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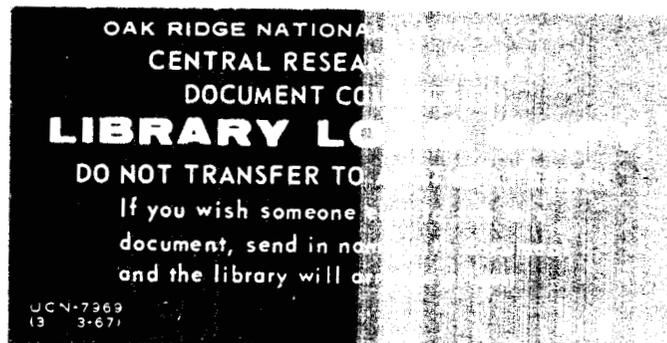


ORNL - TM - 2015

INVESTIGATION OF CERTAIN TERNARY SYSTEMS  
CONTAINING THORIUM AND URANIUM

(Thesis)

John Thomas Venard



Submitted as a thesis to the Graduate Council of the University of Tennessee  
in partial fulfillment of the requirements for the degree of Master of Science.

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JANUARY 1968

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## ABSTRACT

Potential advantages of thermal-breeder fuels having a metallic thorium matrix with a dispersion of either (Th,U)C or (Th,U)N led to an investigation of the Th-U-C and Th-U-N ternary systems. This investigation was limited to the 1000°C. isotherm at 50 atomic per cent carbon or nitrogen and below. Alloys in the Th-U-C system were made by arc-melting techniques while those in the Th-U-N system were prepared by powder metallurgical techniques. Equilibration times for cast alloys in the Th-U-C system were found to be 240 to 350 hours at 1000°C. and greater than 1000 hours at 600 and 800°C. In the Th-U-N system the 1000°C. equilibration time was found to be 80 to 100 hours. Lattice parameters across the UC-ThC pseudobinary showed a slight negative deviation from Vegard's law and excellent agreement with published data. Across the UN-ThN pseudobinary lattice parameters obey Vegard's law. The most uranium-rich compounds in equilibrium with metallic thorium were found to be  $(\text{Th}_{0.906}, \text{U}_{0.094})\text{C}_{0.712}$  and  $(\text{Th}_{0.944}, \text{U}_{0.056})\text{N}_{0.869}$ , respectively. A thermodynamic analysis was shown to be consistent with the experimental results and yielded an estimate of the 1000°C. free energy of formation of ThN. This value was found to be minus 51,900 calories per gram-mole.

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## CHAPTER I

### INTRODUCTION

Optimum utilization of the world's nuclear fuel supply depends on using not only uranium-235, a naturally occurring fissionable isotope, but also on using uranium-233 and plutonium-239, which are fissionable isotopes formed by thermal neutron capture (1)\*. A thermal-breeder fuel having metallic thorium as both matrix and fertile material, which would utilize the thorium-232 to uranium-233 breeding cycle, offers a considerable potential in this context. An Atomic Energy Commission task force has shown that fuels of this kind must be capable of operation at temperatures in the range 800 to 1000°C. if low fuel cycle costs are to be realized (2).

A thermal-breeder fuel must, however, contain a fissionable isotope of uranium (5 to 20 weight per cent) since thorium will not fission with neutrons having energies less than one million electron volts (3). In the thorium-uranium binary system, metallic uranium is subject to both "irradiation growth" and "irradiation swelling." The first of these occurs at temperatures of 450°C. or below. It results from the anisotropy of the metal, and it is a function of the number of thermal cycles and of fuel burnup. The phenomenon of "irradiation swelling" occurs at temperatures of 450°C. and above. It is the result of fission gas

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\* Denotes reference. See page 69.

nucleation and migration, and is also a function of fuel burnup (4,5). The more isotropic crystal structure of metallic thorium would be expected to be resistant to "irradiation growth," and irradiation experiments (6,7) have shown a thorium-base fuel to be more resistant to "irradiation swelling" than metallic uranium. A fuel having a fine dispersion of a compatible second phase has been shown, by experiment (5) and according to a theoretical model (8), to be more resistant to fuel swelling than the same fuel matrix without the dispersion.

Certain alloys from the ternary systems of thorium plus uranium plus carbon or nitrogen appear to be promising in meeting the fuel criteria of having: (1) an operating capability at central fuel temperatures of 800°C.; (2) a crystal structure which is not subject to "irradiation growth"; (3) a nonmetallic form of uranium which is resistant to "irradiation swelling"; and (4) a finely dispersed, stable second phase for further resistance to "irradiation swelling."

In the thorium-uranium-carbon (Th-U-C) system Rudy (9) has shown that a particularly simple ternary isotherm results. On the metal-rich side of this diagram there is a three-phase region consisting of thorium metal, uranium metal, and the compound (Th,U)C [the symbol (Th,U)C is used to indicate any alloy within the single-phase region bounded by UC and ThC]. The thorium-to-uranium ratio for the (Th,U)C phase in equilibrium with thorium and uranium metal may be estimated from data on the standard free energy of formation of ThC and UC. A nuclear fuel having a composition located within the two-phase field, thorium metal plus (Th,U)C, might be expected to satisfy the fuel criteria set down above.

At the beginning of this investigation, sufficient information existed on the system Th-U-N to indicate that the phase diagram, at least on the metal-rich side, could be expected to be analogous to that of the carbon system.

The original objective of these investigations was to define the stoichiometry of the most uranium-rich compound (Th,U)X in thermodynamic equilibrium with metallic thorium, in the temperature range 600 to 1000°C., for both the Th-U-C and the Th-U-N systems.

## CHAPTER II

### REVIEW OF RELEVANT INVESTIGATIONS IN THE LITERATURE

#### The Uranium-Carbon System

A number of fairly recent reviews of the entire uranium-carbon system have been published (10,11,12) so only those investigations which deal with the diagram at and below 50 atomic per cent carbon will be discussed here. There is still some uncertainty about the details of the diagram despite the considerable amount of work published. The uranium-carbon binary diagram proposed by the International Atomic Energy Agency (IAEA) (12) is shown as Figure 1. Figure 2 shows the diagram proposed by Magnier and Accary (13) based on their metallographic and x-ray diffraction work. The differences between these two diagrams are based on the x-ray work reported by Accary (14) concerning the variation of the solubility of uranium in UC and on the existence of the compound  $UC_{1-x}$  as hypothesized by Magnier and Accary (13).

The existence of three crystallographic forms of uranium is generally accepted and Blumenthal (15) has used thermal analysis techniques to determine the transformation temperatures. Blumenthal (16) has reported the maximum solubility of carbon in solid uranium to be less than or equal to 185 parts per million, as determined metallographically.

Uranium monocarbide has the face-centered cubic (NaCl-type) structure and was first identified by Litz et al. (17) in 1948. Since that time quite a number of investigators have measured the lattice parameter

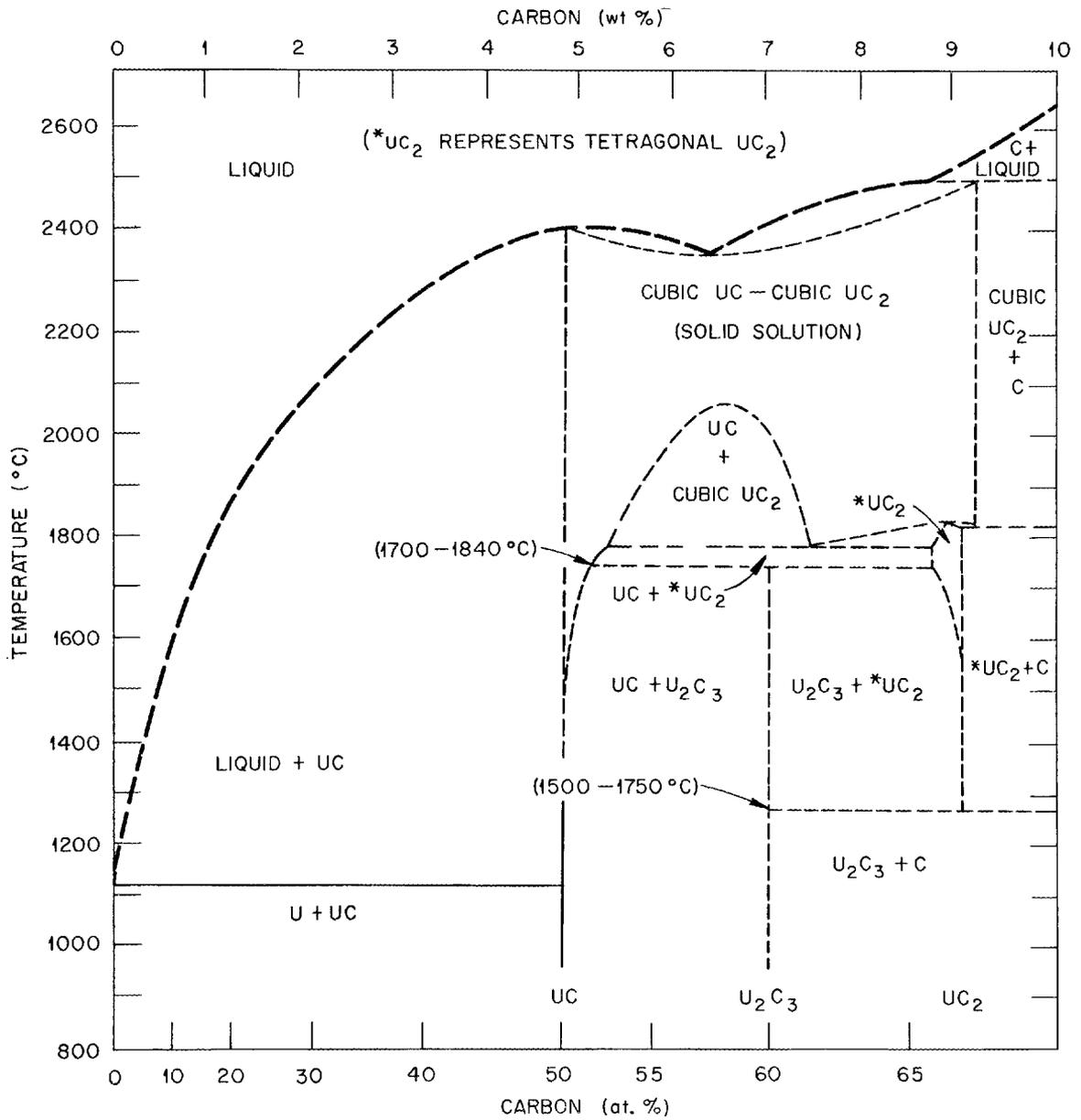


Figure 1. The uranium-carbon binary system after IAEA.

[Reference: "The Uranium-Carbon and Plutonium-Carbon Systems, A Thermochemical Assessment," Technical Report Series No. 14, International Atomic Energy Agency (1963).]

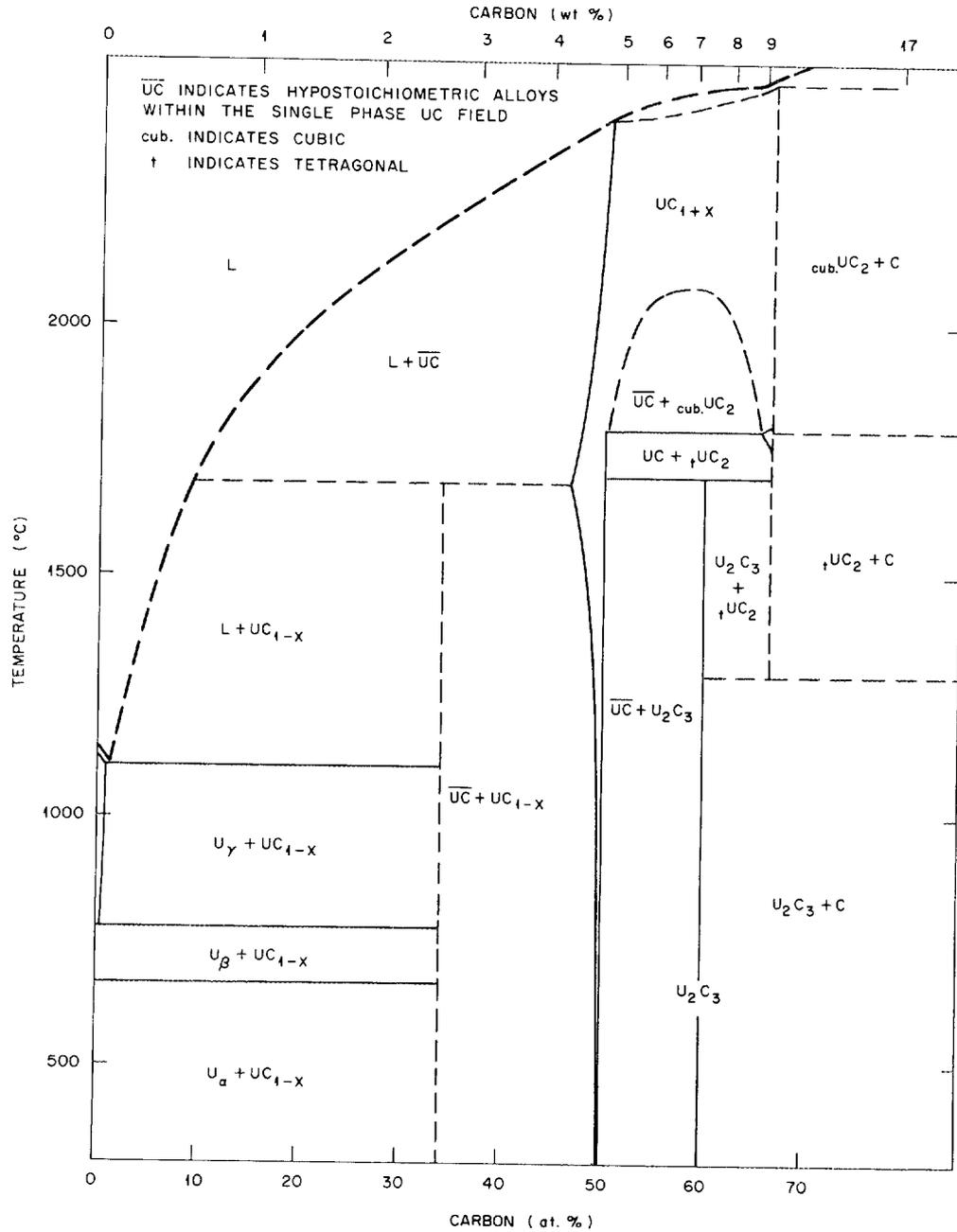


Figure 2. The uranium-carbon binary system after Magnier and Accary.

[Reference: P. Magnier and A. Accary, "The Solubility of Uranium in Uranium Monocarbide," *Carbides in Nuclear Energy* 1, pp. 22-32, London, Macmillan (1964).]

of UC (18 through 34). A value of 4.9597 plus or minus 0.0004 angstroms appears to be the best value for pure UC<sub>1.00</sub> (ref. 35). Magnier (36) has shown that UC exists as a single phase over the approximate composition range 48 to 50 atomic per cent carbon in the temperature range 1600 to 1800°C.

#### The Thorium-Carbon System

Again concentrating on the binary diagram at and below 50 atomic per cent carbon, the reader is referred to the reviews in the literature which cover the entire diagram (10,37,38). Langer et al. (38) have proposed the diagram shown as Figure 3 using what seemed to be the best of their own thermal analysis, room- and high-temperature x-ray, and metallographic data plus data published in the literature. Very recently Chiotti et al. (39) have proposed the diagram shown in Figure 4, based on electrical resistivity determinations. At carbon contents of 50 atomic per cent and below, the major differences between these two diagrams lie in the region of 5 to 35 atomic per cent carbon at temperatures of 1570 to 1700°C.

Wilson et al. (40) have reported that the alpha-to-beta transition for thorium occurs at 1330 plus or minus 20°C. and Chiotti (41) has investigated the crystal structures and lattice parameters of these two phases. The solubility of carbon in solid thorium has been determined by Takeuchi et al. (42) using x-ray, electrical resistivity, and metallographic data.

Thorium monocarbide has the face-centered cubic (NaCl-type) structure reported by Chiotti (43) and confirmed by other

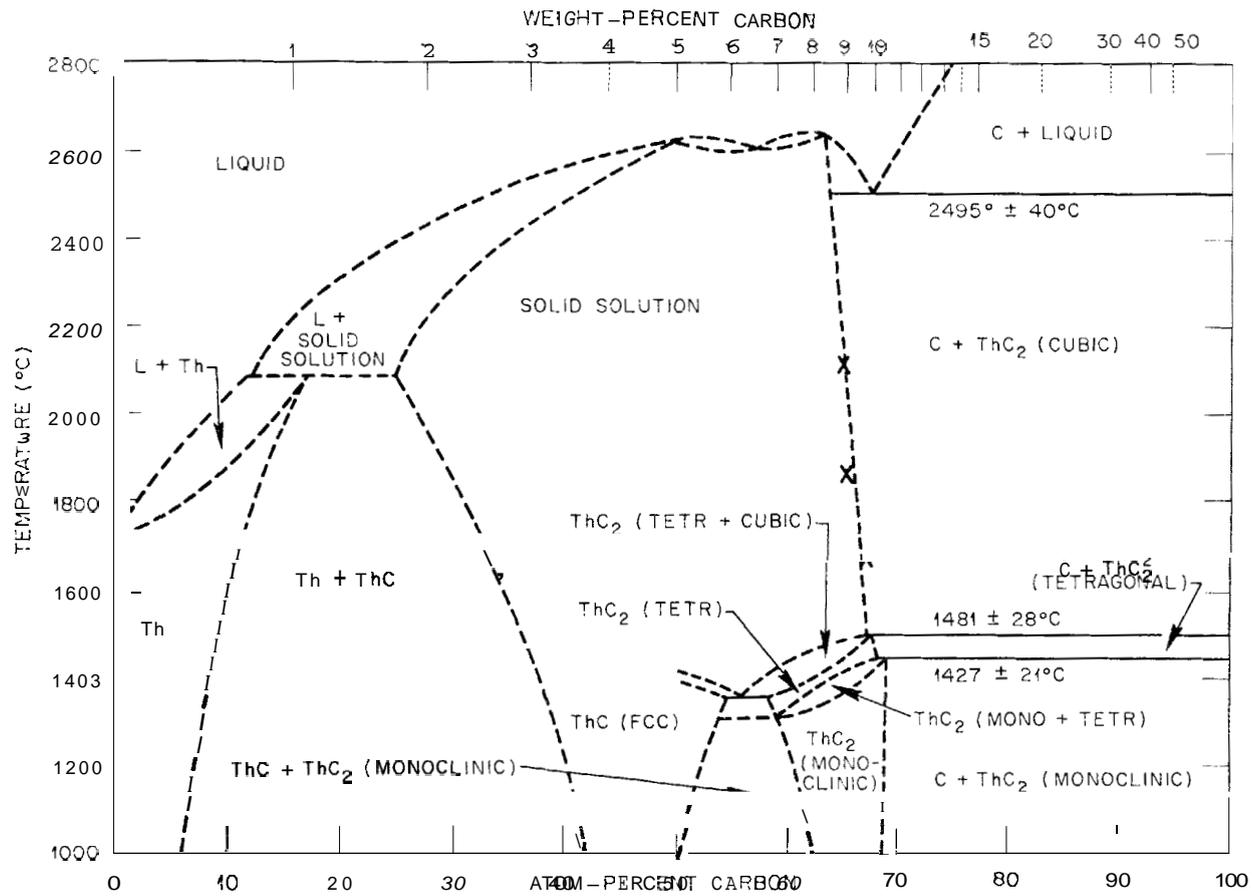


Figure 3. The thorium-carbon binary system after Langer *et al.*

[Reference: S. Langer, N. Baldwin, P. Gantzel, F. Kester, and C. Hancock, "Studies in the Thorium-Carbon Binary System," *Compounds of Interest in Nuclear Technology*, pp. 359-86, AIME Nuclear Energy Series X (1964).]

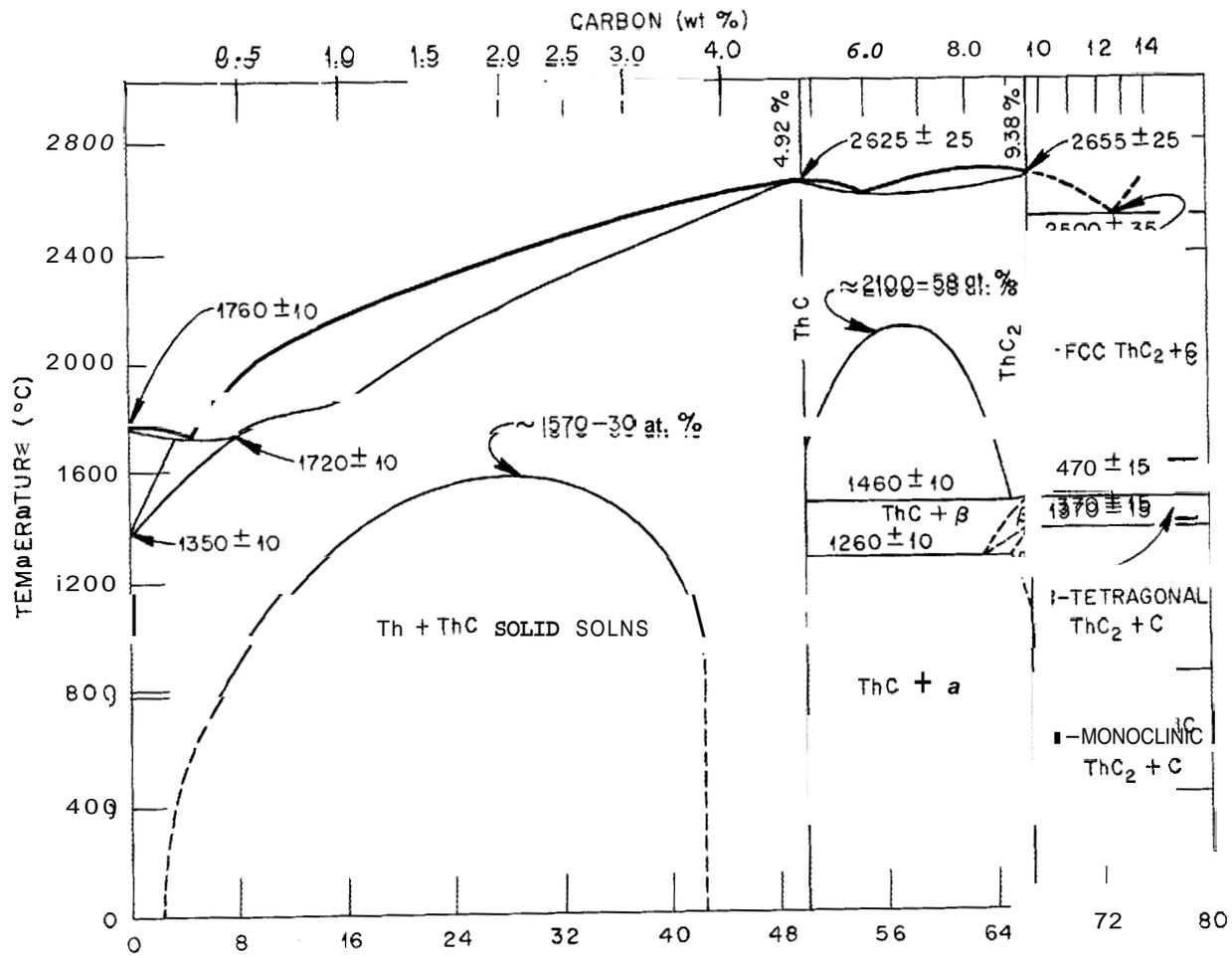


Figure 4. The thorium-carbon binary system after Chiotti *et al.*

[Reference: P. Chiotti, F. W. Korbitz, and G. J. Dooley, III, "Electrical Resistivity and Phase Relations for the Thorium-Carbon System," *J. Nucl. Mater.* **23**, 55-67 (1967).]

investigations (29,44,45). According to Kempter and Krikorian (37) the lattice parameter of  $\text{ThC}_{1.00}$  is about 5.346 angstroms and Takeuchi et al. (42) have shown the single phase to exist over the range 40 to 49 atomic per cent carbon, below 1350°C.

