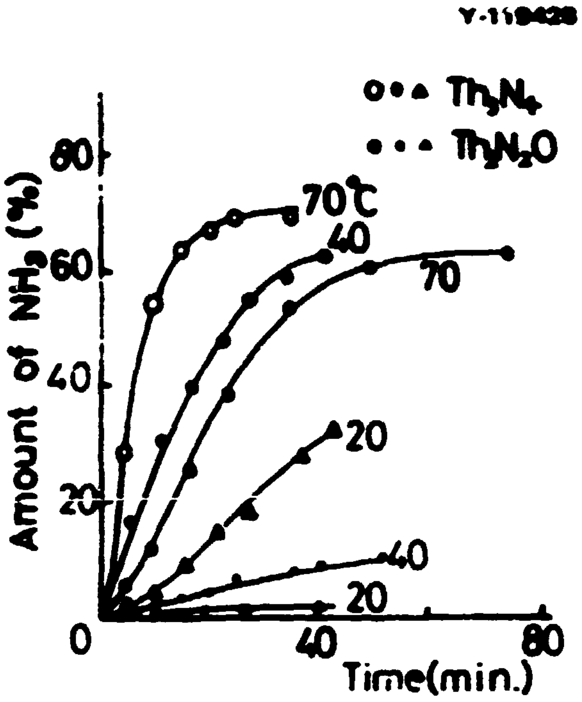

Fig. 20. Hydrolysis Rates of Th_3N_4 and Th_2N_2O. Copied from Sugihara and Imoto.[29]

10. Surface Properties

No information is available.

F. Th_2N_2O

Benz[47] obtained equilibrium between Th_3N_4, Th_2N_2O, and ThO_2 by heating mixtures of thorium, ThN, and ThO_2 in the range 1550 to 2000°C. At equilibrium the phases present were Th_3N_4 and Th_2N_2O, only Th_2N_2O, or Th_2N_2O and ThO_2, depending on whether the initial mixture contained less than, close to, or more than 25 mole % ThO_2 respectively. The Th_2N_2O phase ranged in composition from $ThN_{1.22}O_{0.20}$ to $ThN_{1.0}O_{0.5}$ at 1600 ± 40°C and $ThN_{1.28}O_{0.10}$ to $ThN_{1.0}O_{0.5}$ at 2000 ± 48°C. The ThO_2 phase showed no variability at 1600°C but extended to approximately $ThN_{0.1}O_{1.85}$ at 2000°C. On cooling, precipitation removed nonstoichiometry from these phases. No solubility of oxygen in Th_3N_4 could be detected. The oxynitride was gray to maroon, depending on grain size. Benz and Zachariasen[4] give the crystal structure of Th_2N_2O as hexagonal with a_0 = 3.8833 ± 0.0002 Å and c_0 = 6.1870 ± 0.0003 Å.

Equilibrium between Th_2N_2O and other solids has been investigated by Benz;[32] selected equilibrium diagrams are given in Fig. 19. The decomposition pressure, presumably according to the equation

$$2\,Th_2N_2O \rightleftharpoons 3ThN + ThO_2 + \tfrac{1}{2}\,N_2\ ,$$

was reported by Kusakabe and Imoto[10] over the range 1690 to 1985°C to be fitted by

$$\log p_{N_2}\,(\mathrm{atm}) = 13.544 \quad 3.095 \times 10^4/T$$

or

$$\log p_{N_2}\,(\mathrm{N/m^2}) = 18.550 \quad 3.095 \times 10^4/T\,.$$

From this decomposition pressure they calculated the enthalpy and entropy of formation of Th_2N_2O to be ΔH_{298} = −321.7 kcal/mole = −1346 kJ/mole and ΔS_{298} = −76.2 cal mole^{-1} (°K)$^{-1}$ = −319 J mole^{-1} (°K)$^{-1}$. They also report the following emissivities at the wavelength 0.65 μm:

T (°C)	$\varepsilon_{Th_2N_2O}$
1577	0.331
1667	0.343
1725	0.346
1815	0.345
1925	0.367

Rates of hydrolysis to ThO_2 and dissolved ammonia, measured by Sugihara and Imoto,[29] are shown in Fig. 20.

