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THE URANIUM-NITROGEN-CARBON SYSTEM

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THE URANIUM-NITROGEN-CARBON SYSTEM

by

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June 23, 1958

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THE URANIUM-NITROGEN-CARBON SYSTEM

Alfred E. Austin and Arnold F. Gerds

The ternary system uranium-nitrogen-carbon has been studied at 1800 C under vacuum and under a 1-atm nitrogen pressure. There is complete solid solubility between UN and UC, and essentially no solid solubility of nitrogen in UC_2 or U_2C_3 or of carbon in U_2N_3 . At 1800 C the two-phase field, $U(C,N)$ and UC_2 , and the three-phase field, $U(C,N)$, UC_2 , and C, exist in vacuum or argon. At 1 atm of nitrogen, the uranium nitrides are more stable than the uranium carbides up to 1800 C, but at 2000 C, the uranium carbides $UC_2 + U(C,N)$ become more stable. At 1 atm of nitrogen, U_2N_3 is the stable phase up to 1550 C, and $U(N,C)$ solid solution is stable at 1800 C.

INTRODUCTION

Uranium carbides and uranium mononitride are stable in inert atmospheres to high temperatures. The structures⁽¹⁾ of UC and UN are isomorphous and the high-temperature structure of UC_2 ⁽²⁾ is isomorphous with UN_2 ⁽¹⁾. Therefore, solid solution between the carbides and nitrides seemed likely. It also appeared possible that mixed carbide-nitride phases may be formed. The composition of solid solutions and the stability of the various phases would be dependent upon nitrogen pressure as are the higher nitrides of uranium, U_2N_3 and UN_2 .⁽³⁾ Exploratory experiments were undertaken to study these factors. Solid-solid reactions between phases of the binary systems, as well as solid-gas reactions between carbide and nitrogen, were used for the study.

EXPERIMENTAL WORK

Methods

The uranium carbides, nominally UC, U_2C_3 , and UC_2 , were made by arc melting biscuit uranium and carbon under helium. The U_2C_3 ingot was heat treated at 1700 C for 4 hr to form the sesquicarbide phase. The carbides were crushed to minus 200 mesh under argon. Powdered uranium nitride, nominally U_2N_3 , was prepared by nitriding small pieces of uranium metal at 850 C with prepurified nitrogen at 1 atm. The nitrogen was dried before reaction by passing through a Dry Ice-acetone trap. The uranium was cleaned by pickling in nitric acid before reaction. The mononitride was made from the sesquinitride by heating to 1300 C in vacuum.

The lots of carbides and nitrides were kept sealed under dry argon. Table 1 gives the chemical analyses and cell constants for these materials.

Mixtures to be employed for solid-solid reactions were prepared by weighing and mixing in a dry argon atmosphere. The mixtures were compacted by moistening with a

(1) References at end.

solution of 2 w/o paraffin in cp benzene (using about 1 cm³ of solution to 10 g of powders), packing into a 1/8-in.-ID rubber tube, and hydrostatically pressing at 100,000 psi. The compacts were removed from the rubber tubing under argon and kept in sealed vials until used. The compacts were placed on powders of the same composition and sintered in a high-frequency induction-heating furnace. The solid-solid reactions were carried out generally by heating at 1800 C in argon and holding for 2 hr. The compacts were cooled at about 50 C per min to black heat in argon and then cooled to room temperature at the cooling rate of the furnace. Initially, some compacts had been heated in BeO crucibles. However, a surface reaction occurred to form UO₂ and Be₃N₂.

TABLE 1. CHEMICAL ANALYSES AND CELL CONSTANTS OF URANIUM CARBIDES AND NITRIDES

Material	Analysis, w/o				Phases and Cell Constants, A
	U	C	N	O	
UC	95.3	4.64	0.04	--	4.9598 ± 0.0003
UC ₂	91.4	8.39	0.04	--	a ₀ = 3.509 ± 0.003, c ₀ = 5.980 ± 0.005 + UC
UN	94.8	0.01	5.35	--	4.8897 ± 0.0003
U ₂ N ₃	91.2	0.03	7.0(a)	0.1 to 0.5	10.659 ± 0.001
U ₂ C ₃	92.5	7.51	0.008	--	a ₀ = 8.0885 ± 0.0005 + UC ₂

(a) Nitrogen is low and the analysis is questioned; the cell size would indicate about 8.4 w/o nitrogen.