#### Binary Systems of Nitrogen with Uranium and Thorium

Benz and co-workers (46,47) have surveyed the significant literature and have combined this information with their own metallographic, chemical, and thermal analysis data to produce the binary diagrams shown in Figures 5 and 6.

The mononitrides of uranium and thorium were identified as face-centered cubic (NaCl-type) by Rundle et al. (26,48). Others who have used x-ray diffraction to determine the crystal structure and lattice parameter of UN are Dunn (49), Williams and Sambell (50), Kempter et al. (51,52), Keller (53), Olson and Mulford (54), Evans and Davies (55), Carrol (56), and Weber (57). These studies indicate that UN has a lattice parameter of about 4.890 angstroms and this value has been further confirmed by the neutron diffraction determination of Mueller and Knott (58). A value of about 5.159 angstroms for the lattice parameter of ThN has been confirmed by the x-ray diffraction work of Street and Waters (59), Olson and Mulford (60), and that of Aronson and Auskern (61).

#### The Thorium-Uranium System

Figure 7 from Hansen and Anderko (62) and Figure 8 from Elliot (63) represent the most thorough compilation and review of the work published concerning the Th-U binary system. Of particular

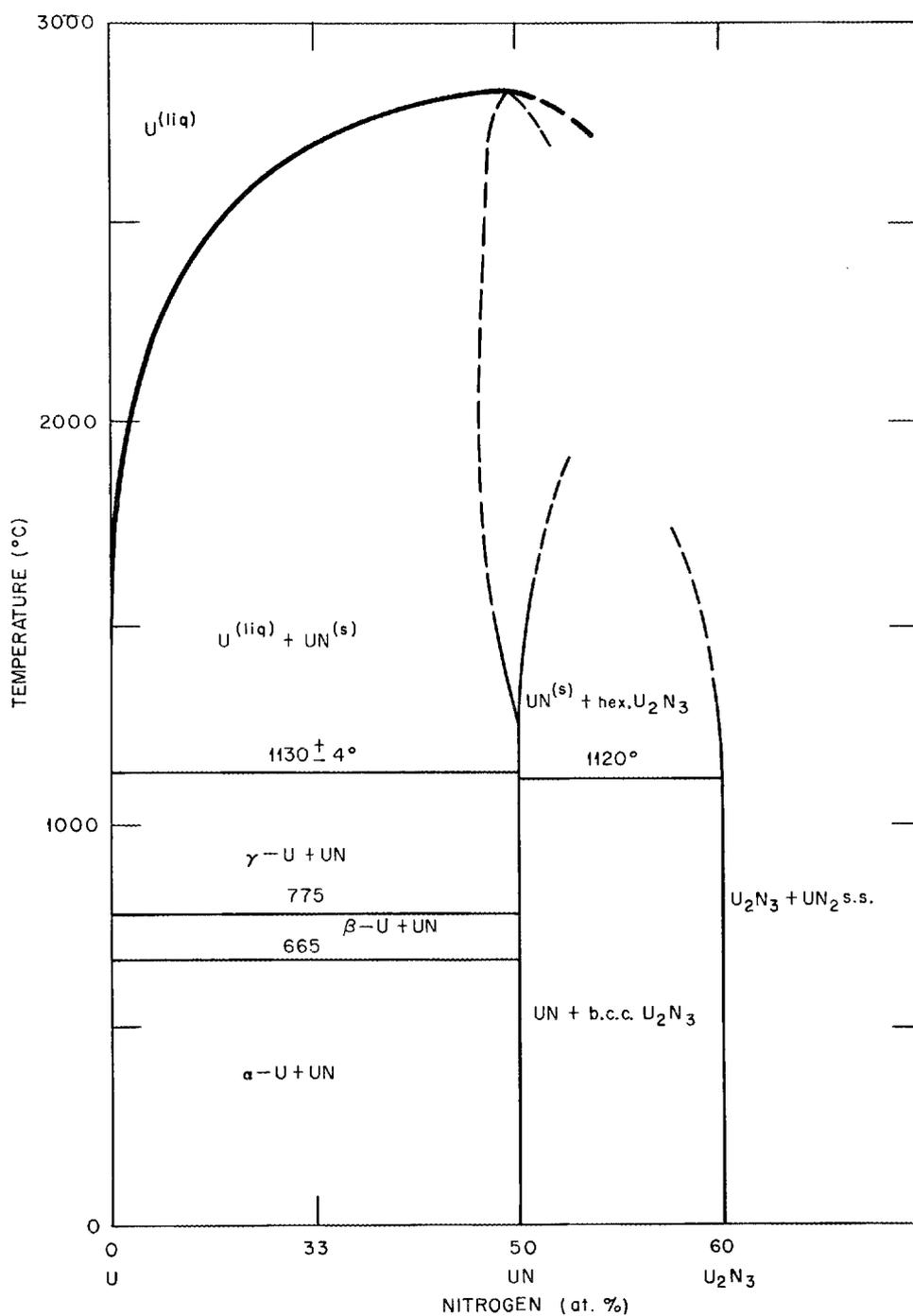


Figure 5. The uranium-nitrogen binary system after Benz and Bowman.

[Reference: R. Benz and M. G. Bowman, "Some Phase Equilibria in the Uranium-Nitrogen System," *J. Am. Chem. Soc.* 88(2), 264-68 (1966).]

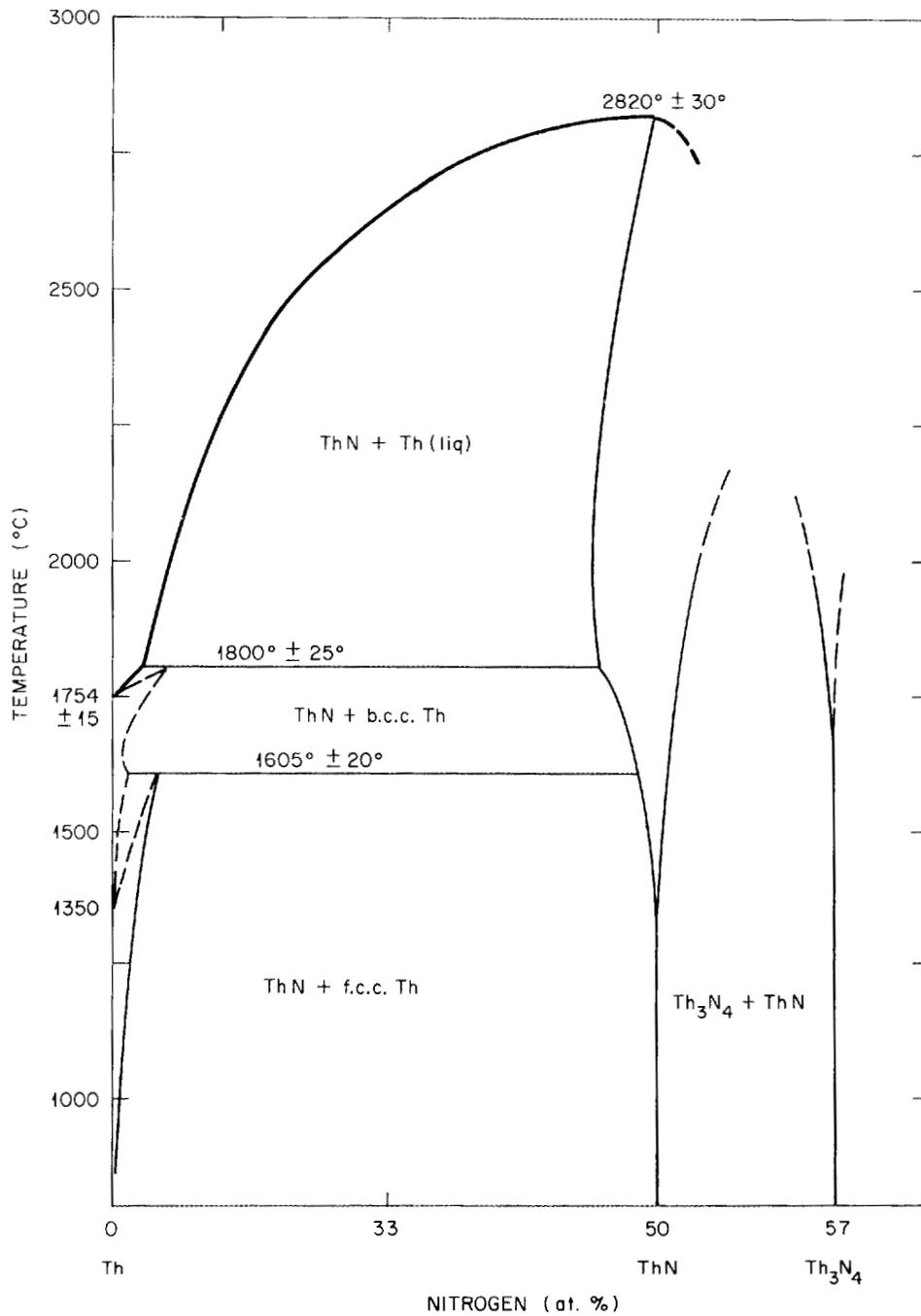


Figure 6. The thorium-nitrogen binary system after Benz et al.

[Reference: R. Benz, C. G. Hoffman, and G. N. Rupert, "Some Phase Equilibria in the Thorium-Nitrogen System," J. Am. Chem. Soc. 89(2), 191-97 (1967).]

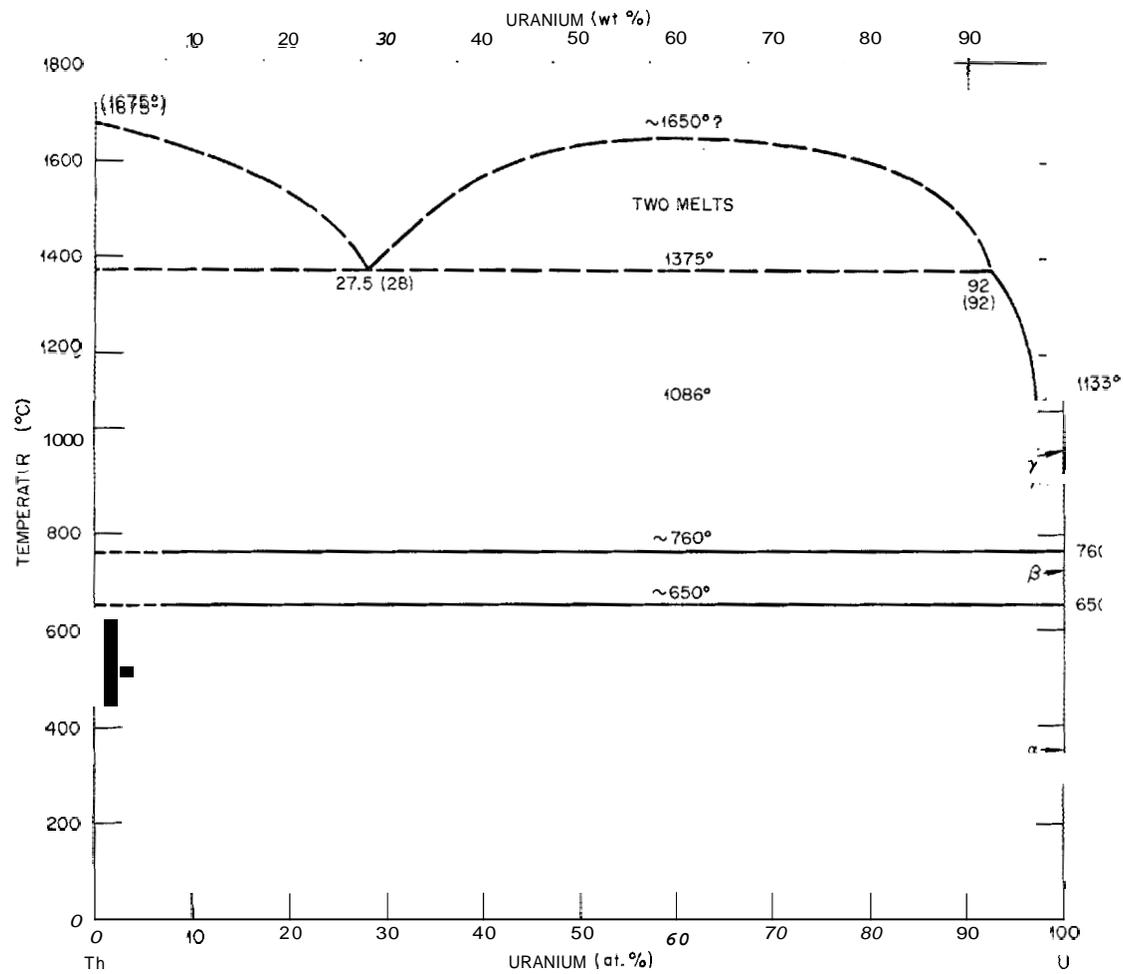


Figure 7. The thorium-uranium binary system after Hansen and Anderko.

[Reference: M. Hanson and K. Anderko, "Constitution of Binary Alloys," Second edition p. 1233, New York, McGraw-Hill Book Company, Inc. (1958).]

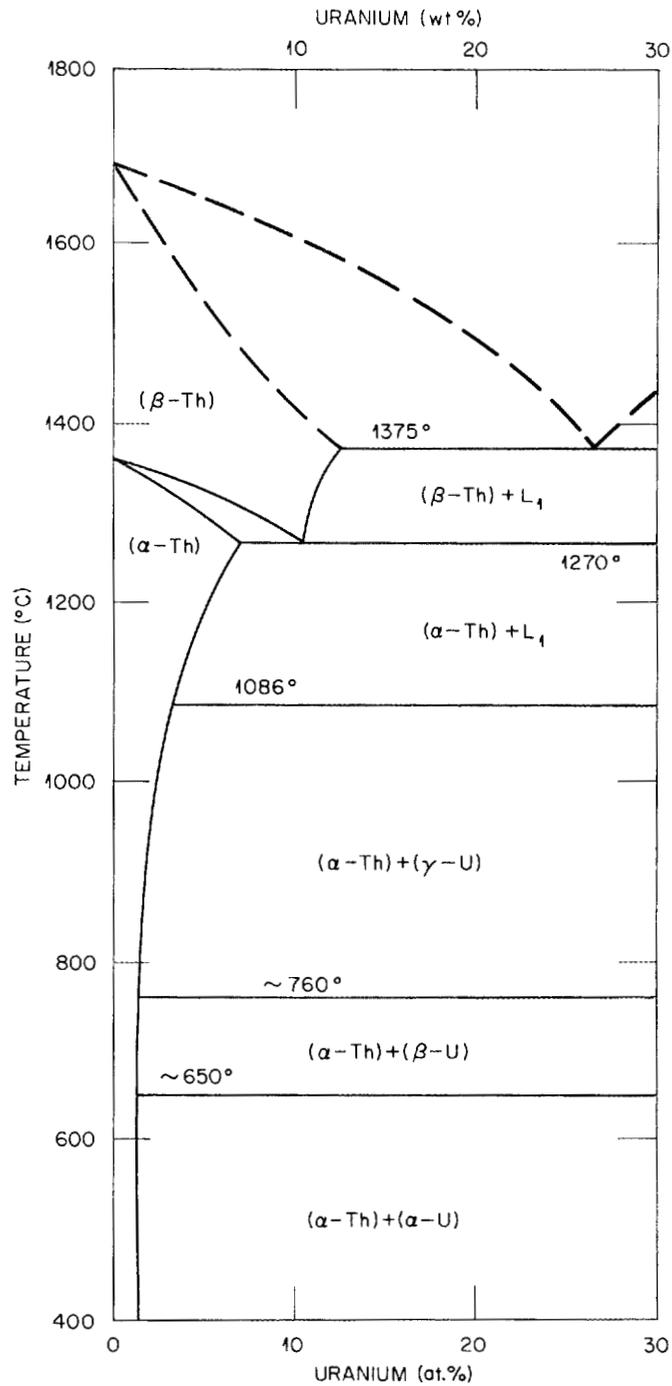


Figure 8. The thorium-uranium binary system after Elliot.

[Reference: R. P. Elliot, "Constitution of Binary Alloys, First Supplement," p. 846, New York, McGraw-Hill Book Co., Inc. (1965).]

importance in this investigation is the very low mutual solid solubility of uranium and thorium. The solubility of uranium in thorium at temperatures below 1000°C. is less than 2.5 atomic per cent according to investigations using metallographic, x-ray, and resistivity data (40,64,65,66). Murray established, by metallographic examination, that the solubility of thorium in uranium is 0.3 atomic per cent at 900°C. (ref. 64).

#### The Thorium-Uranium-Carbon System

Based on data generated through x-ray diffraction and metallographic examination Benesovsky and Rudy (67) proposed the 1000°C. partial isotherm of the Th-U-C system as shown in Figure 9. They have correlated the results with a thermodynamic calculation which predicts where the three-phase field intersects the single-phase (Th,U)C solid solution. This calculation and its implications will be discussed in a later section.

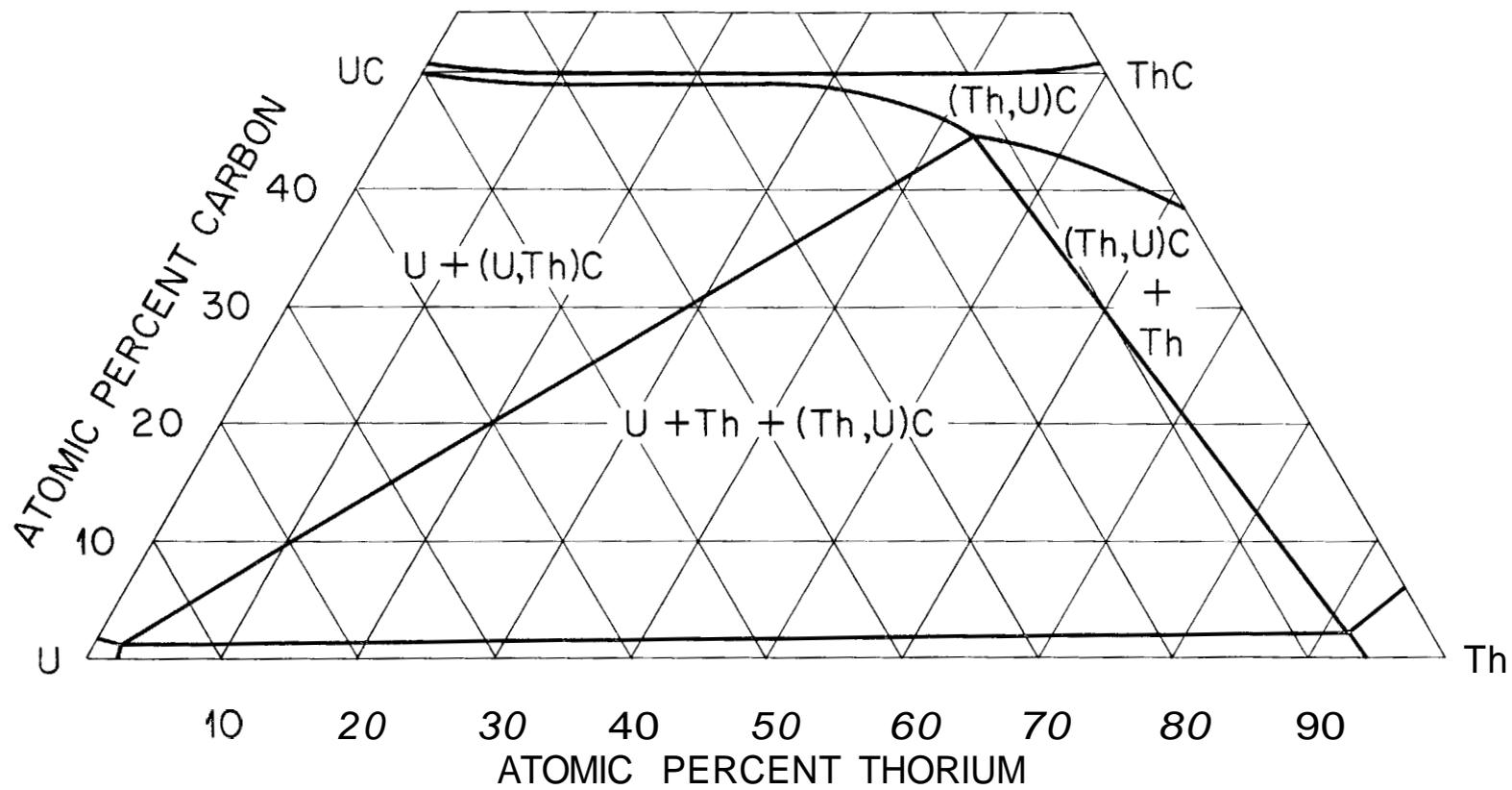


Figure 9. The thorium-uranium carbon partial ternary isotherm at 1000°C. according to Benesovsky and Rudy.

[Reference: F. E. Benesovsky and E. Rudy, "Studies of the Uranium-Thorium-Carbon System," Monatsh. Chem. 92, 1176-83 (1961), AEC-tr-5175, Technical Information Service, Washington, D. C. ]

## CHAPTER III

### SAMPLE PREPARATION AND EXPERIMENTAL PROCEDURE

#### Materials and Preparation

The materials used in preparing the carbon alloys were spectrographic grade carbon, uranium and thorium sheet. The uranium sheet was greater than 99.9 weight per cent pure and the thorium sheet was greater than 99.6 weight per cent pure. Detailed impurity analyses of the metals are given in Tables I through IV in Appendix A. The metallurgical history of the uranium and thorium sheet is shown in the flow diagrams of Figures 10 and 11. The uranium used in this investigation was depleted in uranium-235.