G. Thorium Nitride–Halides

Juza and Sievers[48] have prepared and characterized a series of compounds ThNX, where X is F, Cl, Br, or I. All arise from reaction of the appropriate thorium tetrahalide with ammonia or Th_3N_4. The fluoride is insoluble and stable to aqueous reagents; it decomposes in 3 hr at 1320°C or in 15 min at 1550°C. The other compounds have reactivities that increase with the atomic weight of the halogen. The fluoride can dissolve up to 10% ThO_2.

The crystal structures have been worked out in detail.[48] The fluoride is rhombohedral, and the others are tetragonal. Two intermediate nitride fluorides, ThN_xF_{4-3x}, were also observed, tetragonal with x from 0.88 to 0.94 and orthorhombic with x from 0.79 to 0.87.

H. ThCN

In an investigation of phase equilibria in the Th-N-C system, Benz and Troxel[6] found the compound ThCN with little if any variation in composition near stoichiometric. Figure 13 shows solid-phase relationships involving this compound. The crystal structure was

Table 7. High-Temperature Lattice Parameters of ThCN, Measured by Benz and Balog[15]

Temperature (°C)	Unit-cell dimensions (Å)			β (deg)	N_2 Pressure	
	a_0	b_0	c_0		(torr)	(kN/m²)
25	7.02_3	3.94_6	7.27_5	95.7	vac.	
760	7.02_6	4.00_2	7.30_1	94.1	vac.	
990	7.02_5	4.00_3	7.30_6	93.7	5	0.7
1100	7.02_9	4.00_1	7.33_7	93.6	200	27
1260	7.03_2	4.01_3	7.34_9	93.9	570	76
1400	7.03_5	4.00_6	7.37_1	94.1	570	76
1500	7.06_2	4.01_2	7.36_5	94.7	600	80
1620	7.07_3	4.03_9	7.37_5	94.7	600	80

determined by Benz *et al.*[49] to be C-centered monoclinic, space group *C2/m* (C_{2h}^3), with lattice parameters a_0 = 7.0249 ± 0.0006 Å, b_0 = 3.9461 ± 0.0002 Å, c_0 = 7.2763 ± 0.0009 Å, and β = 95.67 ± 0.01°. Neutron diffraction showed the carbon atoms to be in triply bonded pairs, showing the compound to be a mixed nitride-acetylide. High-temperature parameters measured by Benz and Balog[15] are given in Table 7. Decomposition pressure measurements by Benz[9] over the range 1500 to 1900°C in the presence of the phases ThC_2 and Th(C,N) can be represented by

$$\log p\,(\mathrm{atm}) = 7.82 - 1.76 \times 10^4/T\,,$$

$$\log p\,(\mathrm{N/m^2}) = 12.825 - 1.76 \times 10^4/T\,.$$

I. Complex Thorium Nitrides

Several complex nitrides not separately described have been reported by Benz and Zachariasen.[50,51] Some[50] have the hexagonal Ce_2O_2S-type crystal structure, space group *P*$\bar{3}$*m1*. Others[51] are tetragonal, space group *I4/mmm*. The x-ray diffraction characterization is summarized in Table 8.

Table 8. Some Complex Thorium Nitrides from Benz and Zachariasen

Compound	Lattice Parameter (Å)		Theoretical Density (g/cm³)
	a_0	c_0	
	Hexagonal[50]		
Th_2NOAs	4.041 ± 0.001	6.979 ± 0.002	9.58
Th_2N_2Se	4.0287 ± 0.0002	7.156 ± 0.001	9.43
Th_2NOP	4.0285 ± 0.0003	6.835 ± 0.001	9.08
Th_2N_2S	4.008 ± 0.001	6.920 ± 0.002	9.04
	Tetragonal[51]		
Th_2N_2Sb	4.049 ± 0.001	13.57 ± 0.01	9.17
$Th_4N_3OSb_2$	4.045 ± 0.00[illegible]	13.18 ± 0.04	9.47
Th_2NOSb	4.041 ± 0.001	12.84 ± 0.01	9.76
Th_2N_2Te	4.0939 ± 0.0004	13.014 ± 0.001	9.44
Th_2N_2Bi	4.075 ± 0.001	13.670 ± 0.01	10.30

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