Reaction products were analyzed for uranium, nitrogen, and carbon. Uranium was determined by ignition to U₃O₈ simultaneously with a combustion analysis at 800 C for total carbon. Nitrogen analysis was carried out by the Friederich method⁽⁴⁾ after comparative tests on uranium nitrides with the conventional Kjeldahl analysis. The Friederich method for specimens of both nitride and carbide is as follows: weigh about 0.2 g, add 25 cm³ 1:1 HCl and 1 cm³ fluosilicic acid, cover, and heat until reaction ceases, cool, add 2 cm³ 30 w/o H₂O₂, heat until excess peroxide decomposes, transfer to Parnas-Wagner micro-Kjeldahl, make alkaline with NaOH, distill, collect ammonia in dilute boric acid and titrate with standard HCl using methyl red from cresol green indicator. The amount of free carbon was determined by combustion of the residue after hydrolyzing in 50 cm³ 1:1 HCl plus 2 cm³ of 30 w/o H₂O₂, washing with HCl, water, and ethyl ether, and drying at 110 C. Oxygen and hydrogen were determined by the vacuum-fusion method. Metallographic examination and X-ray diffraction analyses were used to determine the phases present in samples cooled from 1800 C.

The cell sizes of the cubic phases and solid solutions were determined by graphical extrapolation of the X-ray diffraction data taken with FeK radiation in a 114.57-mm Debye camera. The densities of the sintered compacts were determined using a pycnometer.

Reactions in nitrogen at a 1-atm pressure were carried out in a high-temperature X-ray camera. Samples consisted of carbide powder, pressed compacts, and solid pieces from arc-melted ingots. Some initial reactions made at 1000 C and a 1-atm pressure of nitrogen indicated complete reaction of a 20-mil rod of sintered carbide in

2 hr to form U_2N_3 . Therefore, reactions of powder and compacts at 1000 to 2000 C or higher were carried out for 2 to 3 hr.

RESULTS

Solid-Solid Reactions

The reactions between UC, UC_2 , UN, U_2N_3 , and graphite were investigated for mixtures heated to 1800 to 1850 C for 2 hr in dry argon. This temperature was selected since prior work with binary carbides had shown complete reaction in 2 hr at about 1800 C. Figure 1 shows the ternary section determined for 1800 C. Tables 2 and 3 give compositions and phase analyses. Uranium mononitride, UN, is the only stable nitride in a vacuum or a nitrogen-free atmosphere at this temperature. There is complete solid solubility between UN and UC.

Figure 2 shows a plot of the U(C,N) cell size as a function of the mol fraction of UC in the solid solution. The compositions for the two-phase U(C,N) + UC_2 specimens, 4, 9, 10, 14, and 15, are shown on the plot. These specimens were each corrected for the presence of carbon or UC_2 by assuming that all of the nitrogen was in the U(C,N) phase. The deviation of the cell size from linearity indicates that carbon and nitrogen are more soluble in U(C,N), in the region of 0.65 to 0.75 mol fraction UC, than expected by additivity between UC and UN.

The cell size, 4.9254 ± 0.0005 A, for 0.50 mol fraction UC, was obtained from the core of a reacted compact of equimolar ratio of UC and UN. The cell size of the UC_2 did not change for the two- and three-phase specimens, indicating very little if any solid solubility of nitrogen in UC_2 .

The single-phase specimens, 8, 12, and 26, were analyzed for oxygen impurity with results of 0.14, 0.05, and 0.10 w/o of oxygen respectively. These amounts of oxygen are too low compared with the carbon and nitrogen contents to account for the deviation of cell size from linearity for Specimens 8 and 26 in Figure 2. Previously reported work⁽⁵⁾ indicated linearity of the cell size for the U(C,O) phase.

Specimens 12A and 25 in the ternary-phase field were fired twice, with crushing to minus 325 mesh and recompaction between firings, to promote complete reaction. The cell size, 4.9417 A, for U(C,N) in Specimen 12A lies between the values for the U(C,H) phase in Specimens 10 [U(C,N) + UC_2] and 12 [U(C,N) + C]. The addition of carbon to Specimen 12 in making Specimen 12A shifted the composition from the two-phase field into the three-phase field. The best estimate for the terminal composition of the U(C,N) for the three-phase field is 0.62 mol fraction UC, 0.38 mol fraction UN, with uranium between 50 and 49 a/o.