Ternary Th-U-C alloys were arc melted in a furnace similar to the one shown in Figure 12 using the techniques described by Bourgette (68). The furnace charge was made up of 100 to 150 grams of freshly pickled uranium and thorium metal sheet, sheared into small (2 to 5 grams) pieces, plus spectrographic carbon. The carbon in the charge was adjusted to give the desired carbon content in the finished alloy, taking into account the amount of carbon present in the uranium and thorium metal. Bourgette (68) demonstrated the extreme sensitivity of these alloys to carbon content and also showed that this charging technique yields alloys that have carbon contents which are very close (plus or minus 60 parts per million by weight) to that desired.

## PREPARATION OF URANIUM SHEET

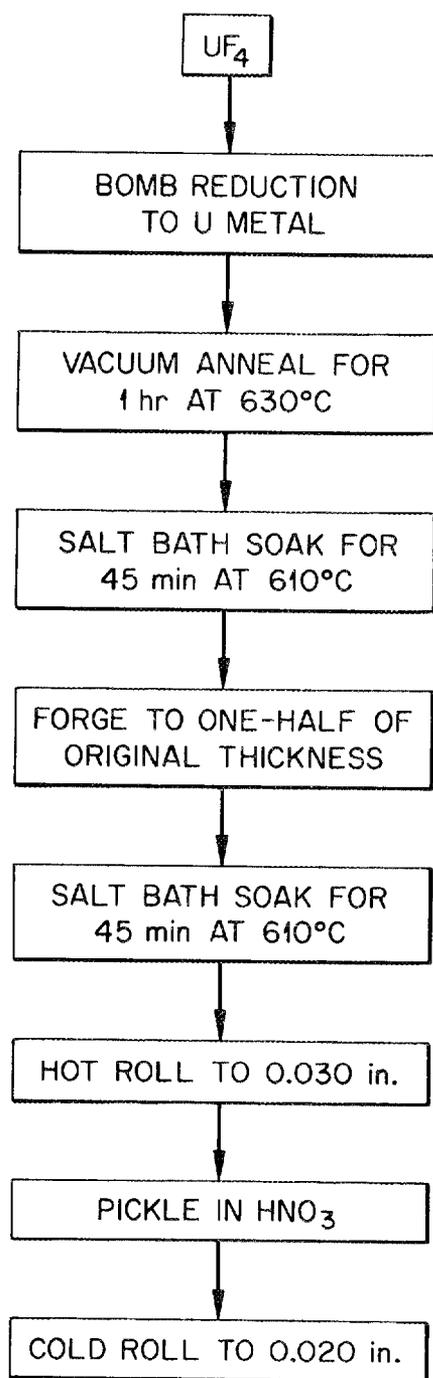


Figure 10. Flow diagram showing the preparation of uranium sheet.

## PREPARATION OF THORIUM SHEET

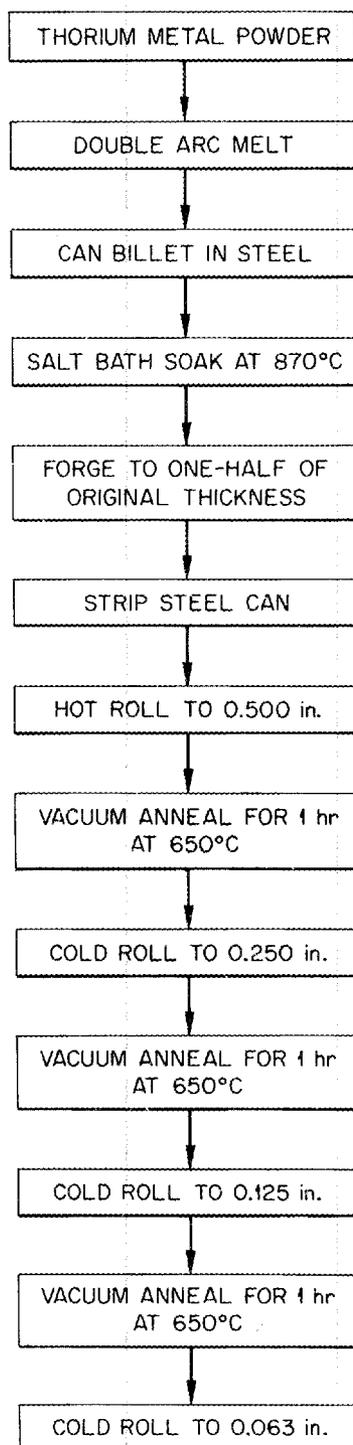


Figure 11. Flow diagram showing the preparation of thorium sheet.

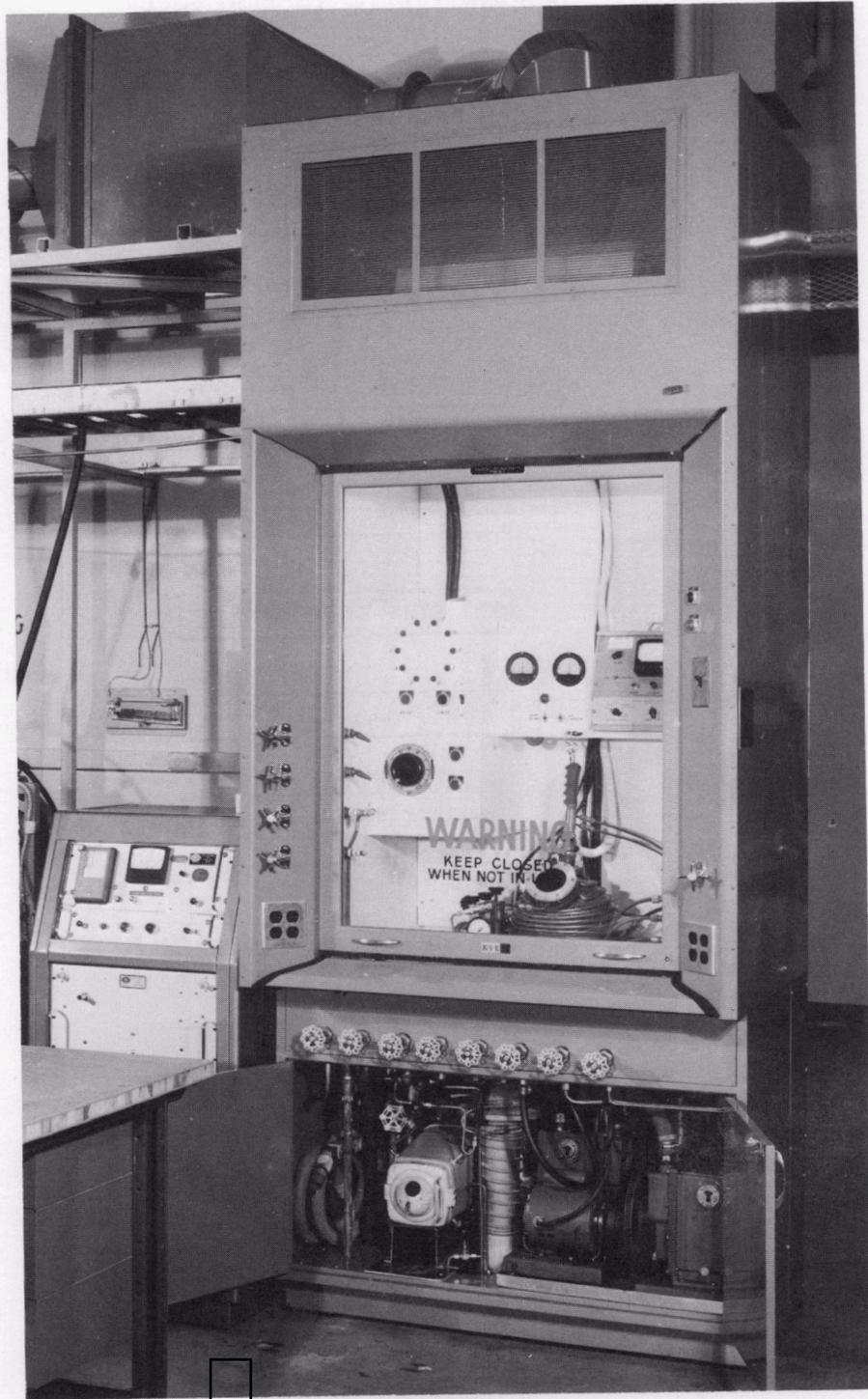


Figure 12. Arc-melting furnace used for melting and drop-casting carbon alloys.

With the charge in the furnace, a vacuum of approximately  $10^{-6}$  torr was established prior to backfilling with high-purity argon (less than 4 parts per million total impurities) to a pressure of approximately 500 millimeters of mercury. A 100-gram zirconium button, used as an oxygen "getter," was melted prior to melting the alloy. Each button was melted from six to ten times, turning the button with the electrode between each remelt, to ensure complete dissolution of carbon and melt homogeneity.

Following button preparation the 4.8 weight per cent alloys were drop-cast into a graphite thimble supported by a hollow copper mold. The graphite thimbles were vacuum degassed at  $2300^{\circ}\text{C}$ . and stored in a vacuum desiccator prior to use. The alloys containing 3.0 and 1.5 weight per cent carbon proved to be very difficult to drop-cast and were therefore remelted into water-cooled finger molds. Figure 13 shows typical drop- and finger-castings.

The completed castings were placed in individual sample bottles under mineral oil and stored under vacuum (less than 10 microns of mercury). Preparation of samples for chemical analysis, annealing, x-ray analysis, and metallography was performed in an argon-filled glove box.

Nitrogen alloy preparation began with the arc-melting of master alloys of uranium plus thorium. These arc-melted buttons were reduced to machine chips, etched in nitric acid, and placed in tungsten crucibles. These crucibles were loaded into the furnace shown in Figure 14. This furnace uses a tungsten-mesh heating element, and has both high-vacuum and purge-gas capability. The stoichiometric mononitrides,  $(\text{Th,U})\text{N}$ , were

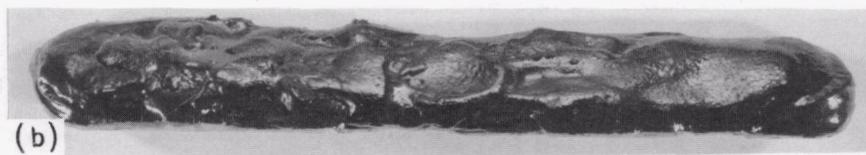
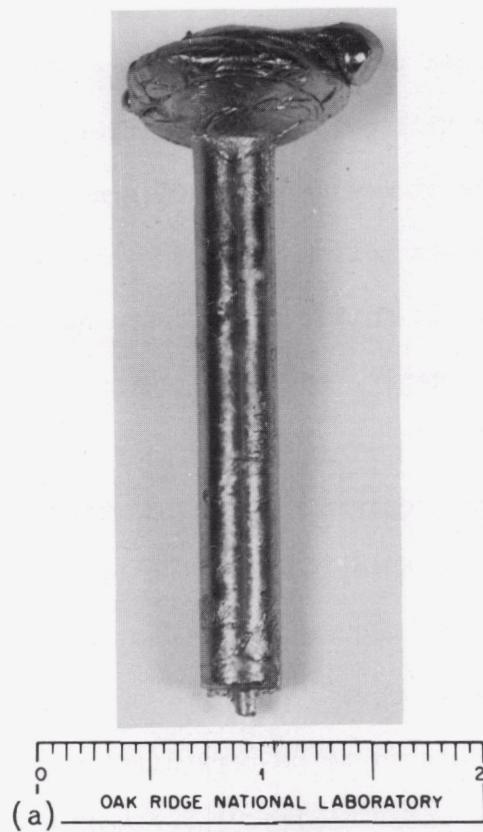


Figure 13. Typical castings. (a) Drop-casting. (b) Finger-casting.

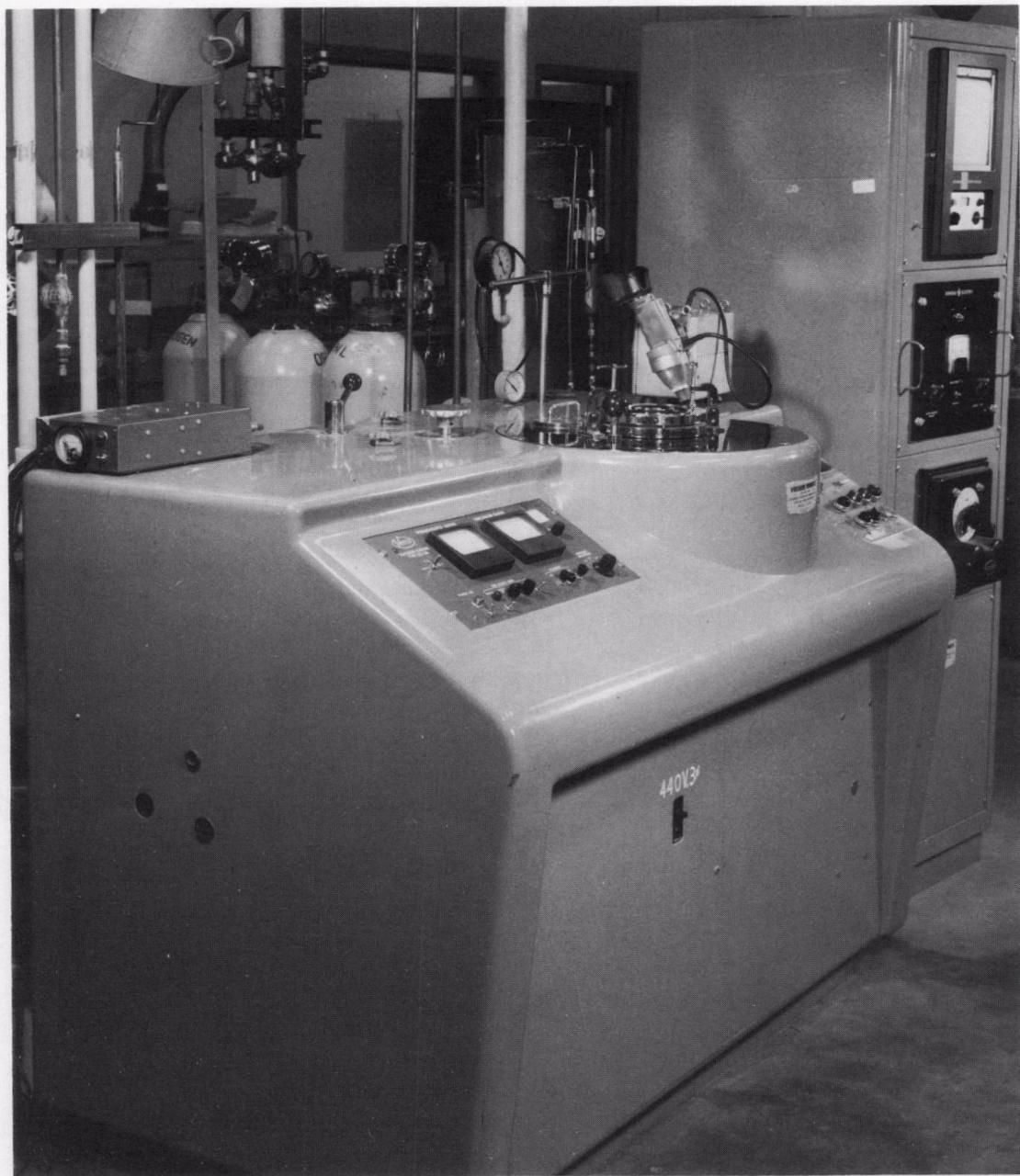


Figure 14. High-temperature tungsten-mesh heating element furnace used for anneals above  $1000^{\circ}\text{C}$ . and for synthesis of the mononitrides.

synthesized by successively hydriding, dehydriding, nitriding to the higher nitrides, and vacuum decomposition to the mononitrides, as shown in the flow diagram of Figure 15. The product of the synthesis was a fairly coarse powder which was crushed to pass a 325-mesh screen for incorporation into two- and three-phase alloy pellets, for x-ray analysis, and for chemical analysis.

The pellets which were prepared to investigate the two- and three-phase regions of the diagram were made using -325-mesh powders of the nitrides above, -325-mesh uranium powder from the same stock as used in the carbon alloys, and commercially prepared -325-mesh thorium powder. The thorium powder was of greater than 99.1 weight per cent purity as can be seen from the impurity analysis given in Table V of Appendix A.

The appropriate amounts of powder were weighed out, blended for sixty minutes in individual one-half-ounce bottles in an oblique blender and pressed at 25,000 pounds per square inch in a one-half-inch diameter die using stearic acid lubricant. A flow sheet showing these operations appears as Figure 16. All operations were carried out under an argon atmosphere.

#### Chemical Analysis

During the initial stages of these experiments there was concern that copper and tungsten contamination would be significant in the carbon alloys. Spectrographic and neutron activation analysis of a number of castings, however, showed the copper content to be less than 10 parts per million and the tungsten level to be 10 to 130 parts per million by weight. Vacuum fusion analyses were performed to determine oxygen,

## SYNTHESIS OF (Th,U)N

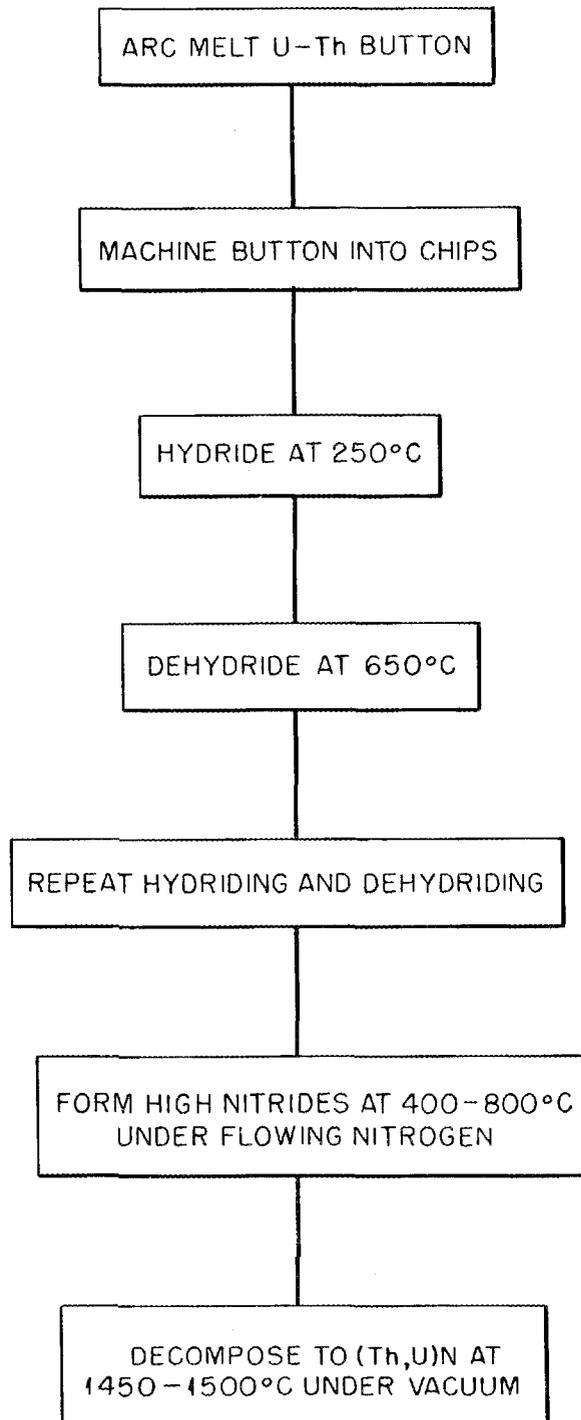


Figure 15. Flow diagram for the synthesis of (Th,U)N alloys.

## PROCESS FOR 2-AND 3-PHASE Th-U-N PELLETS

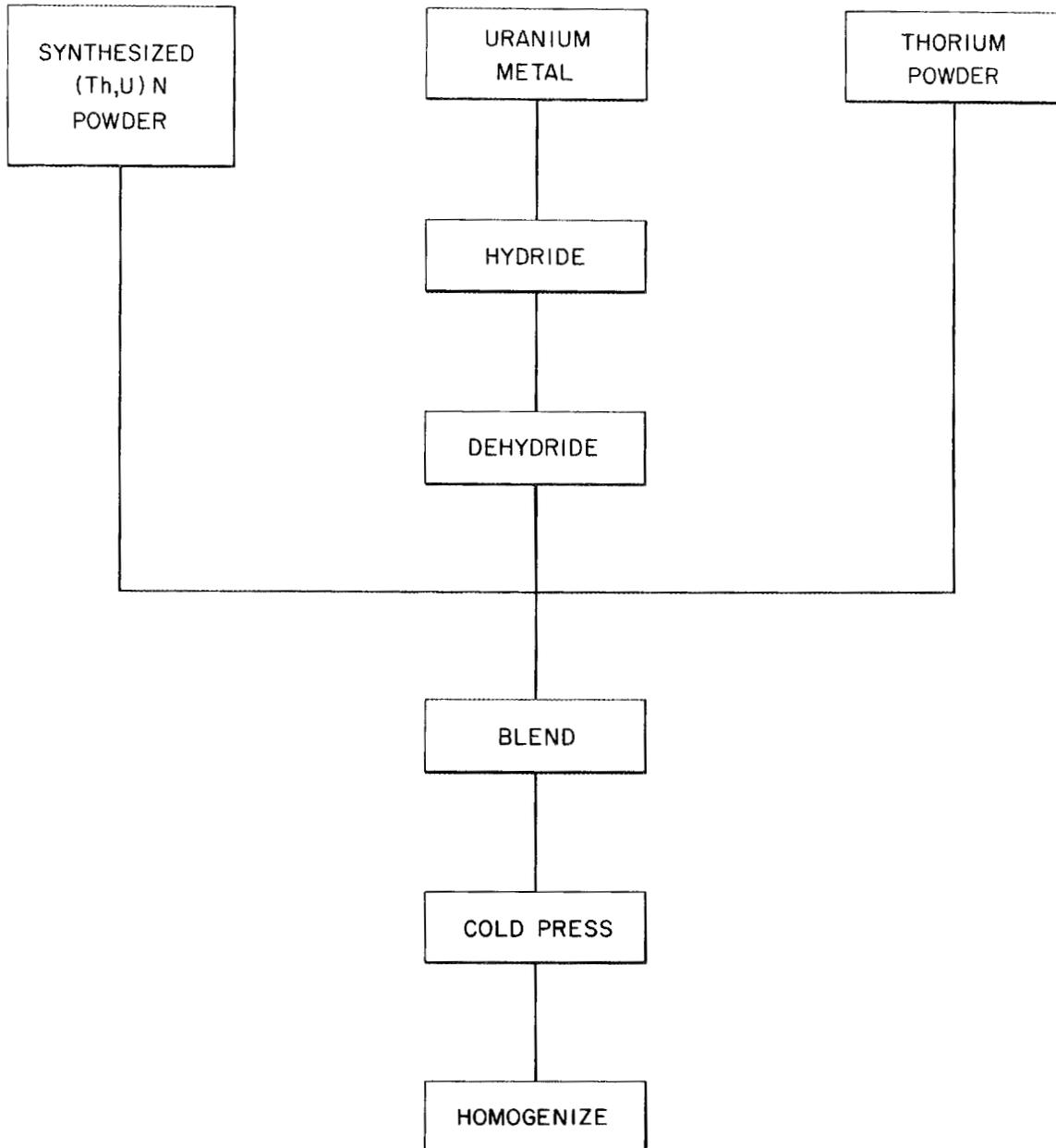


Figure 16. Flow diagram for the preparation of two- and three-phase Th-U-N alloys.

nitrogen, and hydrogen levels in the cast (Th,U)C alloys. There was a wide variation in the amount of these species found in various castings; typical ranges are listed below.