Density measurements, shown in Table 4, can, in general, be correlated with the phase identifications. The theoretical densities calculated from X-ray diffraction data are as follows: UC, 13.6 g per cm^3 ; UC_2 , 11.68 g per cm^3 ; UN, 14.32 g per cm^3 ; and U_2N_3 , 11.24 g per cm^3 . An experimental density of 13.06 g per cm^3 was determined for UC. This is lower than the theoretical density, probably because of the presence of some UC_2 , which has a lower density, in the structure. The U(C,N) solid solution was

TABLE 2. COMPOSITIONS OF URANIUM-NITROGEN-CARBON SPECIMENS REACTED AT 1800 C IN ARGON

Specimen	Reactants	Compositions								
		Initial, a/o			Products, w/o			Products, a/o		
		U	C	N	U	C	N	U	C	N
3	UC + U ₂ N ₃	43.1	20.5	34.8	94.7	1.67	3.53	51.0	16.8	32.3
4	U ₂ N ₃ + UC ₂	36.9	33.2	30.0	94.9	3.70	1.52	49.0	37.8	13.3
8	UC + UN	51.0	34.6	13.3	94.8	2.91	2.11	50.3	30.6	19.1
9	UN + UC ₂	41.6	37.4	21.1	94.7	3.76	1.35	49.4	38.4	11.8
10	UN + C	33.4	33.2	33.4	94.1	4.44	1.55	45.2	42.3	12.6
11	UN + UC	50.1	15.1	35.0	94.8	1.14	3.72	51.5	12.5	35.2
12	UN + C	24.9	51.0	23.9	89.8	8.22	1.98	31.3	57.9	11.8
13	UC + U ₂ N ₃	41.5	13.8	44.8	94.8	1.34	3.71	51.3	14.4	34.2
14	UC + U ₂ N ₃	48.2	39.2	12.6	95.0	3.52	1.52	49.9	36.6	13.6
15	U ₂ N ₃ + UC ₂	35.7	55.4	8.8	92.6	7.01	0.43	38.7	58.2	3.1
25	UN + UC ₂ + C	27.9	66.5	5.6	89.8	10.0	0.1	31.0	68.4	0.6
12A(a)	UN + C	--	--	--	89.6	9.3	1.0	30.8	63.3	5.8
26	UN + UC	50.8	39.5	9.8	94.9	3.62	1.40	49.9	37.6	12.5

(a) Specimen 12A was Specimen 12 crushed and repressed with slight additional carbon from paraffin binder.

TABLE 3. PHASES FORMED IN URANIUM-NITROGEN-CARBON SPECIMENS AT 1800 C IN ARGON

Specimen	Phases Identified		Cubic Solid-Solution Cell Constant ^(b) , Å
	By Metallography ^(a)	By X-Ray Diffraction	
3	U(N, C) + trace UO ₂	U(N, C)	4.9415 for minor phase 4.9068 for major phase
4	U(C, N) + UC ₂	U(C, N) + UC ₂	4.9480
8	U(N, C)	U(N, C)	4.9454
9	U(C, N) + UC ₂	U(C, N) + UC ₂	4.9487
10	U(C, N) + UC ₂	U(C, N) + UC ₂	4.9474
11	U(N, C)	U(N, C)	4.9088
12	U(C, N) + C	U(C, N) + C	4.9393
13	U(N, C) + trace UO ₂	U(N, C)	4.9096
14	U(C, N) + UC ₂	U(C, N)	4.9495
15	UC ₂ + U(C, N)	UC ₂ + U(C, N)	4.9565
25	UC ₂ + U(C, N) + C	UC ₂ + U(C, N) + C	(c)
26	U(C, N)	U(C, N)	4.9482
12A	UC ₂ + U(C, N) + C	UC ₂ + U(C, N) + C	4.9417

(a) UC phase stains and UN phase does not. Therefore, U(C, N) denotes a stained solid solution phase and U(N, C) denotes an unstained solid-solution phase. C indicates graphite.

(b) Error in cell constants was 0.0005 Å.

(c) Cell constant not determined.

FIGURE 2. PLOT OF $U(C,N)$ CELL SIZE VERSUS MOL FRACTION OF UC IN SOLID SOLUTION

more dense than UC, as might be expected, because the density of UN is higher than that of UC. The presence of graphite in the microstructure lowers the density appreciably, as can be seen for Specimen 12. UN and the U(N,C) solid solutions have appreciably higher densities than UC and the U(C,N) solid solutions. Thus, qualitatively, there is agreement between the experimental density measurements and the phases present in test samples.

TABLE 4. DENSITY MEASUREMENTS ON URANIUM-NITROGEN-CARBON SPECIMENS FORMED AT 1800 C IN ARGON

Specimen ^(a)	Phases Present in Specimen ^(b)	Density ^(c) , g per cm ³
--	UC	13.06
26	U(C,N)	13.81
14	U(C,N) + UC ₂	13.52
10	U(C,N) + UC ₂	13.06
9	U(C,N) + UC ₂	13.81
12	U(C,N) + C	10.43
--	UC ₂	11.38
--	UN	14.18
8	U(N,C)	13.94
3	U(N,C)	13.65
11	U(N,C)	14.54
13	U(N,C)	14.03
--	U ₂ N ₃	11.26

(a) Specimens as numbered in Tables 2 and 3.

(b) Phases determined by metallographic methods.

(c) Calculated densities from X-ray diffraction data are as follows:

	G per Cm ³
UC	13.6
UC ₂	11.68
UN	14.32
U ₂ N ₃	11.24

Figures 3 through 10 show typical microstructures of specimens, reacted at 1800 to 1850 C, that were used in the study. All of the photomicrographs are at 500X. The gray material between the particles is mounting resin used to facilitate handling of the specimens. Figure 3 shows a typical field of the U(N,C) solid solution which was formed by reaction at 1750 to 1800 C of equal parts of UC and UN. Lattice-parameter measurements and analytical data indicate the nonstaining matrix to be a nitrogen-rich compound composed of uranium, nitrogen, and carbon, and designated U(N,C) in this report. The small dark-etching particles in the matrix phases are not identified.

Figure 4 shows a typical field in a specimen composed of equal parts of U₂N₃ and UC₂ reacted in argon for 2 hr at 1750 to 1800 C. The major phase stained similar to UC. X-ray diffraction studies and analyses for uranium, nitrogen, and carbon indicated that the stained phase is a carbon-rich solid solution of uranium in the form U(C,N). The few, isolated, light-etching particles in the stained matrix are probably UC₂.

Figure 5 shows the typical microstructure in a specimen produced by reaction of equal parts of UN and UC_2 at 1750 to 1800 C. The matrix of the stained particles is U(C,N), while the light-etching grain-boundary phase is UC_2 . The several light-etching particles containing the stained bands in the center of the field have a UC_2 matrix. The stained bands within these particles probably are composed of the U(C,N) solid solution precipitated in the UC_2 matrix.

Figure 6 shows the structure produced by reaction of 19 parts of UN with 1 part of graphite. The light-etching material in the center of the field appears to contain a UC_2 matrix with bands of a dark-etching phase, probably U(C,N). The smaller particles surrounding this material are the stained U(C,N) phase. The small amount of light-etching material associated with the stained particles is UC_2 .

Figure 7 shows the microstructure produced by reaction of 9 parts of UN with 1 part of graphite. The discrete particles are the U(C,N) solid solution. The small dark inclusions within the particles were not identified. The gray patches between the particles are graphite. These can be distinguished from the smooth gray mounting resin.

Figure 8 shows the microstructure produced by reaction of 5 parts of UC with 1 part of U_2N_3 . The stained particles are the U(C,N) solid solution. Within the particles, wavy lines of a fine, light-etching Widmanstätten precipitate of UC_2 are evident.

Figure 9 shows the microstructure produced by reaction of 5.5 parts of UC_2 with 1 part of U_2N_3 at 1800 C for 2 hr. The light-etching particles are UC_2 . The dark-etching bands in the light-etching particles are U(C,N). This photomicrograph shows that U(C,N) can replace UC in a UC_2 -rich material without appreciably changing its appearance under the microscope.

Figure 10 shows the microstructure produced by reaction at 1700 C for 2 hr of 16 parts of UC_2 , 4 parts of UN, and 1 part of graphite. The UC_2 appears as the light-to-gray etching matrix, depending upon grain orientation. The dark precipitated bands in the particles are U(C,N). The swirly black material between some of the particles is graphite, while the dark-gray material between the particles is the mounting resin.