<u>Element</u>	<u>Range, Parts Per Million by Weight</u>
Oxygen	500-1500
Nitrogen	100-1000
Hydrogen	5-50

The effect of these impurities on the results will be discussed in a later section.

It became apparent early in the investigation that the available techniques for carbon analysis were not sufficiently accurate to establish the stoichiometry of the (Th,U)C alloys. This observation agrees with that of Bourgette (68) and that of Chiotti and White (69). It was found that carbon analyses were lower than expected by from 0.05 to 0.20 weight per cent. Rather than develop a technique for carbon analysis, which was not the purpose of the investigation, the techniques of Bourgette (68) have been used and the stoichiometry defined according to the proportions charged to the arc-melting furnace. There has been no evidence, during the course of these investigations, which suggests that this approach is not valid.

It was also found that, as in the case of the carbon alloys, the available chemical analysis techniques did not give results which were precise enough to define the stoichiometry of the nitride alloys. A material balance on the arc-melted Th-U buttons showed, however,

that the desired thorium-to-uranium atom ratio was achieved within plus or minus 0.8 per cent. Because of the control of the thorium-to-uranium ratio and the fact that higher nitrides of uranium and thorium decompose to pure mononitride during vacuum annealing (26,52,54,60,70,71) we are confident that the nominal compositions of our alloys are correct within plus or minus one atomic per cent. The principal contaminant in the nitride alloys was oxygen, the extent and possible effects of which will be discussed in a later section.

#### Annealing

All anneals at temperatures above 1000°C. were performed in vacuum in the tungsten-mesh heating element furnace mentioned earlier. The temperatures in this furnace were measured by use of a manually operated optical pyrometer and were controlled by manual adjustment of the furnace power.

Those samples annealed at temperatures of 1000°C. and below were placed in resistance-heated vacuum furnaces. Temperatures were measured by Chromel-P-Alumel thermocouples through time-proportioning controllers. All anneals were performed in a vacuum of approximately  $10^{-5}$  torr, in flowing, high-purity argon, or in a static partial pressure (approximately 5 inches of mercury) of high-purity argon.

#### X-Ray Diffraction

Samples for x-ray diffraction were crushed in a hardened steel mortar until the entire sample passed a 325-mesh screen. The crushed material was placed in a 0.3-millimeter-inside diameter lithium-glass

capillary which was then removed from the argon-filled glove box and quickly sealed with a match flame.

X-ray patterns were obtained with a North American Philips 114.59-millimeter diameter Debye-Scherrer camera using Straumanis film mounting and copper radiation ( $\lambda K_{\alpha_1} = 1.54051$  angstroms,  $\lambda K_{\alpha_2} = 1.54433$  angstroms,  $\lambda K_{\alpha} = 1.54178$  angstroms,  $\lambda K_{\beta} = 1.39217$  angstroms). The powder patterns were measured using a conventional North American Philips film reader and an auxiliary table-mounted 5X magnifier. The back-reflection region of the film was measured and where practical, in the single-phase alloys, unfiltered radiation was used.

In the interest of accuracy and speed in analyzing these films, use was made of the computer code developed by Vogel and Kempter (72) as modified by Godfrey and Leitnaker (73). This program utilizes the measured diameter of the back-reflection rings, and using the extrapolation parameter of Nelson and Riley (74), calculates the best value of the lattice parameter, the standard deviation of the lattice parameter, and errors in the measured ring diameter.

#### Metallographic Preparation

To avoid oxidation, samples were transferred from the argon-filled glove box to the metallographic specimen preparation area under mineral oil or alcohol. The general outline of the metallographic preparation was as follows.

The samples were washed in alcohol to remove all traces of the mineral oil and then incorporated into standard 1 1/4-inch diameter metallographic mounts using room-temperature setting epoxy resin.

Grinding was done on an eight-inch diameter grinding wheel with successively finer grits of silicon carbide paper (180 to 600 grit) using silicone oil or absolute, anhydrous ethyl alcohol as a vehicle. The final polish was obtained using a vibratory polisher with nylon cloth and a slurry of 0.3-micron  $\text{Al}_2\text{O}_3$  abrasive. The vehicle in the case of (Th,U)C alloys was made up of 500 cubic centimeters of water plus 10 cubic centimeters of chromic acid plus 10 cubic centimeters of a saturated solution of sodium dichromate. For Th-U-C and Th-U-N alloys the vehicle was silicone oil. Various etching solutions were tried and the most successful one for (Th,U)C proved to be thirty parts (by volume) nitric acid plus thirty parts acetic acid plus thirty parts water. Thorium-uranium-carbon alloys were electroetched with a solution containing fifty parts acetic acid plus fifty parts phosphoric acid at ten volts direct current for five to ten seconds using a stainless steel cathode. Thorium-uranium-nitrogen alloys were etched in sixty parts lactic acid plus thirty parts nitric acid plus two parts hydrofluoric acid. The metallographic samples were examined using both bright field and polarized light illumination.

The as-polished and etched alloys are susceptible to room-temperature oxidation and become increasingly sensitive to the atmosphere as the thorium content increases. It was also noted that (Th,U)C alloys which had not been annealed sufficiently to bring about both homogenization and recrystallization were extremely susceptible to reaction with the atmosphere.

## CHAPTER IV

### EXPERIMENTAL RESULTS AND DISCUSSION

#### Equilibrium Anneals

As-cast samples of (Th,U)C alloys were annealed at 1800°C. to remove coring and quenching strains. Anneals ranging from 72 to 216 hours were necessary in order to produce Debye-Scherrer films of good quality.

Originally it was intended that the 600, 800, and 1000°C. isotherms for the Th-U-C system would be investigated. These alloys reached equilibrium at 1000°C. in 240 to 350 hours, as indicated by the value of the lattice parameter of the (Th,U)C phase. Figure 17 is a plot demonstrating how four of these alloys equilibrated. Anneals of 1000 hours at 600 and 800°C. failed, however, to produce equilibrium. The goal of determining these isotherms in a reasonable length of time was, therefore, abandoned.

The vacuum decomposition of the higher nitrides at 1500°C. to form (Th,U)N alloys was found to produce strain-free material which did not require further annealing.

Pellets which were prepared to give alloy compositions across the Th-U-N isotherm were annealed for 100 to 200 hours at 1000°C. As can be seen from Figure 18 these times are sufficient to produce equilibrium.

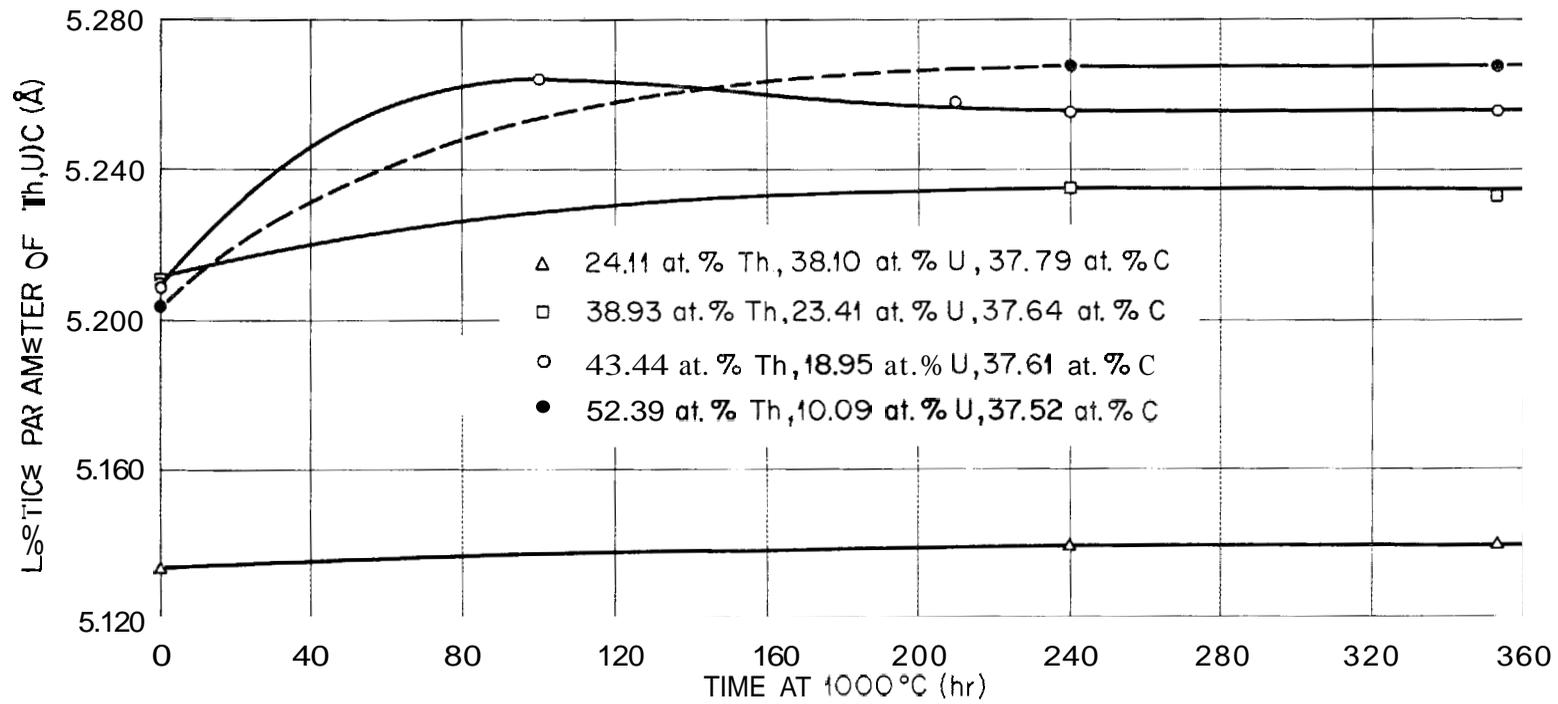


Figure 17. Lattice parameter of the (Th,U)C phase versus annealing time at 1003°C. for four Th-U-C alloys.

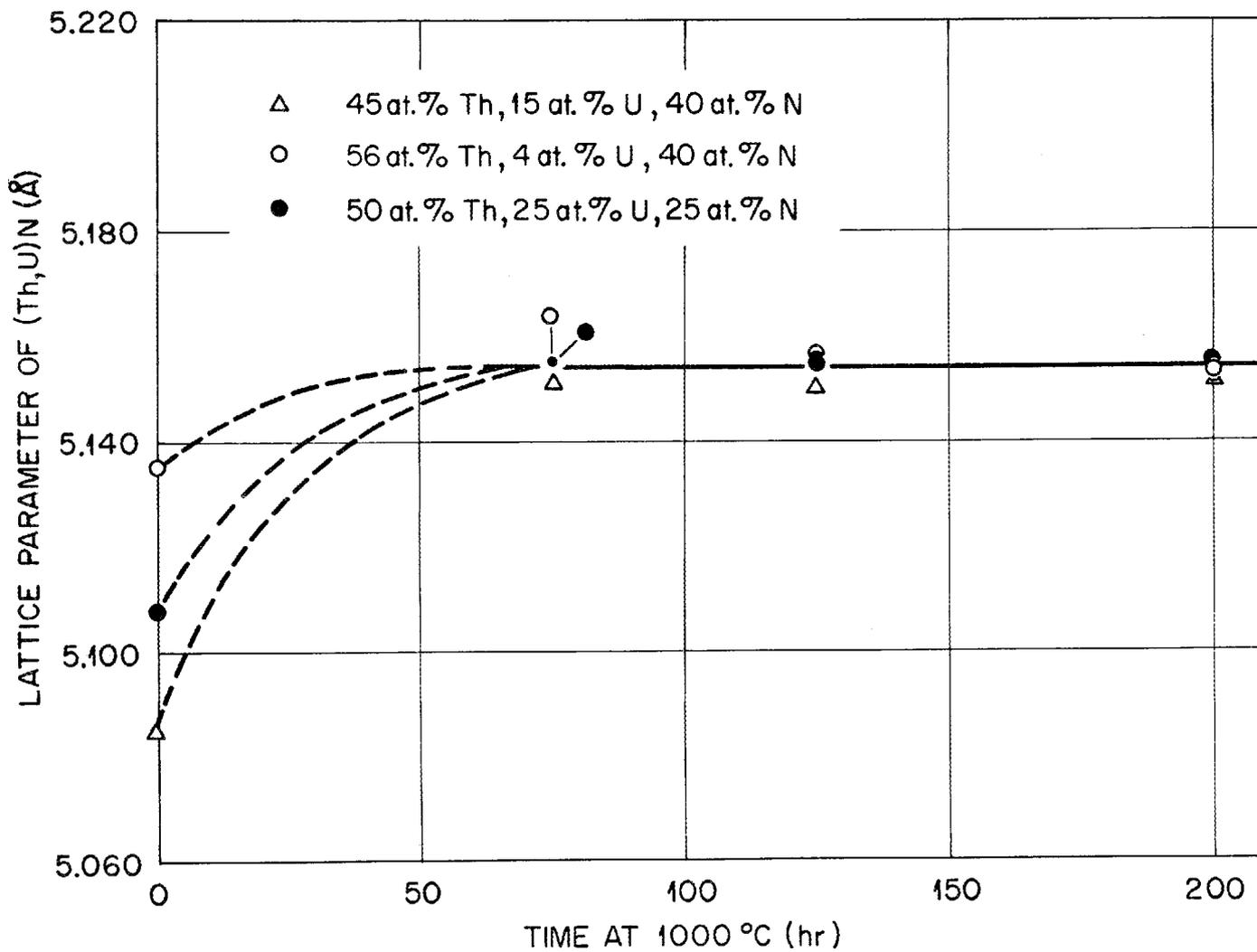


Figure 18. Lattice parameter of the (Th,U)N phase versus annealing time at 1000°C. for three Th-U-N alloys.

Lattice Parameters of (Th,U)C and (Th,U)N

Lattice parameters across the UC-ThC pseudobinary have been plotted in Figure 19. The nominal compositions of these alloys, their lattice parameters, and the standard deviation of the lattice parameter are listed in Table VI of Appendix B. Note that there is a slightly negative deviation from Vegard's law in these data. The agreement between these data and those of earlier investigators (67,75,76) is quite good as can be seen from Figure 20. The data from the present investigation show the greatest deviation from Vegard's law.

As was mentioned earlier, the major contaminants in these (Th,U)C alloys were oxygen and nitrogen. The maximum levels found were 1500 parts per million oxygen and 1000 parts per million nitrogen.

The change in the lattice parameter of UC due to oxygen and nitrogen substitution for carbon has been investigated by Stoops and Hamme (77), by Magnier and co-workers (35), and by Magnier (36). The latter two investigations are of more interest here since they deal with oxygen and nitrogen levels of the magnitude found in these samples. According to these investigators one might expect 1500 parts per million oxygen contamination to increase the lattice parameter of (Th,U)C by about 0.03 per cent while 1000 parts per million nitrogen may decrease the lattice parameter by 0.0009 per cent. Changes of these magnitudes are of the same order as the experimental error for the present measurements of the lattice parameters and have been neglected.

A plot of lattice parameters across the pseudobinary UN-ThN is shown as Figure 21. The agreement with Vegard's law is seen to be quite

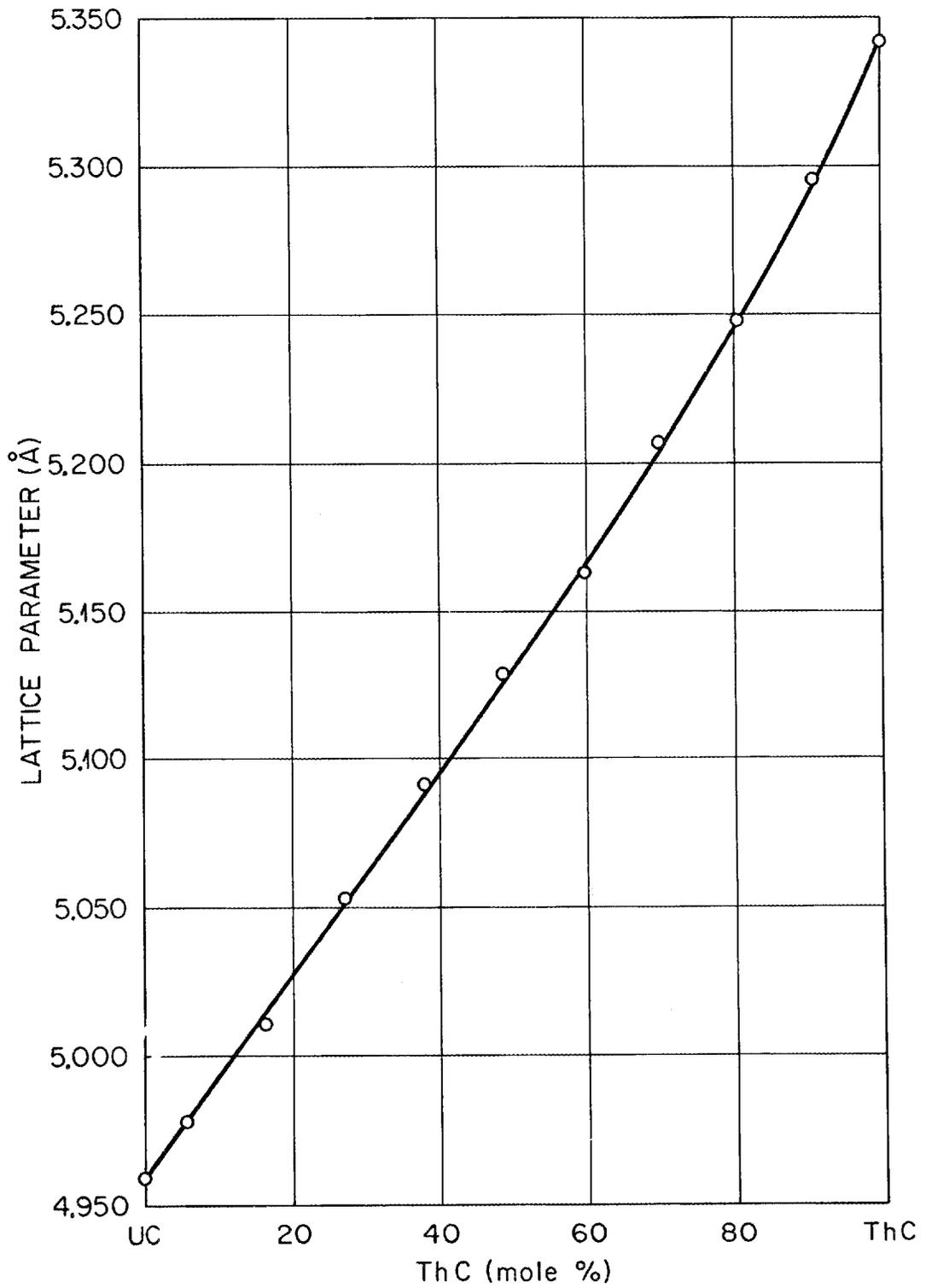


Figure 19. Lattice parameters of (Th,U)C across UC-ThC pseudobinary.

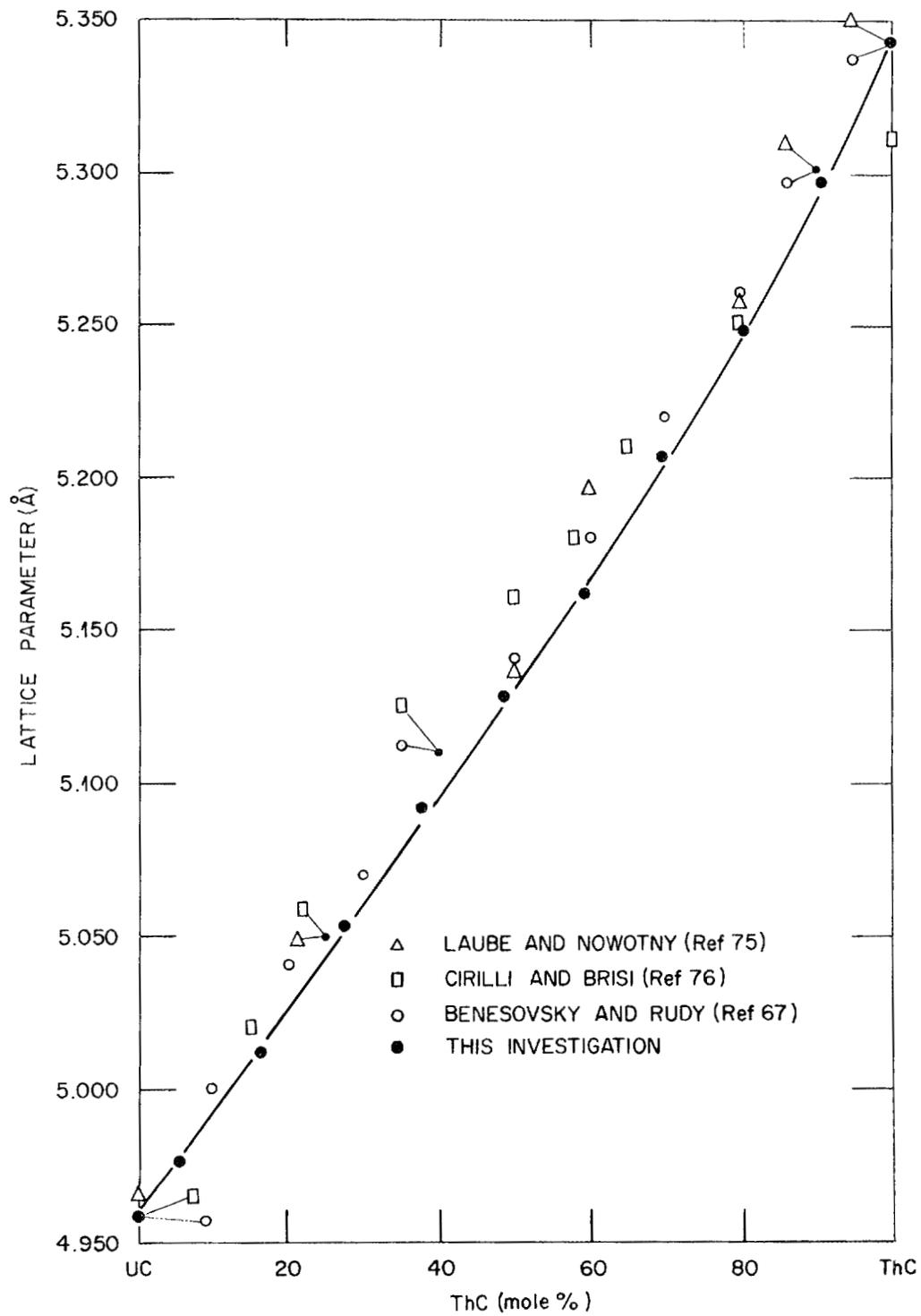


Figure 20. Lattice parameters of (Th,U)C across the UC-ThC pseudo-binary according to the literature compared with this investigation.