Solid-Gas Reactions

The reaction of uranium carbides with nitrogen at a 1-atm pressure was investigated from 1000 to 2000 C. Rods of UC, 20 mils in diameter, were heated at 1000 C under 1 atm of dried prepurified nitrogen in a high-temperature X-ray diffraction camera. Within 2 hr the specimen was changed from UC with a lattice parameter of 5.0110 Å to a face-centered-cubic fluorite-type structure with a lattice parameter of 5.36 Å. A duplicate run gave the same result. The crushed rod at room temperature had the typical doubled fluorite cell of the U_2N_3 structure⁽¹⁾. Apparently at 1000 C the U_2N_3 structure shifts to the smaller defect fluorite cell. There was complete reaction of the UC with the nitrogen.

500X

Nitric-Acetic Etch

N44653

Shows U(N, C) matrix containing a few small particles of a darker etching phase. Dark gray material between particles is mounting resin.

FIGURE 3. SPECIMEN 1, PREPARED WITH EQUAL WEIGHTS OF UN AND UC

Powders mixed, compacted, and argon sintered at 1750 to 1800 C for 2 hr and slowly cooled.

500X

Nitric-Acetic Etch

N44647

Shows stained U(C, N) matrix with occasional unidentified light-etching particles, probably UC_2 . Dark gray material between particles is mounting resin.

FIGURE 4. SPECIMEN 4, PREPARED WITH EQUAL WEIGHTS OF U_2N_3 AND UC_2

Powders mixed, compacted, and argon sintered at 1750 to 1800 C for 2 hr and slowly cooled.

500X

Nitric-Acetic Etch

N45745

Shows stained U(C, N) particles. Light-etching phase in stained particles as well as light-etching banded particles are UC_2 . Dark material between particles is mounting resin.

FIGURE 5. SPECIMEN 9. PREPARED WITH EQUAL WEIGHTS OF UN AND UC_2

Powders mixed, compacted, and argon sintered at 1750 to 1800 C for 2 hr and slowly cooled.

500X

Nitric-Acetic Etch

N45747

Shows patch of light-etching UC_2 in a matrix of stained U(C, N). Gray material between particles is mounting resin.

FIGURE 6. SPECIMEN 10, PREPARED WITH 19 PARTS OF UN AND 1 PART OF GRAPHITE

Mixed, compacted, and argon sintered at 1750 to 1800 C for 2 hr and slowly cooled.

500X

Nitric-Acetic Etch

N46742

Shows particles of stained U(C, N). Light-gray swirly patches are graphite in a slightly darker gray mounting resin.

FIGURE 7. SPECIMEN 12, PREPARED WITH 9 PARTS OF UN AND 1 PART OF GRAPHITE

Powders mixed, compacted, and sintered in argon at 1750 to 1800 C and slowly cooled.

500X

Nitric-Acetic Etch

N46239

Shows stained U(C, N) particles containing a small amount of lighter etching phase, probably UC_2 . Gray material between particles is mounting resin.

FIGURE 8. SPECIMEN 14, PREPARED WITH 5 PARTS OF UC AND 1 PART OF U_2N_3

Powder mixed, compacted, and sintered at 1750 to 1800 C in argon and slowly cooled.

500X

Nitric-Acetic Etch

N46241

Shows particles typical of UC₂. Dark bands within particles are U(C, N).
Gray material between particles is mounting resin.

FIGURE 9. SPECIMEN 15. PREPARED WITH 5.5 PARTS OF UC₂ AND 1 PART OF U₂N₃

Powder mixed, compacted, and sintered in argon at 1750 to 1800 C for 2 hr and slowly cooled.

500X

Nitric-Acetic Etch

N48144

Shows light-etching UC₂ particles with dark-etching U(C, N) precipitate.
Black material adjacent to particles is graphite. Gray material between particles is mounting resin.

FIGURE 10. SPECIMEN 25, PREPARED WITH 4 PARTS OF UN, 16 PARTS OF UC₂, AND 1 PART OF CARBON

Mixed, compacted, and sintered at 1700 C for 2 hr in argon and slowly cooled. Resintered in argon at 1800 to 1850 C for 2 hr and slowly cooled.