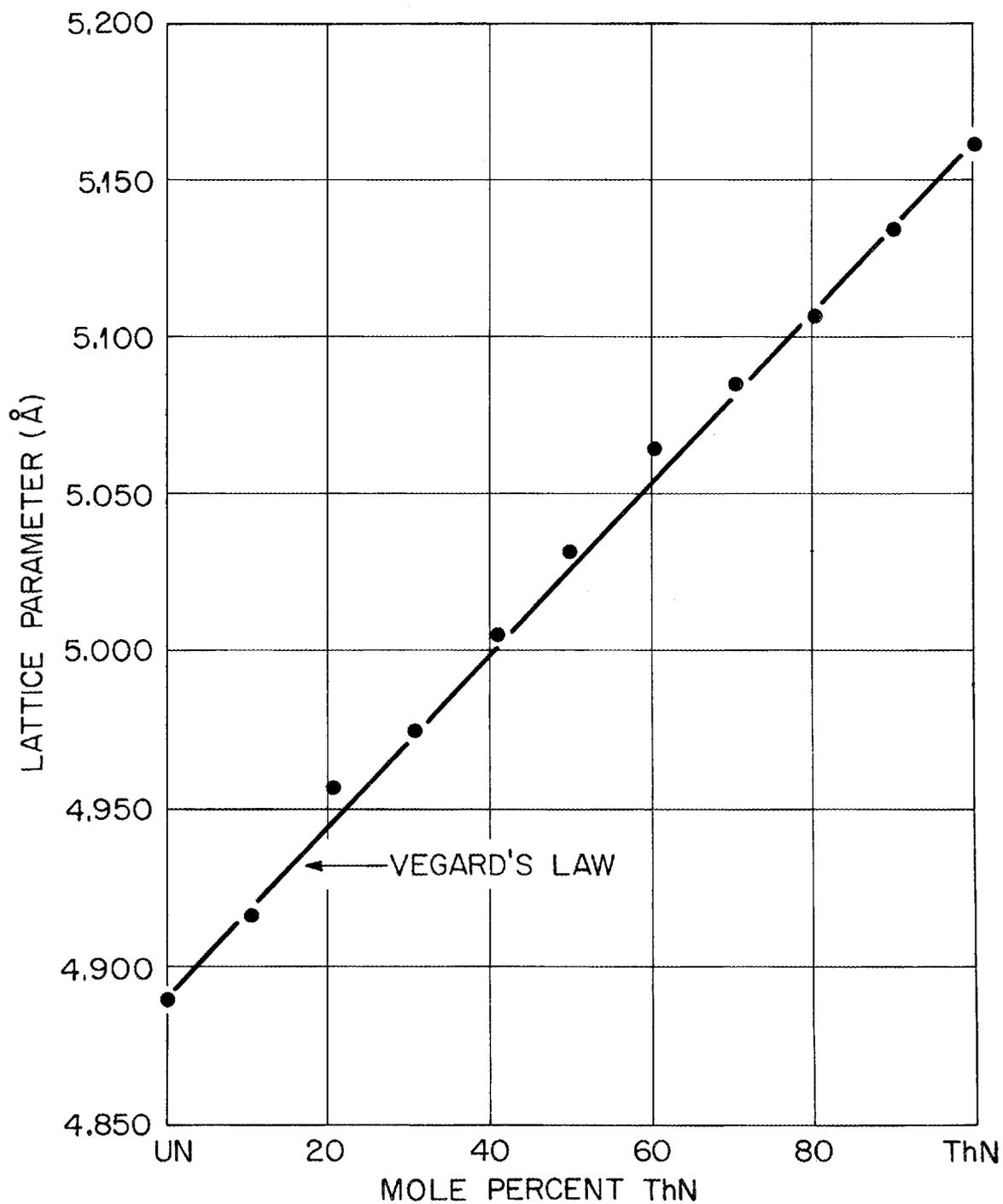


Figure 21. Lattice parameters of (Th,U)N across the UN-ThN pseudobinary.

good. Table VII of Appendix B gives the nominal compositions of these alloys, their lattice parameters and the standard deviation of the lattice parameters.

The major contaminant in these alloys was found to be oxygen. The 40.60 mole per cent ThN alloy, containing the greatest amount of oxygen (less than 1 weight per cent) gave one of the poorest x-ray patterns and showed ThO<sub>2</sub> lines. The remainder of the (Th,U)N alloys contained less than 0.5 weight per cent oxygen and did not show ThO<sub>2</sub> lines. The lack of CuK<sub>α1</sub>-K<sub>α2</sub> doublet separation in some of these alloys accounts for the large standard deviation of the lattice parameters.

The agreement between the lattice parameter measurements for the UN and ThN of this investigation and values reported in the literature (47,52,54,55,58,60,61) leads one to conclude that the lattice parameters across the UN-ThN pseudobinary are little affected by less than 1.0 weight per cent oxygen contamination.

#### Partial Ternary Isotherms

Recalling Figure 9, page 16, it is seen that in moving from the U-X limiting binary across the ternary isotherm one expects to pass through a two-phase region, a three-phase region, and finally a second two-phase region. For both the carbon and the nitrogen systems two series of alloys were prepared across the isotherm at constant carbon or nitrogen levels. As expected, based on Figures 19, page 35, and 21, page 37, the lattice parameter of the (Th,U)X phase continually increases across the uranium plus (Th,U)X two-phase region. On reaching the three-phase region, thorium plus uranium plus (Th,U)X, the lattice parameter of

(Th,U)X remains essentially constant and then rises again as the thorium plus (Th,U)X two-phase region is entered. The nominal compositions of these alloys, the lattice parameter of the (Th,U)X phase in each alloy, the standard deviation of the lattice parameter, and the phases observed are given in Tables VIII and IX of Appendix C. The major phases present in these alloys were determined using an x-ray diffractometer on metallographic samples, the front-reflection lines in the Debye-Scherrer patterns, and metallographic examination under an optical microscope.

The position of each alloy on the ternary isotherm and the lattice parameter of that alloy's (Th,U)C phase are plotted in Figure 22 for the Th-U-C system. Similarly, Figure 23 indicates the major phases identified in these alloys. In addition, most of these alloys showed weak ThO<sub>2</sub> lines in their x-ray patterns; however, ThO<sub>2</sub> was not identified by optical metallography.

The phase boundaries in these figures, representing the equilibrium 1000°C. partial ternary isotherm for the Th-U-C system, were established using the present data and data previously cited from the literature concerning composition ranges and solid solubilities. In addition to this information a point-count analysis for phase distribution was made on the nominal 69.55 atomic per cent thorium, 7.66 atomic per cent uranium, 22.79 atomic per cent carbon alloy. An extrapolation of a constant lattice parameter value of 5.267 angstroms [the average value for (Th,U)C in the three-phase region] and the point-count analysis of the alloy mentioned established the terminal point of the three-phase region at the UC-ThC single-phase boundary at 52.8 atomic per cent thorium,



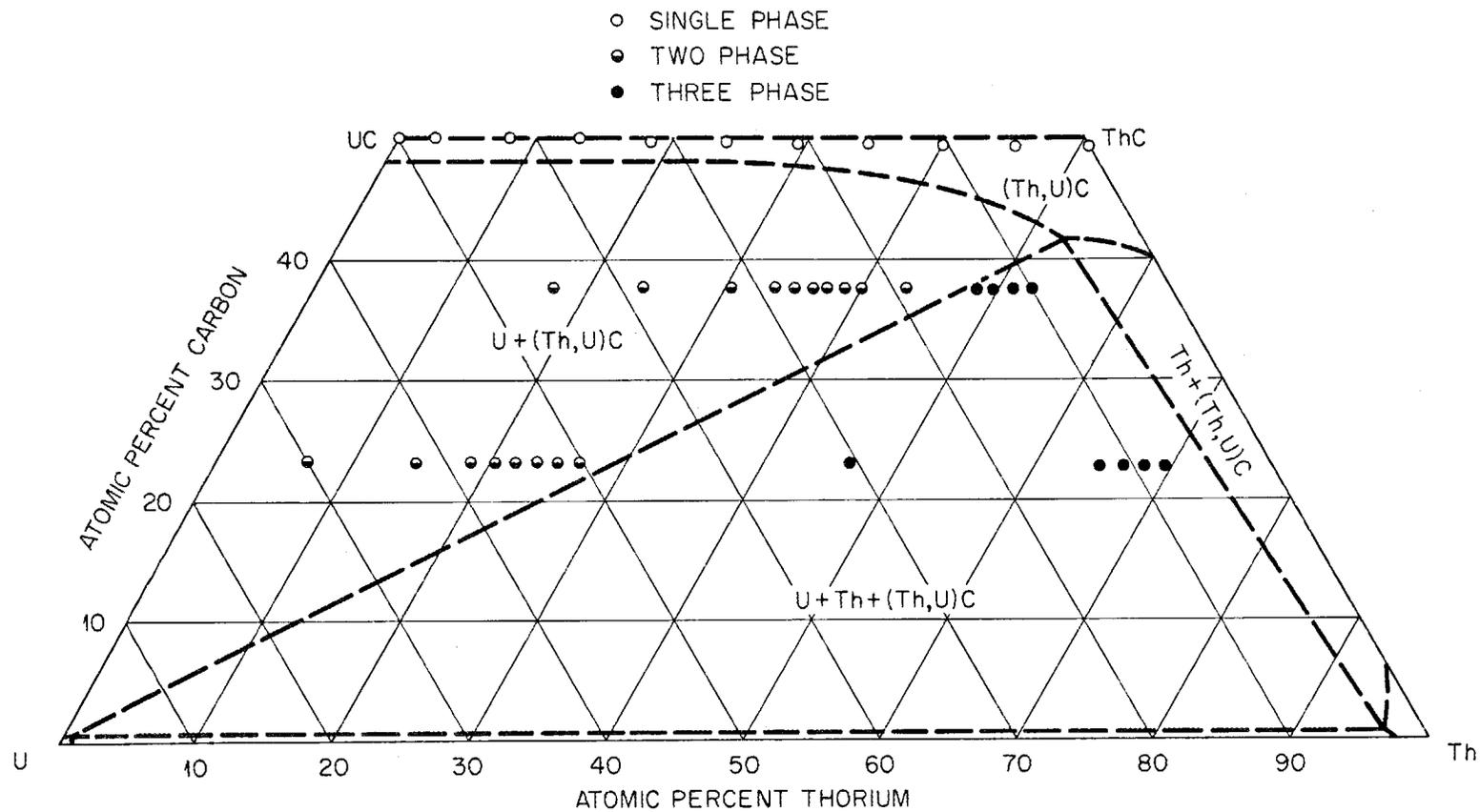


Figure 23. The equilibrium 1000°C. partial isotherm of the Th-U-C system showing alloys examined and the number of major phases identified by x-ray and metallographic examination.

5.5 atomic per cent uranium, and 41.6 atomic per cent carbon. The corresponding compound in the single-phase region is  $(\text{Th}_{0.906}, \text{U}_{0.094})\text{C}_{0.712}$ . This same analysis established the point at 96.63 atomic per cent thorium, 2.67 atomic per cent uranium, and 0.71 atomic per cent carbon as the terminal point of the three-phase region at the thorium single-phase boundary. Solubilities at the pure uranium corner of the diagram are quite low, as can be seen from the figures, and the composition 0.6 atomic per cent thorium, 99.0 atomic per cent uranium, and 0.4 atomic per cent carbon was assumed to be the third corner of the three-phase region.

Figures 24 and 25 show Th-U-N system alloy compositions, their (Th,U)N phase lattice parameters, and the major phases present as determined by metallographic and x-ray examination. The phase boundaries shown are based on previously cited solubility data and the information presented in the figures. In this case, the terminal point of the three-phase region occurs at 50.5 atomic per cent thorium, 3.0 atomic per cent uranium, and 46.5 atomic per cent nitrogen. The corresponding compound is  $(\text{Th}_{0.944}, \text{U}_{0.056})\text{N}_{0.869}$ . Oxidation of these samples was a problem even when the pellets were wrapped with tantalum foil and subsequently vacuum (approximately  $10^{-5}$  torr) sealed in quartz for homogenization. Oxides were not identified by optical microscopy though most samples showed weak  $\text{ThO}_2$  lines in their x-ray patterns. Chemical analysis indicated that the oxygen contents were of the order of one weight per cent.

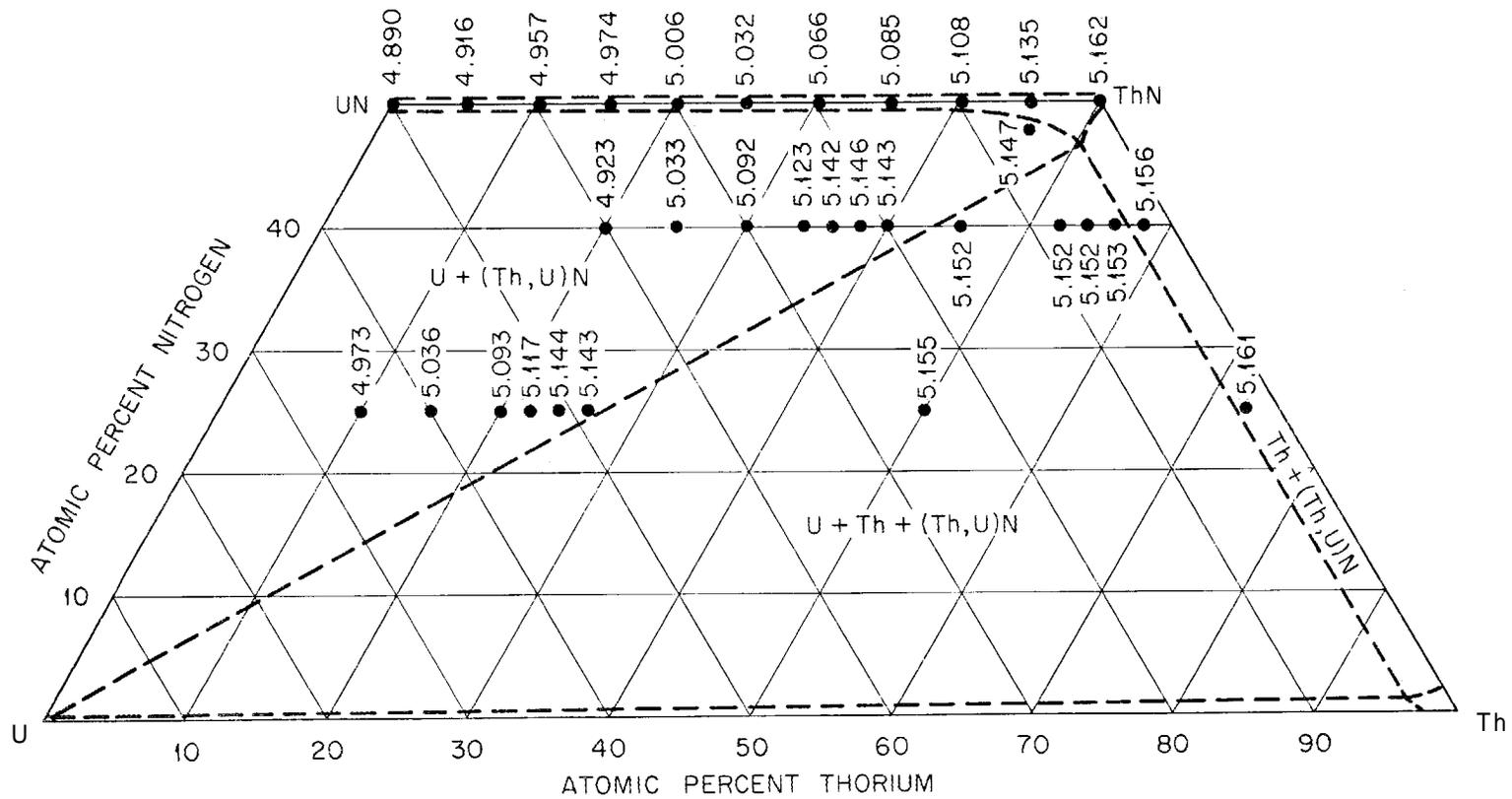


Figure 24. The equilibrium 1000°C. partial isotherm of the Th-U-N system showing alloys examined and the lattice parameter of their (Th,U)N phase.

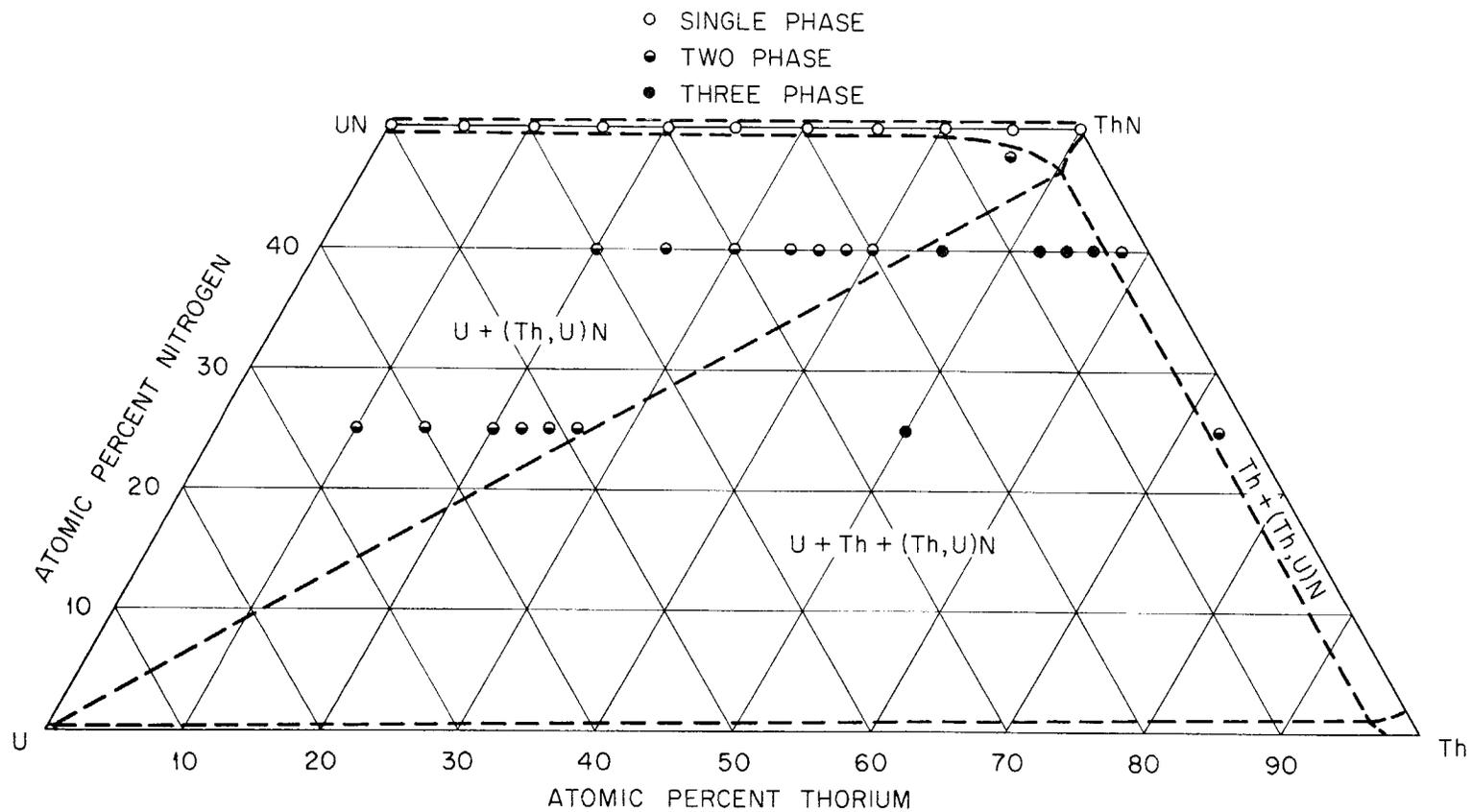


Figure 25. The equilibrium 1000°C. partial isotherm of the Th-U-N system showing alloys examined and the number of major phases identified by x-ray and metallographic examination.

### Thermodynamic Calculations

As was mentioned in the introduction, Rudy (9) has given a thermodynamic analysis of ternary isotherms of the kind found in this investigation. The treatment is as follows.

By definition, the partial molal free energy of component  $i$ ,  $\bar{G}_i$ , at a particular temperature, pressure, and composition is

$$\bar{G}_i \equiv \left( \frac{\partial G'}{\partial n_i} \right)_{T, P, n_j} \quad (1)$$

where  $G'$  is the free energy of the solution containing  $n_A$  moles of component A,  $n_B$  moles of component B, et cetera. It is easily shown (78) that

$$G' = \bar{G}_A n_A + \bar{G}_B n_B + \dots \quad (2)$$

The free energy of the solution per mole,  $G$ , is given by

$$G \equiv \frac{G'}{n_A + n_B + \dots} \quad (3)$$

and, hence,

$$G = \bar{G}_A X_A + \bar{G}_B X_B + \dots, \quad (4)$$

where  $X_i$  is the mole fraction of component  $i$  in the solution. We may also write (78)

$$\bar{G}_i = RT \ln a_i + \dot{G}_i, \quad (5)$$

where  $\dot{G}_i$  is the free energy per gram-atom of the pure component  $i$  and  $a_i$  is the activity of component  $i$  in the solution. Combining the latter two expressions one obtains

$$G = X_A(RT \ln a_A + \dot{G}_A) + X_B(RT \ln a_B + \dot{G}_B) + \dots \quad (6)$$

Assuming ideal solution conditions for a binary system equation 6 becomes

$$G_{(A,B)} = \dot{G}_A + X_B(\dot{G}_B - \dot{G}_A) + RT(X_A \ln X_A + X_B \ln X_B) \quad (7)$$

By analogy, in the BC-AC pseudobinary we may write

$$G_{(A,B)C} = \Delta G_{AC} + X_{BC}(\Delta G_{BC} - \Delta G_{AC}) + RT(X_{AC} \ln X_{AC} + X_{BC} \ln X_{BC}) \quad (8)$$

where  $G_{(A,B)C}$  is the free energy per gram-atom of a BC-AC solid solution,  $\Delta G_{AC}$  and  $\Delta G_{BC}$  are free energies of formation of the pure compounds AC and BC and  $X_{AC}$  and  $X_{BC}$  are mole fractions of those compounds.