Further reactions of bulk UC and UC₂ powder with nitrogen were carried out. At 1000, 1300, and 1550 C, reactions were performed with the carbide powder in platinum crucibles heated in a Globar-tube furnace for 3 hr. At 1800 and 2000 C, UC₂ was heated as a compacted powder and also as massive pieces from arc-melted ingots. The samples were placed on UC₂ chips in a graphite crucible and heated slowly in dry prepurified nitrogen to temperature. They were heated at temperature for 3 hr and slowly cooled in nitrogen to room temperature. Table 5 gives data on the chemical analyses and phase identifications. The weak graphite diffraction pattern in the U₂N₃ products was masked by the U₂N₃ pattern. Calculation from weight gains for the reactions indicated the product was UN_{1.67} at 1000 C and UN_{1.48} at 1300 C. The 1000 C value is slightly higher than expected according to vapor-pressure data⁽⁶⁾ (UN_{1.565}). Chemical analysis of the reaction products at 1000, 1300, and 1550 C did not give a material balance. Vacuum-fusion analysis of the product of UC₂ reacted at 1000 C gave 6.27 w/o nitrogen and 1.72 w/o oxygen. This gave close balance, and indicated an oxygen contamination which caused an error in the chemical analysis for nitrogen. This oxygen is apparently in solid solution in the U₂N₃ structure, for no uranium oxide phase could be detected. The closeness of total- and free-carbon values would indicate very little carbon combined in solid solution in the U₂N₃ phases. All compositions were on the nitrogen-rich side of the binary tie line between U₂N₃ and C.

TABLE 5. ANALYSIS OF PRODUCTS OF URANIUM CARBIDE REACTIONS WITH NITROGEN AT 1 ATM

Starting Material	Temperature, C	Composition, w/o				X-Ray Phase Determination
		U	N	Total C	Free C	
UC	1000	86.8	3.40	4.35	4.20	U ₂ N ₃
UC ₂	1000	83.5	4.10	7.71	7.60	U ₂ N ₃
UC	1300	87.8	3.00	3.87	3.80	U ₂ N ₃ a ₀ = 10.658 ± 0.005 Å
UC ₂	1300	84.5	2.70	7.36	7.30	U ₂ N ₃
UC	1550	87.3	6.60	4.21 ^(a)	3.80	U ₂ N ₃ a ₀ = 10.646 ± 0.005 Å
UC ₂	1550	86.7	6.10	4.72 ^(a)	4.30	U ₂ N ₃
UC ₂	1800	87.7	4.60	7.70	2.20	U(N,C) a ₀ = 4.8923 ± 0.0008 Å
UC ₂	2000	90.3	1.50	8.10	2.60	U(C,N) a ₀ = 4.9416 ± 0.0008 Å + UC ₂ + C

(a) The UC and UC₂ powders reacted at 1550 C were partially mixed during the heating.

Figures 11 and 12 show at 500X the microstructures of the solid UC₂ samples reacted with nitrogen for 3 hr at 1800 and 2000 C. The sample reacted at 1800 C (Figure 11) contains a light-etching matrix phase composed of U(N,C). The small dark-etching particles appear to be graphite, as does a slight amount of the material in the large cracks. The gray material in the cracks is mounting resin.

The UC₂ specimen reacted with nitrogen at 2000 C contains relatively coarse light-etching particles of UC₂, as can be seen in Figure 12. Each particle contains a dark-etching material, probably U(C,N), as a rim around the particles and also as thin bands within the light-etching particles. The black mottled areas between the light-etching particles are graphite. The gray mounting resin fills some void areas in the graphite.

Shows light-etching U(N, C) matrix with small dark-etching graphite particles.
Coarse dark gray material in cracks is mounting resin.

FIGURE 11. UC_2 REACTED WITH DRY NITROGEN AT 1800 C FOR 3 HR AND SLOWLY COOLED IN NITROGEN

Shows light-etching metallic UC_2 containing thin bands of U(C, N). Coarse mottled dark gray-to-black bands are graphite.