Differentiating equation 7 with respect to  $X_B$  and equation 8 with respect to  $X_{BC}$  gives equation 9 and 10 below.

$$\frac{\partial G_{(A,B)}}{\partial X_B} = (\dot{G}_B - \dot{G}_A) + RT \ln \frac{X_B}{X_A} \quad (9)$$

$$\frac{\partial G_{(A,B)C}}{\partial X_{BC}} = (\Delta G_{BC} - \Delta G_{AC}) + RT \ln \frac{X_{BC}}{X_{AC}} \quad (10)$$

Rudy (79) has shown that in the rather special case of equilibrium between A, B, and the compound (A,B)C

$$\left[ \frac{\partial G_{(A,B)}}{\partial X_B} \right]_{T,P} = \left[ \frac{\partial G_{(A,B)C}}{\partial X_{BC}} \right]_{T,P} \quad (11)$$

This being the case equation 9 is subtracted from equation 10 to give, on rearranging terms,

$$RT \ln \frac{X_B}{X_A} \frac{X_{AC}}{X_{BC}} = (\Delta G_{BC} - \Delta G_{AC}) - (\dot{G}_B - \dot{G}_A) \quad (12)$$

The two systems Th-U-C and Th-U-N show very small solid solubilities of the metals in one another while the monocarbides and mononitrides exhibit complete solid solubility.

This being the case, equation 7 may be written as

$$G_{(A,B)} = \dot{G}_A + X_B (\dot{G}_B - \dot{G}_A) \quad (13)$$

Differentiating with respect to  $X_B$ ,

$$\frac{\partial G_{(A,B)}}{\partial X_B} = (\dot{G}_B - \dot{G}_A) \quad (14)$$

Equations 10, 11, and 14 now give

$$RT \ln \frac{X_{BC}}{X_{AC}} = (\dot{G}_B - \dot{G}_A) - (\Delta G_{BC} - \Delta G_{AC}) \quad (15)$$

Using specific heat data from the literature Rudy (9) has calculated

$$\begin{aligned}\dot{G}_{\text{Th}}^{1000} &= -21,490 \text{ calories/gram-atom, and} \\ \dot{G}_{\text{U}}^{1000} &= -21,558 \text{ calories/gram-atom.}\end{aligned}$$

These values are essentially equal, considering the uncertainty in this kind of data, and thus the quantity  $(\dot{G}_{\text{Th}} - \dot{G}_{\text{U}})$  in equation 15 can be neglected.

The relationship which results,

$$RT \ln \frac{X_{\text{ThC}}}{1 - X_{\text{ThC}}} = (\Delta G_{\text{UC}} - \Delta G_{\text{ThC}}), \quad (16)$$

allows one to estimate the composition of the (Th,U)C phase in equilibrium with thorium and uranium. If we now define the quantity

$$\beta_{\text{C}} \equiv \frac{X_{\text{ThC}}}{X_{\text{UC}}}, \quad (17)$$

where  $X_{\text{ThC}}$  and  $X_{\text{UC}}$  are mole fractions in the UC-ThC solid solution it follows that

$$\beta_{\text{C}} = \frac{X_{\text{Th}}}{X_{\text{U}}}, \quad (18)$$

where  $X_{\text{Th}}$  and  $X_{\text{U}}$  are atom fractions in the terminal compound  $(\text{Th}_x, \text{U}_{1-x})\text{C}_y$ . This compound has been determined to be  $(\text{Th}_{0.906}, \text{U}_{0.094})\text{C}_{0.712}$  as previously discussed. Equation 16 can be rewritten as

$$RT \ln \beta_{\text{C}} = (\Delta G_{\text{UC}} - \Delta G_{\text{ThC}}) \quad (19)$$

and by substituting  $\beta_C = 9.64$  at  $1000^\circ\text{C}$ . we find

$$(\Delta G_{\text{UC}}^{1000} - \Delta G_{\text{ThC}}^{1000}) = 5745 \text{ calories/gram-mole.}$$

McIver (80) has determined, using a galvanic cell, the free energy of formation of UC as a function of temperature and Langer (81) gives an estimate of the same quantity for ThC. Using these data one obtains

$$\Delta G_{\text{UC}}^{1000} = -22,000 \text{ calories/gram-mole,}$$

$$\Delta G_{\text{ThC}} = -25,290 \text{ calories/gram-mole,}$$

$$(\Delta G_{\text{UC}}^{1000} - \Delta G_{\text{ThC}}^{1000}) = 3290 \text{ calories/gram-mole.}$$

The agreement between the two independently determined values for  $(\Delta G_{\text{UC}}^{1000} - \Delta G_{\text{ThC}}^{1000})$  is considered to be good and offers evidence of consistency between the experiments and the thermodynamic analysis.

Since  $\Delta G_{\text{ThN}}^{1000}$  has not been experimentally determined, equation 16 can now be used to estimate its value. The calculation requires

$$RT \ln \beta_N = (\Delta G_{\text{UN}} - \Delta G_{\text{ThN}}), \quad (20)$$

where equation 20 is analogous to equation 19 and  $\beta_N$  is analogous to  $\beta_C$  defined above. The value for  $\Delta G_{\text{UN}}^{1000}$  can be obtained from the expression given by Rand and Kubaschewski (82),

$$\Delta G_{\text{UN}} = -70,000 + 20.5 T^\circ\text{K so that}$$

$$\Delta G_{\text{UN}}^{1000} = -43,900 \text{ calories/gram-mole.}$$

Substituting this value into equation 20 along with a value of 16.85 for  $\beta_N$  at 1000°C.,

$$\Delta G_{\text{ThN}}^{1000} = -51,900 \text{ calories/gram-mole .}$$

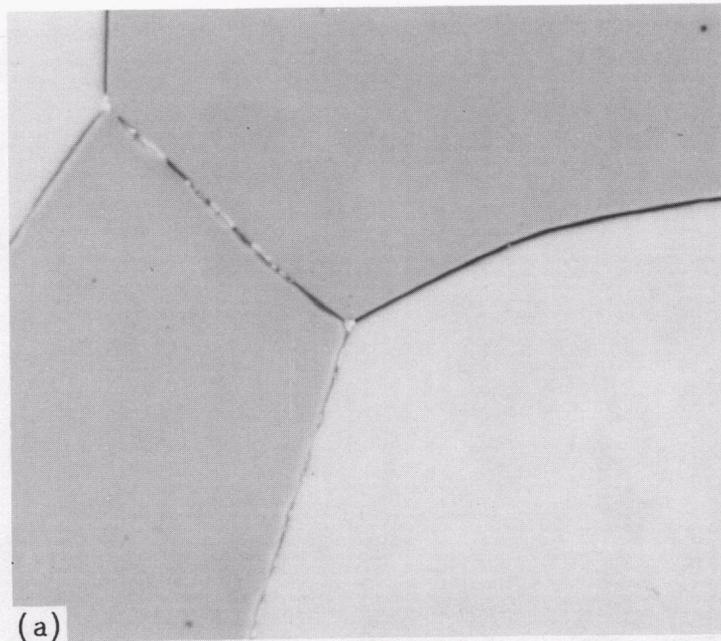
The various uncertainties associated with the value for  $\Delta G_{\text{UN}}^{1000}$  and the approximations associated with the thermodynamic analysis make the error in the estimated value of  $\Delta G_{\text{ThN}}^{1000}$  difficult to assess. We believe, however, that the estimated value is within plus or minus 5000 calories per gram-mole of the true value.

### Metallography

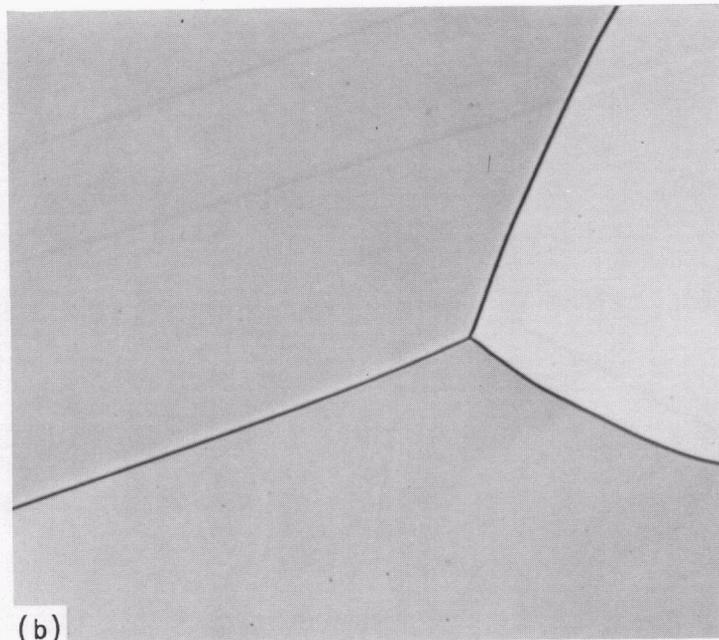
Photomicrographs of a number of the alloys examined in this investigation are presented as Figures 26 through 36 and while most are self-explanatory a few of the structures need amplification. Note that in order to properly show the structure, magnifications of 500 and 1000x have been used. Consequently the relative phase distribution seen in the photomicrographs must not be taken as typical of the entire sample.

During quenching from the melt free uranium is often formed in the grain boundaries of UC. Figure 26 illustrates the dissolution of the free uranium during an 1800°C. homogenization.

A particularly striking difference in alloy appearance can be seen by comparing Figures 26(b), 27(b), and 28(b) with Figures 27(a) and 28(a). The latter photomicrographs illustrate coring in the as-cast (Th,U)C alloys. This coring is revealed by the variation in etching response across a given grain. These alloys are quite beautifully



(a)



(b)

Figure 26. Alloy containing 50 atomic per cent uranium and 50 atomic per cent carbon. (a) As cast. Note the small amount of free uranium in the grain boundaries. 1000X. (b) Annealed at 1800°C. for 72 hours. 500X. Etchant: 30 parts  $\text{HNO}_3$ , 30 parts acetic acid, and 30 parts  $\text{H}_2\text{O}$ .

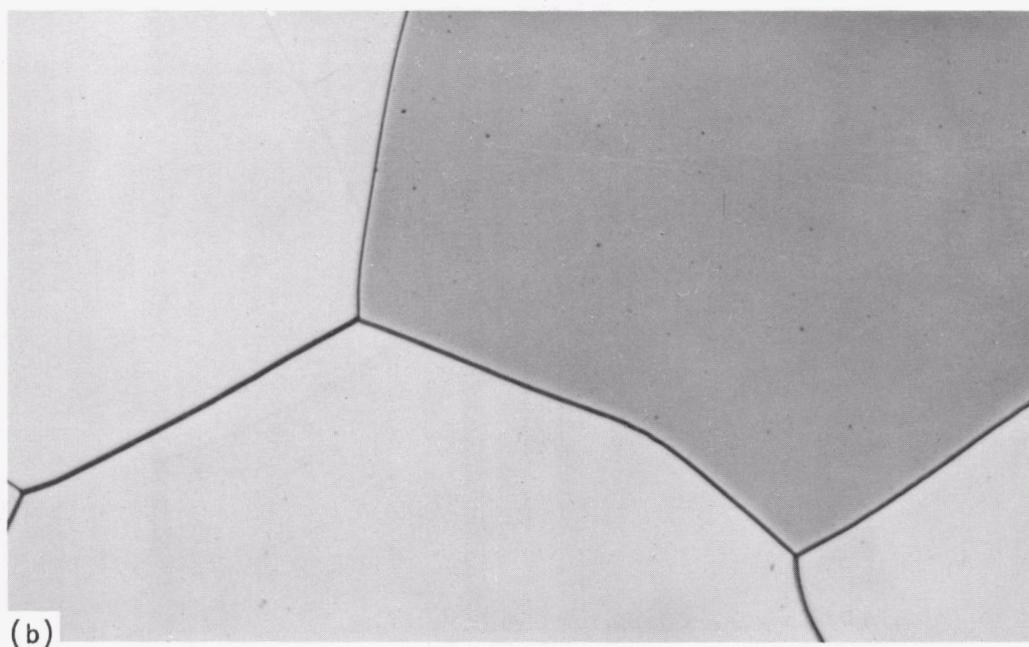
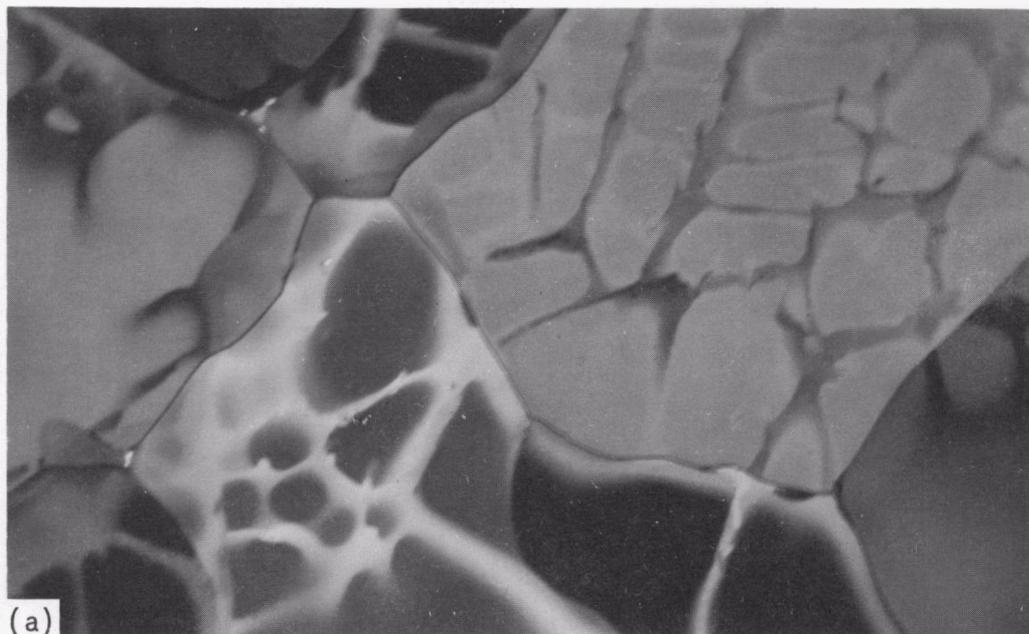


Figure 27. Alloy containing 2.80 atomic per cent thorium, 47.24 atomic per cent uranium, and 49.96 atomic per cent carbon. (a) As cast. 1000X. (b) Annealed at 1800°C. for 72 hours. 500X. Etchant: 30 parts  $\text{HNO}_3$ , 30 parts acetic acid, and 30 parts  $\text{H}_2\text{O}$ .

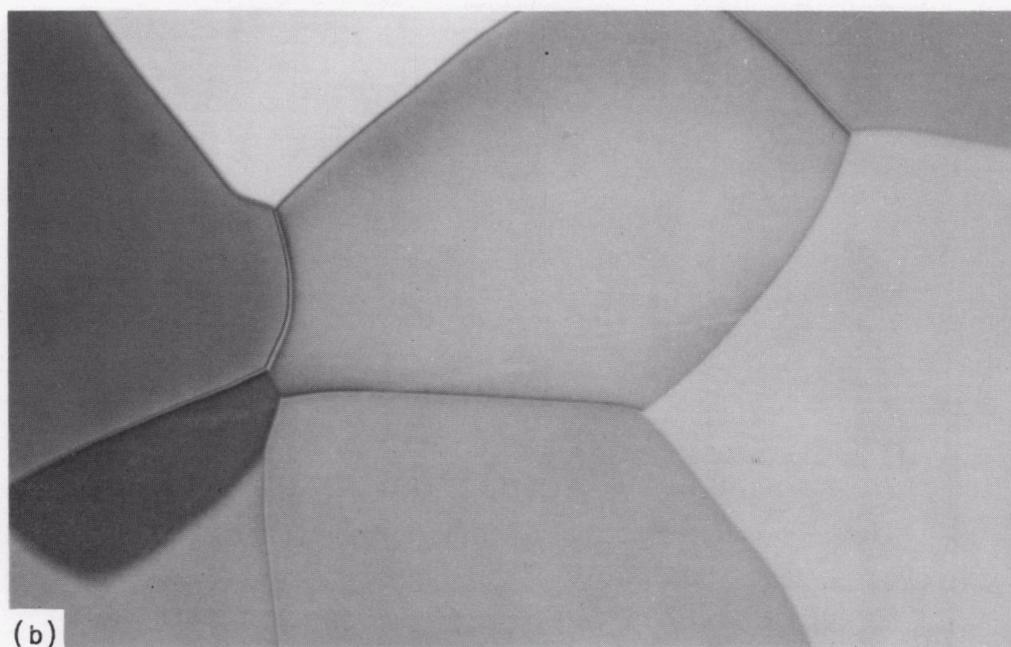
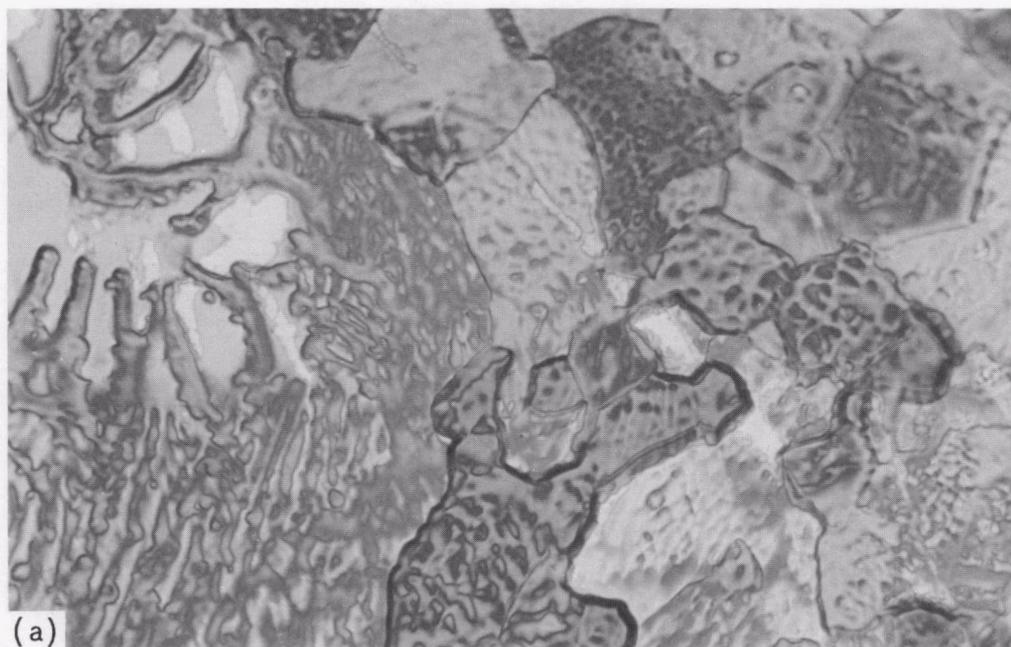


Figure 28. Alloy containing 29.52 atomic per cent thorium, 20.86 atomic per cent uranium, and 49.63 atomic per cent carbon. (a) As cast. (b) Annealed at 1800°C. for 216 hours. Etchant: 30 parts  $\text{HNO}_3$ , 30 parts acetic acid, and 30 parts  $\text{H}_2\text{O}$ . 1000X

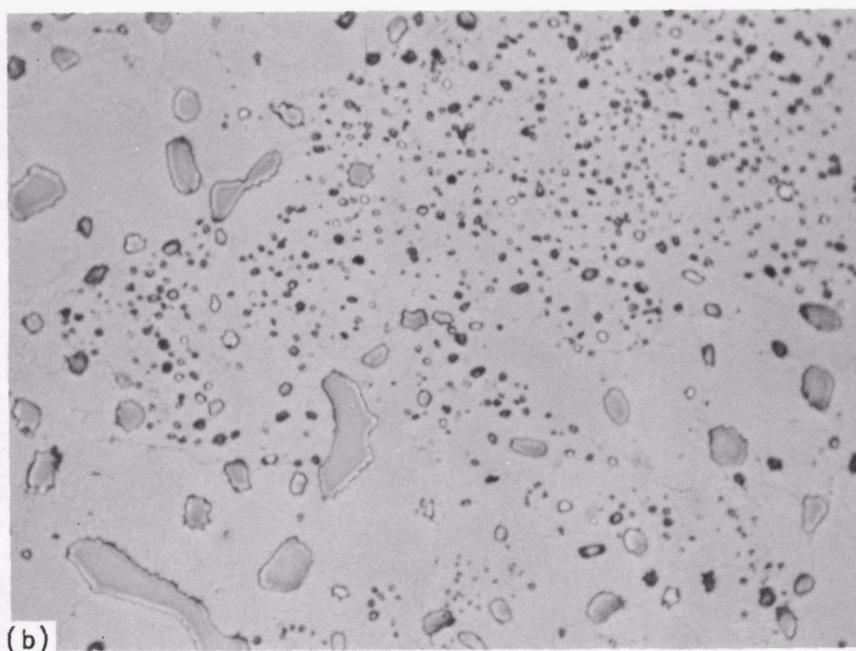
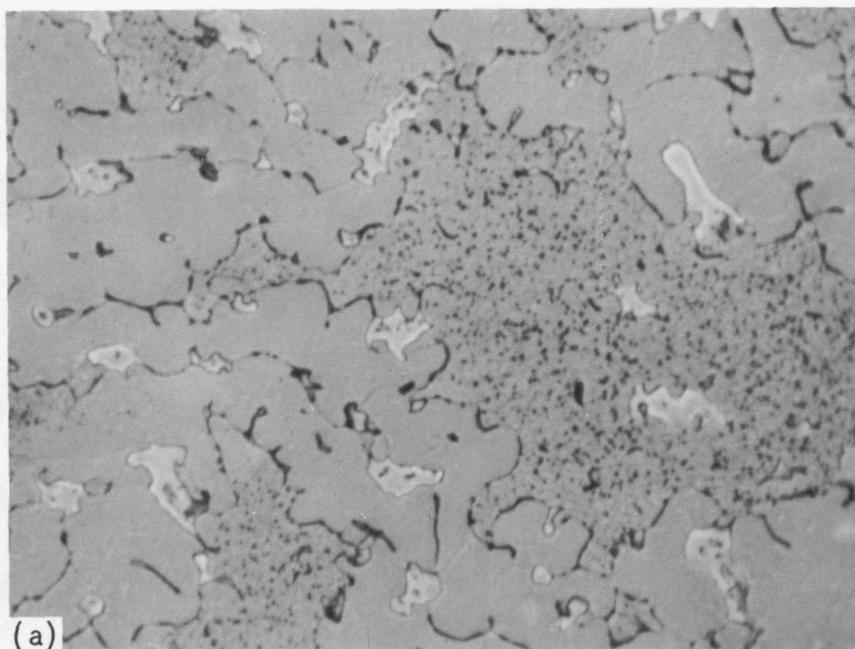


Figure 29. Alloy containing 43.44 atomic per cent thorium, 18.95 atomic per cent uranium, and 37.61 atomic per cent carbon. (a) As cast. Gray phase is (Th,U)C and white phase is uranium. (b) Annealed at 1000°C. for 350 hours. Darkest phase is uranium and matrix phase is (Th,U)C. Electroetched. 1000X.

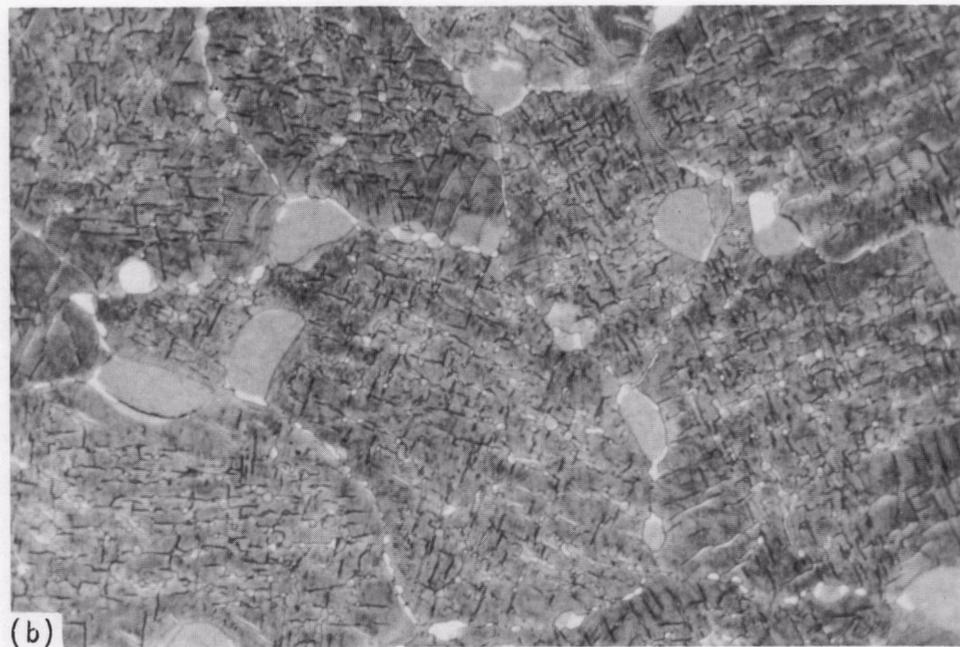
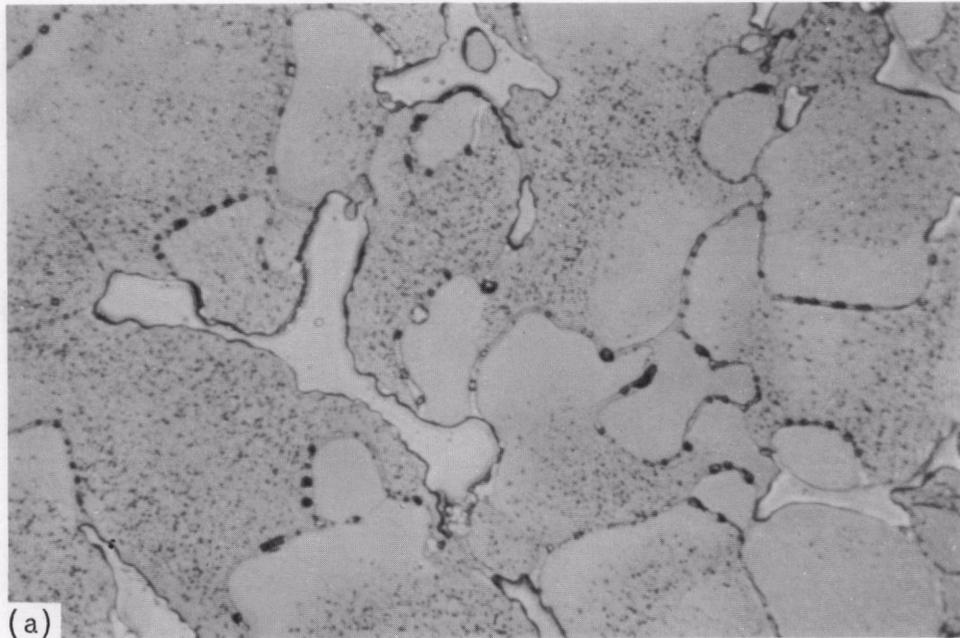


Figure 30. Alloy containing 49.84 atomic per cent thorium, 12.61 atomic per cent uranium, and 37.54 atomic per cent carbon. (a) As cast. Matrix phase is (Th,U)C, white phase is uranium, and dark phase in grain boundaries is thorium. (b) Annealed at 1000°C. for 350 hours. Matrix phase is (Th,U)C, light gray dispersant is uranium, and white phase in grain boundaries is thorium. Electroetched. 1000X.

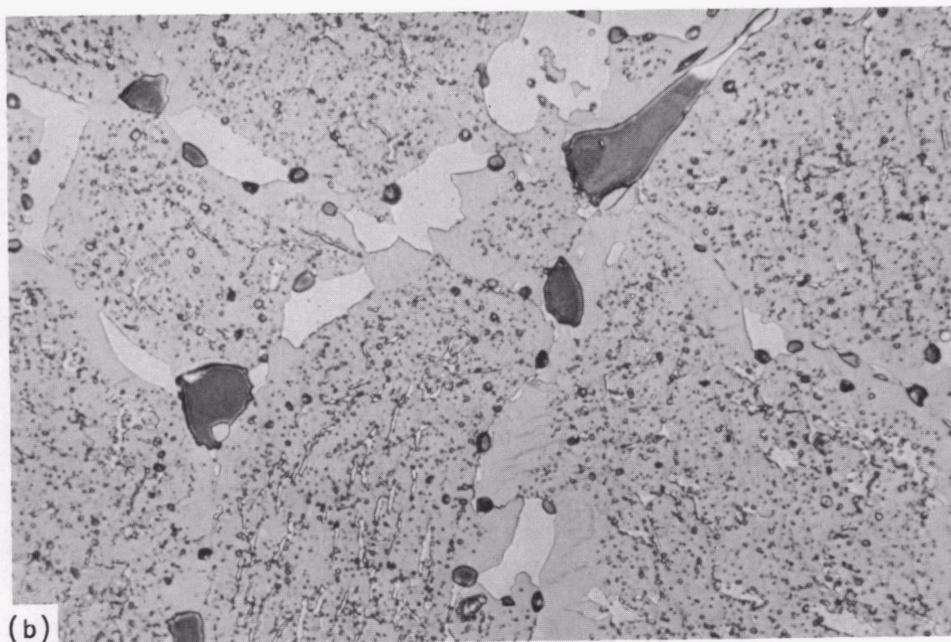
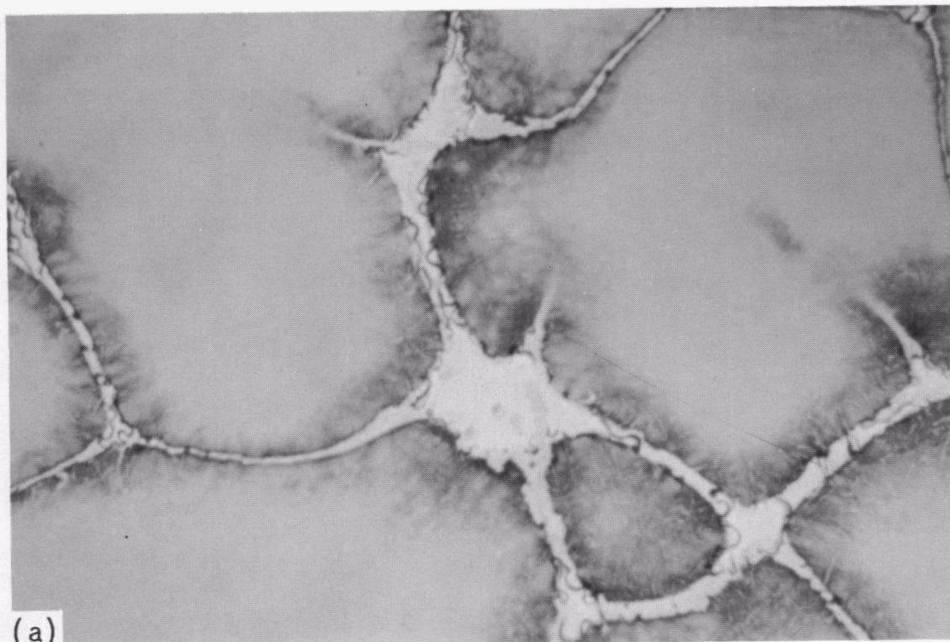


Figure 31. Alloy containing 52.39 atomic per cent thorium, 10.09 atomic per cent uranium, and 37.52 atomic per cent carbon. (a) As cast. Gray matrix is  $(Th,U)C$ , dark gray particles are uranium, and white material is thorium. (b) Annealed at  $1000^{\circ}C$ . for 350 hours. Gray matrix is  $(Th,U)C$ , dark gray particles are uranium, and white particles are thorium. Electroetched. 1000X.

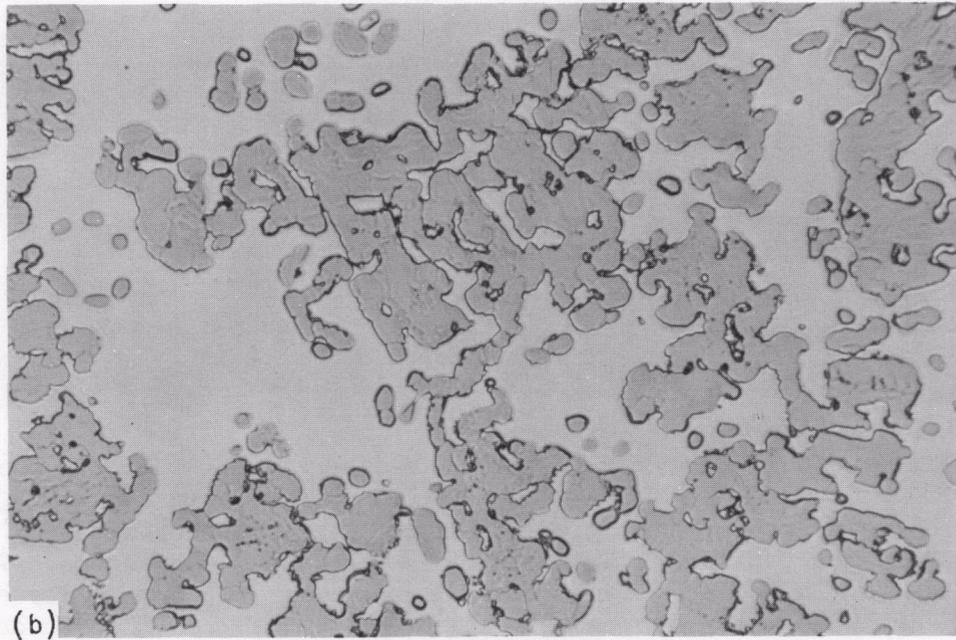
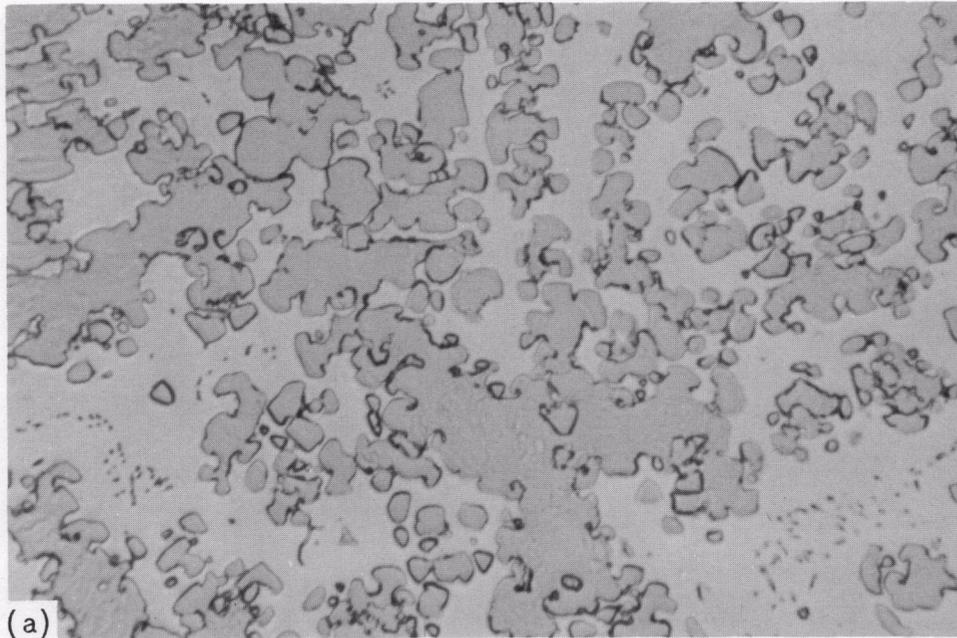


Figure 32. Alloy containing 14.74 atomic per cent thorium, 62.15 atomic per cent uranium, and 23.11 atomic per cent carbon. (a) As cast. (b) Annealed at 1000°C. for 350 hours. Gray phase is (Th,U)C and matrix is uranium. Electroetched. 1000X. •

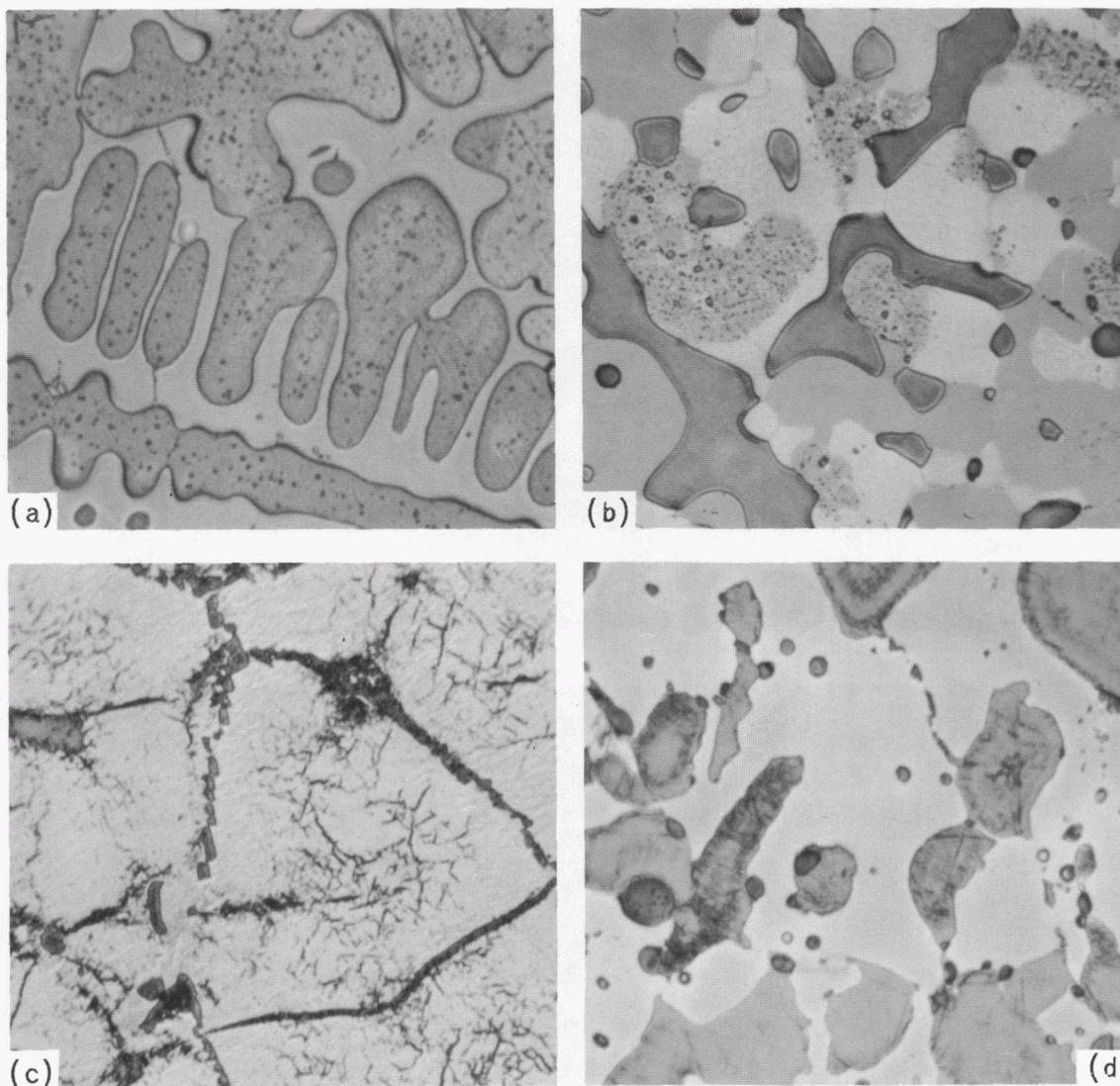


Figure 33. Differences between as-cast and annealed structures of two alloys within the three-phase region uranium plus thorium plus (Th,U)C. (a) Alloy containing 46.28 atomic per cent thorium, 30.81 atomic per cent uranium, and 22.91 atomic per cent carbon. As cast. Dark phase is (Th,U)C and light phase is uranium. (b) Same alloy as (a) annealed at 1000°C. for 350 hours. Light gray phase is (Th,U)C, dark phase is uranium, and white phase is thorium. (c) Alloy containing 69.55 atomic per cent thorium, 7.66 atomic per cent uranium, and 22.79 atomic per cent carbon. As cast. Matrix is thorium, gray phase in grain boundaries is uranium, and the very finely dispersed phase is (Th,U)C. (d) Same alloy as (c) annealed at 1000°C. for 350 hours. White phase is thorium, light gray phase is (Th,U)C, and dark gray phase is uranium. Electroetched. 1000X.

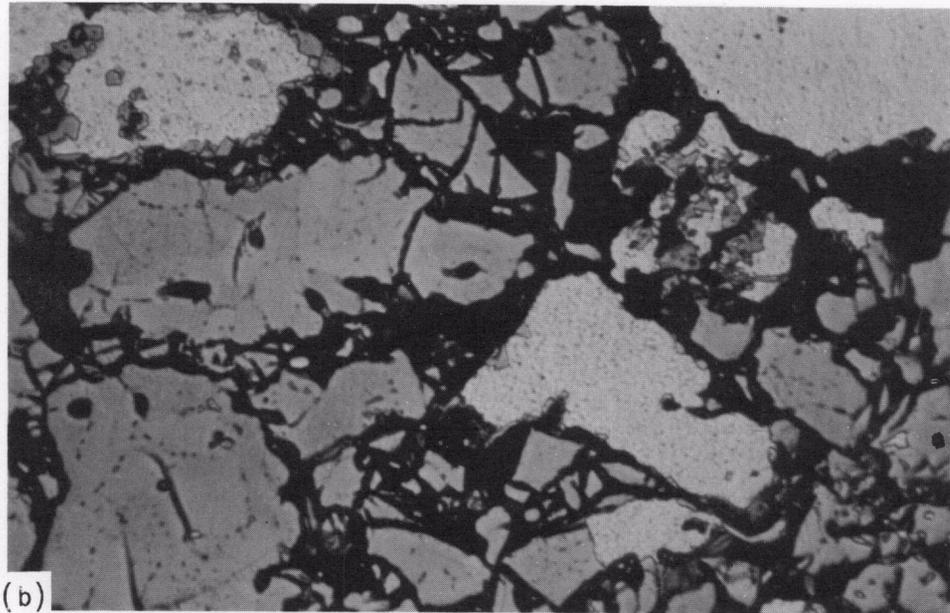
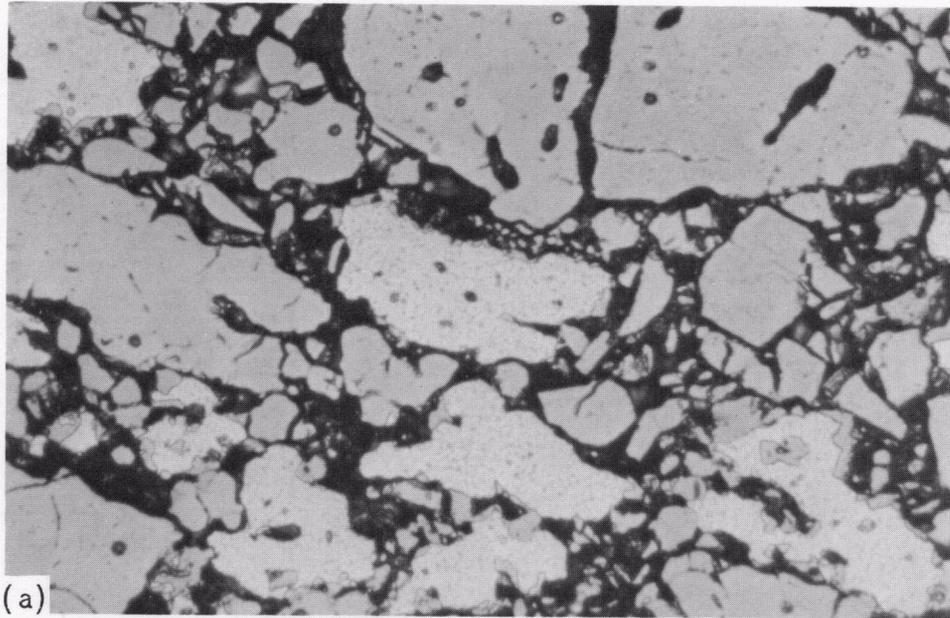
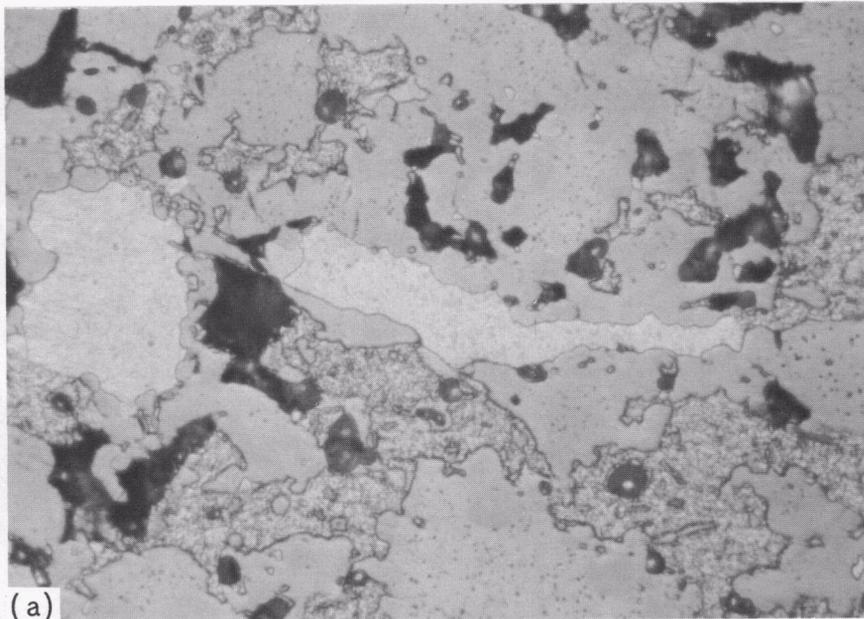
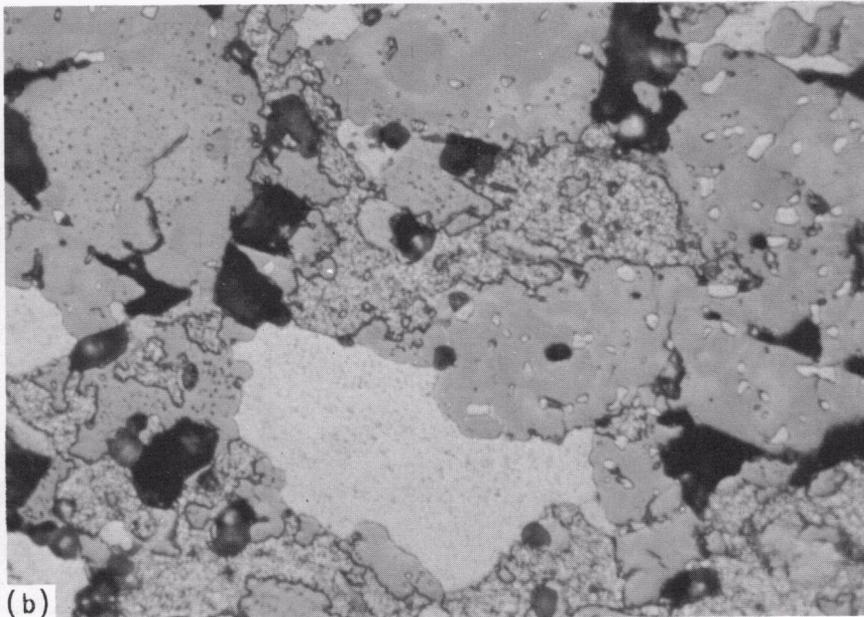


Figure 34. Representative alloys in the Th-U-N system. (a) Alloy containing 22 atomic per cent thorium, 53 atomic per cent uranium, and 25 atomic per cent nitrogen. (b) Alloy containing 30 atomic per cent thorium, 30 atomic per cent uranium, and 40 atomic per cent nitrogen. Annealed at 1000°C. for 100 hours. Dark phase is (Th,U)N, light phase is uranium, and black regions are voids. Etchant: 60 parts lactic acid, 30 parts  $\text{HNO}_3$ , and 2 parts HF. 1000X.