FIGURE 12. UC_2 REACTED WITH DRY NITROGEN AT 2000 C FOR 3 HR AND SLOWLY COOLED IN NITROGEN ATMOSPHERE

The X-ray diffraction data for the solid UC_2 specimens reacted with nitrogen at 1800 and 2000 C agreed with those reported in Table 5 for powder compacts used in the same experiments. The UC_2 reacted with nitrogen at 1800 C contained $U(N,C)$ + graphite and was located in the $U(N,C)$ + C field on the diagram (Figure 1). This $U(N,C)$ solid solution contains 0.95 mol fraction of UN according to the unit-cell parameter. The absence of appreciable amounts of the UC_2 phase indicates that the amount of combined carbon should be low, about 0.5 w/o. The difference in chemical analysis between total and free carbon is normally assumed to be combined carbon. However, the free carbon is obtained from the residue after an oxidizing dissolution of the uranium phase, and the finely divided graphite shown in the photomicrograph (Figure 11) could be oxidized during this treatment. Therefore, the analysis for combined carbon is considered not reliable for this sample.

The relative stability under 1 atm of nitrogen of uranium nitride and uranium carbide shifts between 1800 and 2000 C. At 1800 C, the nitride phase is more stable than the carbide. At 2000 C, the carbide phase is more stable, UC_2 existing with $U(C,N)$ and graphite. The $U(C,N)$ phase in the UC_2 , reacted at 2000 C with nitrogen, had a unit-cell parameter essentially the same as for $U(C,N)$ phase in the three-phase sample at 1800 C under argon. This indicates that the mol fraction of UC in $U(C,N)$ is about 0.62. From the estimates of the heat of formation⁽⁷⁾, the free-energy change was calculated for the reaction $UC_2 + 1/2N_2 \rightleftharpoons UN + 2C$. At 1800 C the ΔF was +1.6 kcal per g mol and at 2000 C it was +6 kcal per g mol. The experimental observations indicated the reaction was almost complete at 1800 C. This would indicate some error in the estimated free energy at 1800 C, which could be in the heat of formation, ΔH , or in the assumption that $\Delta C_p = 0$. The free energy of the $U(N,C)$ solid solution would be somewhat different from that of UN. With decreased nitrogen pressure the carbides would become more stable as observed for reaction in argon or vacuum. It is estimated that at 2000 C 3.8 atm of nitrogen would be needed to form UN from UC_2 .

Formation of U_2C_3

To determine the possibility of nitrogen solubility in U_2C_3 , attempts were made to form U_2C_3 by reaction of compressed powders of UN, UC, and UC_2 at 1650 to 1700 C. The reaction between UC and UC_2 was checked in the same experiment as a control. Very little U_2C_3 was formed. Phase analyses are given in Table 6. Specimen 16, composed of UC, UN, and UC_2 , formed $U(C,N)$. Uranium sesquicarbide, U_2C_3 , was made by arc melting an alloy containing 7.03 w/o carbon and then heat treating pieces of the ingot at 1650 C for about 2 hr. The product of this treatment was U_2C_3 plus UC_2 , with the composition 92.5 w/o uranium-7.51 w/o carbon-0.008 w/o nitrogen. This material was crushed to minus 325 mesh, mixed with UN, and heated at 1650 to 1700 C for 4 hr in vacuum. The resulting product, Specimen 27, was essentially all U_2C_3 with the composition 92.8 w/o uranium-7.00 w/o carbon-0.001 w/o nitrogen. The analysis showed practically no nitrogen, and the U_2C_3 unit-cell parameter given in Table 6 was the same as in the starting material. Calculation of the mols of carbon and nitrogen relative to uranium before and after firing indicated a loss of both carbon and nitrogen. The UN evidently reacted with the UC_2 to form U_2C_3 and to evolve nitrogen and CN. This result, together with the finding of $U(C,N)$ in Specimen 16, indicates very little solubility of nitrogen in U_2C_3 .

TABLE 6. PHASES OF U_2C_3 REACTIONS AT 1650 TO 1700 C

Specimen	Initial Phases	Product Phases Identified After Reaction at 1700 C in Vacuum	
		By Metallography	By X-Ray Diffraction
15A	$UC_2 + U(C, N)$	$UC_2 + U(C, N)$	$UC_2 + U(C, N)$
16	$UN + UC + UC_2$	$UC_2 + U(C, N) + \text{trace } U_2C_3$	$UC_2 + U(C, N)$ with $a_0 = 4.9497 \pm 0.0005 \text{ \AA}$
17	$UC_2 + UC$	$UC_2 + UC + \text{trace } U_2C_3$	$UC_2 + UC$ with $a_0 = 4.9564 \pm 0.0005 \text{ \AA}$
27	$UC_2 + U_2C_3$ with $a_0 = 8.0885 \pm 0.0005 \text{ \AA}$	U_2C_3	U_2C_3 with $a_0 = 8.0892 \pm 0.0005 \text{ \AA}$

TABLE 7. RELATIVE LOSS OF CARBON AND NITROGEN FOR REACTIONS IN URANIUM-NITROGEN-CARBON SYSTEM AT 1800 C IN ARGON

Specimen	Reactants	Atomic Ratio					
		Initial		Final		Loss	
		C/U	N/U	C/U	N/U	$\Delta C/U$	$\Delta N/U$
3	$UC + U_2N_3$	0.48	0.81	0.33	0.63	0.15	0.18
4	$UC_2 + U_2N_3$	0.90	0.82	0.72	0.27	0.18	0.55
9	$UN + UC_2$	0.90	0.51	0.78	0.24	0.12	0.27
10	$UN + C$	1.00	1.00	0.94	0.28	0.06	0.72
11	$UN + UC$	0.30	0.70	0.24	0.68	0.06	0.02
12	$UN + C$	2.00	0.96	1.85	0.38	0.15	0.58
13	$UC + U_2N_3$	0.33	1.08	0.28	0.67	0.05	0.41
14	$UC + U_2N_3$	0.81	0.26	0.74	0.27	0.07	0.01
15	$U_2N_3 + UC_2$	1.55	0.25	1.51	0.08	0.04	0.17
25	$UN + UC_2 + C$	2.38	0.20	2.22	0.02	0.16	0.18
26	$UN + UC_2$	0.78	0.19	0.75	0.25	0.03	0.07 ^(a)
27	$UN + U_2C_3 + UC_2$	1.53	0.05	1.49	0	0.04	0.05

(a) Weight gain.

DISCUSSION AND CONCLUSIONS

The compositions for the ternary-diagram section at 1800 C in argon (Figure 1) were made by reacting mixtures of UN, U_2N_3 , UC, UC_2 , and C. The reactions can be grouped as follows:

- (1) $UN + UC \rightarrow U(C, N)$
- (2) $UN + UC_2 \rightarrow U(C, N) + N_2 + CN$
- (3) $U_2N_3 + UC \rightarrow U(C, N) + N_2 + CN$
- (4) $U_2N_3 + UC_2 \rightarrow U(C, N) + N_2 + CN$
- (5) $UN + C \rightarrow U(C, N) + UC_2 + N_2 + CN.$

The equations are not balanced because proportions of the products depend upon the initial proportions of the reactants chosen for a given experiment. The formation of CN is inferred from the loss of nitrogen and carbon from the preparations during reaction, as shown in Table 7. This table gives the atomic ratios of carbon and nitrogen to uranium before and after reaction. The molecule of CN presumably decomposes at 1 atm of nitrogen since there was no appreciable loss of carbon in the reactions with nitrogen gas.

The only solid-solution field found at 1800 C for the uranium-nitrogen-carbon system is between UN and UC with a slight excess of carbon and nitrogen. Since at temperatures above 2200 C the UC and the high-temperature cubic phase of UC_2 form solid solutions^(2, 8), one would expect continuous solid solution for the ternary field UC- UC_2 -UN. The composition of this solid solution would depend upon the nitrogen pressure. However, at lower temperatures such a solid solution should dissociate into $U(C, N) + UC_2$ and/or C and at a sufficiently high nitrogen pressure to $U_2N_3 + C$.

Since the composition of U_2N_3 increases to UN_2 with increasing nitrogen pressure⁽¹⁾ (126 atm) the same variation in equilibrium with carbon is expected. UN_2 has the fluorite structure⁽¹⁾ similar to the high-temperature form of UC_2 . Therefore, at high temperatures, above 2200 C, and at high nitrogen pressures, the solid-solution field may be between UN_2 and UC_2 . However, no experimental proof for this hypothesis has been obtained in this study.

The lack of solid solubility of nitrogen in UC_2 and U_2C_3 would indicate that single carbon bonds do not exist in these compounds, but rather double to triple bonds. Concurrent neutron-diffraction-structure studies⁽⁹⁾ have determined that there are carbon double bonds in UC_2 and also in U_2C_3 .

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