(a)



(b)

Figure 35. Representative alloys in the Th-U-N system. (a) Alloy containing 54 atomic per cent thorium, 6 atomic per cent uranium, and 40 atomic per cent nitrogen. (b) Alloy containing 50 atomic per cent thorium, 25 atomic per cent uranium, and 25 atomic per cent nitrogen. Annealed at  $1000^{\circ}\text{C}$ . for 100 hours. Dark phase is (Th,U)N, light phase is uranium, mottled phase is thorium, and black areas are voids. Etchant: 60 parts lactic acid, 30 parts  $\text{HNO}_3$ , and 2 parts HF. 1000X.

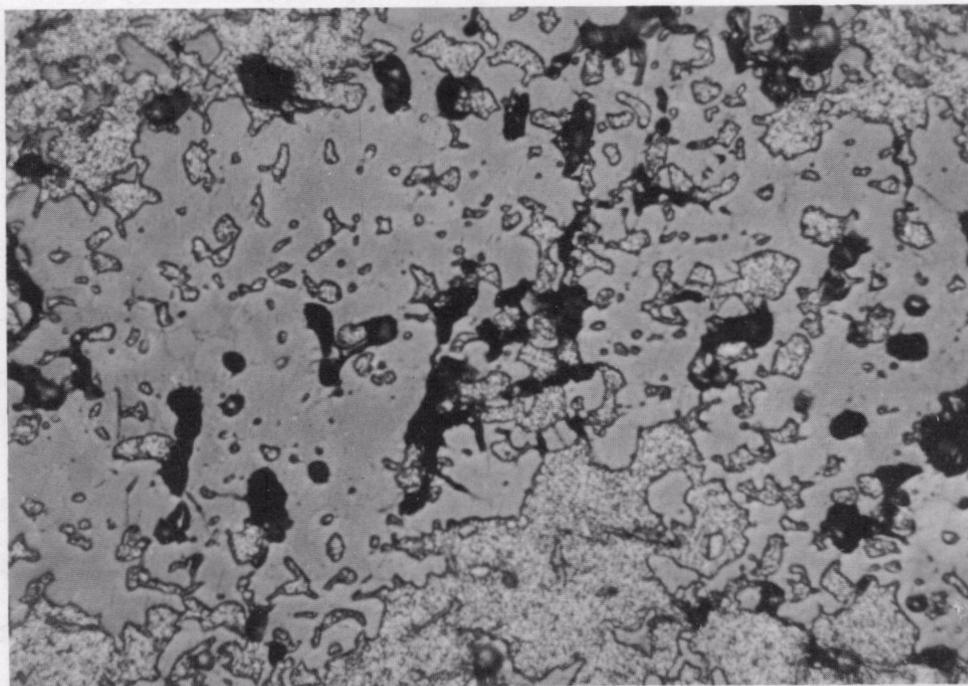


Figure 36. Alloy containing 73 atomic per cent thorium, 2 atomic per cent uranium, and 25 atomic per cent nitrogen. Annealed at 1000°C. for 100 hours. Dark phase is (Th,U)N, mottled phase is thorium, and black areas are voids. Etchant: 60 parts lactic acid, 30 parts HNO<sub>3</sub>, and 2 parts HF. 1000X.

colored when observed on the metallograph but unfortunately color photographs could not be reproduced here. The varied etching response of an unequilibrated alloy serves as an excellent gage of whether the structure has been fully homogenized.

Figures 26(b), 27(b), and 28(b) are examples of fully homogenized (Th,U)C alloys where the lack of free metal in the grain boundaries or of dicarbide needles within the grains gives excellent testimony to the stoichiometric composition (68).

The structures shown in Figure 29 show the typical as-cast and annealed structures of alloys rich in (Th,U)C located in the uranium plus (Th,U)C two-phase region of the Th-U-C system. Note the somewhat cleaner structure after equilibration. The very fine structure seen in these and other photomicrographs was not identified; however, it is probably made up of the major dispersed phases with some ThO<sub>2</sub> particles since ThO<sub>2</sub> was known to exist in most of the samples. The darker appearance of uranium in Figure 29(b) is due to staining during the time between etching and photographing the samples. This staining or "air etching" was found to be variable and its severity quite unpredictable.

Although the same phases are present in the as-cast and annealed conditions of the alloy of Figure 30, note the rearrangement of the small metal inclusions within the (Th,U)C matrix upon annealing.

Striking differences between as-cast and homogenized structures are evident in Figure 31. The metallic phases are located almost exclusively in the grain boundaries of the as-cast material. The pattern around the grain boundaries suggests that diffusion has been taking place

during cooling. By contrast the homogenized alloy distinctly shows agglomeration of thorium and uranium metal into distinct particles.

Alloys rich in uranium located within the uranium plus (Th,U)C two-phase field do not change their apparent structure significantly on annealing, as can be seen from Figure 32, page 57.

Figure 33, page 58, presents two alloys within the three-phase region uranium plus thorium plus (Th,U)C and shows striking differences between as-cast and annealed structures. Note that in Figure 33a no free thorium was identified in the as-cast condition. Figure 33c does show all three phases in the as-cast condition; however, Figure 33d shows that both uranium and (Th,U)C have migrated and agglomerated to form a much coarser structure.

Figures 34 through 36, pages 59 through 61, are representative of alloys in the Th-U-N system. Since these samples were prepared by powder metallurgical techniques no metallography was done before annealing.

## CHAPTER V

### CONCLUSIONS AND RECOMMENDATIONS

This investigation was concerned with the determination of the partial ternary isotherms of the Th-U-C and Th-U-N systems in the range 600 to 1000°C. During the course of the experimental work certain conclusions have been arrived at concerning this and other investigations. Concurrently it became clear that information is lacking in certain areas. A summation of the more important conclusions and recommendations for related investigations follows.

There was no evidence, in the many samples examined by x-ray and metallographic techniques, that the compound  $UC_{1-x}$  exists and thus the U-C binary diagram of Figure 1, page 5, as proposed by IAEA (12), is more nearly correct. At the same time, because of the temperature range over which these experiments were performed, we were unable to choose between the Th-C binary diagram as proposed by either Langer et al. (38) or by Chiotti et al. (39).

The success in making stoichiometric (Th,U)C, as evidenced by metallographic examination, further verifies the value of the arc-melting technique developed by Bourgette (68). It was found that, while stoichiometric (Th,U)C could be drop cast, alloys containing significantly less than the stoichiometric amount of carbon could not be cast successfully by this technique; therefore, finger castings were made. The use of finger castings did not hamper these experiments; however, this lack of

castability could be troublesome if fuel elements in large quantities were needed.

The technique of hydride, dehydride, nitride, and thermal decomposition to stoichiometric (Th,U)N from master alloys of U-Th has been demonstrated to be successful. In making Th-U-N alloys containing less than 50 atomic per cent nitrogen it has been demonstrated that powder metallurgical techniques are satisfactory.

No new metallographic techniques have been developed but it was observed that Th-U-C alloys which had been cast and not fully homogenized are very difficult to properly etch and photograph.

Time to reach equilibrium at 1000°C. was found to be 240 to 350 hours in the Th-U-C system at less than 50 atomic per cent carbon. At 600 and 800°C. equilibration times are in excess of 1000 hours. In the Th-U-N system, at less than 50 atomic per cent nitrogen, the 1000°C. equilibration time is 80 to 100 hours.

Oxidation of all samples during annealing was a problem to which no satisfactory solution was found. In the case of powder metallurgically prepared Th-U-N alloys it was hoped that wrapping the pellets with 0.003-inch-thick tantalum foil and subsequent sealing in quartz under vacuum (approximately  $10^{-5}$  torr) would prevent oxidation. Although there may have been some improvement, specimen oxidation was not prevented. The effect of this oxygen contamination on the phase relationships is unknown.

The lattice parameters of (Th,U)C across the UC-ThC pseudobinary, as determined in this investigation, show a slight negative deviation

from Vegard's law and agree quite favorably with the data of earlier investigators (67,75,76). In the UN-ThN system Vegard's law has been seen to fit the lattice parameters of (Th,U)N alloys.

The 1000°C. ternary isotherm below 50 atomic per cent carbon or nitrogen has been determined for both the Th-U-C system and the Th-U-N system. The most uranium-rich compounds in equilibrium with metallic thorium were found to be  $(\text{Th}_{0.906}, \text{U}_{0.094})\text{C}_{0.712}$  and  $(\text{Th}_{0.944}, \text{U}_{0.056})\text{N}_{0.869}$  in the Th-U-C and Th-U-N systems, respectively.

A thermodynamic analysis of these ternary diagrams, as proposed by Rudy (9), has given good agreement with the experiments and has allowed a value of -51,900 calories per gram-mole to be estimated as the free energy of formation of ThN at 1000°C.

Certainly not all these results have been positive and during the course of the investigation certain problems have come to light which need clarification. Perhaps the the most vexing problem is the lack of precision chemical analysis techniques for the carbides and nitrides of thorium and uranium. Here is an area which seems ripe for investigation by chemists in the nuclear industry.

A second area, which could be explored, concerns the lack of information on the effect of oxygen contamination, at levels up to approximately two weight per cent, on the lattice parameter of (Th,U)N and on the phase relationships in the Th-U-N and Th-U-C systems.

Finally, due to time limitations, this investigation covers only the 1000°C. isotherms for the Th-U-C and Th-U-N systems. As was pointed out in the introduction, these materials are potential thermal-breeder

fuels to operate at 800 to 1000°C. and therefore it is recommended that the 600 and 800°C. isotherms below 50 atomic per cent carbon or nitrogen be determined. At the very least the equilibration kinetics in these systems, at temperatures of 600 to 800°C., should be determined.

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## REFERENCES

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APPENDICES

## APPENDIX A

## CHEMICAL ANALYSES OF STARTING MATERIALS

TABLE I  
IMPURITY ANALYSIS OF LOT NUMBER 1  
URANIUM STARTING STOCK

Element	Parts Per Million by Weight
Aluminum	3
Barium	< 0.02
Beryllium	1
Bismuth	< 0.03
Boron	0.05
Cadmium	< 0.05
Calcium	2
Carbon	90
Cerium	< 0.02
Cobalt	0.7
Copper	1
Hydrogen	12
Iron	2
Magnesium	4
Manganese	0.7
Nickel	4
Nitrogen	27
Oxygen	140
Phosphorus	< 10
Silicon	10
Silver	< 0.03
Thorium	< 0.03
Tin	< 0.05
Tungsten	< 0.6
Zinc	2

TABLE II

IMPURITY ANALYSIS OF LOT NUMBER 2  
URANIUM STARTING STOCK

Element	Parts Per Million by Weight
Aluminum	30
Barium	< 0.08
Beryllium	0.1
Bismuth	< 0.1
Boron	0.1
Cadmium	< 0.2
Calcium	0.5
Carbon	80
Cerium	< 0.06
Copper	1
Hydrogen	13
Iron	25
Magnesium	3
Manganese	3
Nickel	1
Nitrogen	36
Oxygen	160
Phosphorus	20
Silicon	90
Silver	0.1
Thorium	40
Tin	< 0.2
Tungsten	< 0.3
Zinc	2

TABLE III

IMPURITY ANALYSIS OF LOT NUMBER 1  
THORIUM STARTING STOCK

Element	Parts Per Million by Weight
Aluminum	100
Barium	
Beryllium	4
Bismuth	
Boron	0.6
Cadmium	
Calcium	20
Carbon	320
Cerium	
Copper	4
Hydrogen	24
Iron	25
Magnesium	3
Manganese	2
Nickel	30
Nitrogen	73
Oxygen	1800
Phosphorus	121
Silicon	< 250
Silver	< 0.1
Tin	< 0.2
Tungsten	4
Uranium	3
Zinc	0.6

TABLE IV

IMPURITY ANALYSIS OF LOT NUMBER 2  
THORIUM STARTING STOCK

Element	Parts Per Million by Weight
Aluminum	35
Barium	< 0.08
Beryllium	100
Bismuth	0.09
Boron	0.5
Cadmium	< 0.2
Calcium	5
Carbon	1330
Cerium	20
Chromium	8
Copper	10
Hydrogen	16
Iron	70
Magnesium	4
Manganese	2
Nickel	100
Nitrogen	53
Oxygen	1700
Phosphorus	20
Silicon	50
Silver	< 0.1
Tin	< 0.2
Tungsten	2
Uranium	17
Zinc	< 0.1
Zirconium	2

TABLE V

## IMPURITY ANALYSIS OF THORIUM METAL POWDER

Element	Parts Per Million by Weight
Aluminum	35
Boron	1.5
Barium	< 5
Beryllium	< 0.1
Bismuth	< 1
Calcium	1500
Cadmium	< 0.1
Carbon	220
Cobalt	< 5
Chromium	15
Copper	4
Iron	40
Lead	< 1
Lithium	< 50
Magnesium	10
Manganese	5
Molybdenum	< 1
Nickel	91
Nitrogen	29
Oxygen	810
Potassium	< 2
Phosphorus	< 10
Silicon	8
Silver	< 0.1
Sodium	< 40
Tin	< 1
Titanium	1.5
Vanadium	< 2.5
Zinc	< 25
Zirconium	10
ThO <sub>2</sub> (in per cent)	0.64

APPENDIX B

DATA ON THE UC-ThC AND UN-ThN PSEUDOBINARIES

TABLE VI

NOMINAL COMPOSITIONS AND LATTICE PARAMETERS OF ALLOYS  
ACROSS THE UC-ThC PSEUDOINARY

Thorium (at. %)	Uranium (at. %)	Carbon (at. %)	Thorium Monocarbide (mole %)	Lattice Parameter of (Th,U)C	Standard Deviation
	50.00	50.00		4.95865	0.00021
2.80	47.24	49.96	5.6	4.97757	0.00022
8.17	41.94	49.89	16.4	5.01115	0.00027
13.53	36.64	49.83	27.2	5.05313	0.00041
18.87	31.36	49.76	37.6	5.09185	0.00010
24.20	26.10	49.70	48.4	5.12838	0.00037
29.52	20.86	49.63	59.0	5.16220	0.00022
34.82	15.62	49.56	69.6	5.20686	0.00053
40.11	10.39	49.50	80.4	5.24809	0.00025
45.38	5.19	49.43	90.6	5.29619	0.00020
50.64		49.36	100.0	5.34253	0.00020

TABLE VII

NOMINAL COMPOSITIONS AND LATTICE PARAMETERS OF ALLOYS  
ACROSS THE UN-ThN PSEUDOBINARY

Thorium (at. %)	Uranium (at. %)	Nitrogen (at. %)	Thorium Mononitride (mole %)	Lattice Parameter of (Th,U)N	Standard Deviation
	50.00	50.00		4.89034	0.00025
5.12	44.88	50.00	10.24	4.91561	0.00015
10.20	39.80	50.00	20.40	4.95712	0.00086
15.27	34.73	50.00	30.54	4.97434	0.00079
20.30	29.70	50.00	40.60	5.00608	0.00105
25.00	25.00	50.00	50.00	5.03219	0.00043
30.32	19.68	50.00	60.64	5.06339	0.00115
35.28	14.72	50.00	70.56	5.08531	0.00080
40.19	9.81	50.00	80.38	5.10826	0.00019
45.12	4.88	50.00	90.24	5.13461	0.00046
50.00		50.00	100.00	5.16190	0.00015

## APPENDIX C

## DATA ON TWO- AND THREE-PHASE (Th,U)X ALLOYS

TABLE VIII

NOMINAL COMPOSITIONS OF Th-U-C ALLOYS WITH THE RESULTS  
OF X-RAY AND METALLOGRAPHIC EXAMINATION  
AFTER EQUILIBRATION AT 1000°C.

Thorium (at. %)	Uranium (at. %)	Carbon (at. %)	Lattice Parameter of (Th,U)C	Standard Deviation	Major Phases Identified as Present <sup>a</sup>
17.62	44.53	37.85	5.09605	0.00045	U, (Th,U)C
24.11	38.10	37.79	5.13981	0.00103	U, (Th,U)C
30.57	31.70	37.72	5.18373	0.00391	U, (Th,U)C
33.79	28.51	37.70	5.20859	0.00058	U, (Th,U)C
35.09	27.23	37.68	5.20067	0.00250	U, (Th,U)C
36.37	25.96	37.67	5.22154	0.00026	U, (Th,U)C
37.66	24.69	37.66	5.22459	0.00188	U, (Th,U)C
38.93	23.41	37.64	5.23306	0.00045	U, (Th,U)C
40.22	22.14	37.63	5.25074	0.00037	U, (Th,U)C
43.44	18.95	37.61	5.25560	0.00037	U, (Th,U)C
48.57	13.88	37.55	5.26402	0.00069	U, Th, (Th,U)C
49.84	12.61	37.54	5.26341	0.00045	U, Th, (Th,U)C
51.12	11.35	37.53	5.26848	0.00046	U, Th, (Th,U)C
52.39	10.09	37.52	5.26802	0.00076	U, Th, (Th,U)C
6.78	70.06	23.16	5.03857	0.00782	U, (Th,U)C
14.74	62.15	23.11	5.14474	0.00120	U, (Th,U)C
18.71	59.20	23.09	5.16433	0.00200	U, (Th,U)C
20.29	56.63	23.08	5.19342	0.00707	U, (Th,U)C
21.87	55.06	23.07	5.22195	0.00160	U, (Th,U)C
23.46	53.48	23.06	5.23157	0.00195	U, (Th,U)C
25.04	51.91	23.05	5.25052	0.00049	U, (Th,U)C
26.62	50.34	23.04	5.25655	0.00066	U, (Th,U)C
46.28	30.81	22.91	5.25698	0.00105	U, Th, (Th,U)C
64.91	12.27	22.82	5.26684	0.00055	U, Th, (Th,U)C
66.46	10.73	22.81	5.27699	0.00024	U, Th, (Th,U)C
68.00	9.19	22.80	5.27490	0.00067	U, Th, (Th,U)C
69.55	7.66	22.79	5.26502	0.00030	U, Th, (Th,U)C

<sup>a</sup>Many of these alloys showed a weak set of ThO<sub>2</sub> lines in their x-ray patterns.

TABLE IX

NOMINAL COMPOSITIONS OF Th-U-N ALLOYS WITH THE RESULTS  
OF X-RAY AND METALLOGRAPHIC EXAMINATION  
AFTER EQUILIBRATION AT 1000°C.

Thorium (at. %)	Uranium (at. %)	Nitrogen (at. %)	Lattice Parameter of (Th,U)N	Standard Deviation	Major Phases Identified as Present <sup>a</sup>
46	6	48	5.14705	0.00076	U, (Th,U)N
20	40	40	4.92308	0.00771	U, (Th,U)N
25	35	40	5.03349	0.00085	U, (Th,U)N
30	30	40	5.09227	0.00058	U, (Th,U)N
34	26	40	5.12285	0.00085	U, (Th,U)N
36	24	40	5.14174	0.00052	U, (Th,U)N
38	22	40	5.14607	0.00042	U, (Th,U)N
40	20	40	5.14319	0.00049	U, (Th,U)N
45	15	40	5.15174	0.00105	U, Th, (Th,U)N
52	8	40	5.15201	0.00036	U, Th, (Th,U)N
54	6	40	5.15184	0.00042	U, Th, (Th,U)N
56	4	40	5.15265	0.00031	U, Th, (Th,U)N
58	2	40	5.15577	0.00068	Th, (Th,U)N
10	65	25	4.97301	0.00185	U, (Th,U)N
15	60	25	5.03577	0.00137	U, (Th,U)N
20	55	25	5.09314	0.00175	U, (Th,U)N
22	53	25	5.11741	0.00202	U, (Th,U)N
24	51	25	5.14360	0.00090	U, (Th,U)N
26	49	25	5.14252	0.00066	U, (Th,U)N
50	25	25	5.15527	0.00049	U, Th, (Th,U)N
73	2	25	5.16068	0.00076	Th, (Th,U)N

<sup>a</sup>Many of these alloys showed a weak set of ThO<sub>2</sub> lines in their x-ray patterns.



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