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A STUDY OF AS-CAST AND HEAT-TREATED
URANIUM-URANIUM CARBIDE ALLOYS BY
OPTICAL AND ELECTRON MICROSCOPY

BY

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AEC RESEARCH AND DEVELOPMENT REPORT

RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

FEED MATERIALS PRODUCTION CENTER
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ABSTRACT

Examinations of as-cast uranium-base dilute-carbon alloys revealed the growth characteristics of primary carbides in the liquid state, and as-cast and heat-treated samples showed the nature of the network phases. A tentative peritectic phase diagram is proposed to explain the structures seen in as-cast samples.

Age-hardening treatments revealed that uranium-base dilute-carbon alloys were not suitable for dispersion hardening processes. A fine random dispersion of carbides was unobtainable with gamma heat treating followed by alpha annealing.

1. INTRODUCTION

Fuel cores fabricated from certain uranium alloys show a fine dispersion of second-phase particles. These particles tend to inhibit irradiation growth and swelling in reactor service. At one time carbon had been considered to have little effect on the fabrication or irradiation behavior of fuel cores. However, more recent studies of uranium containing carbon in a range of 140 to 860 ppm have shown dispersions of coarse and fine particles which are now thought likely to affect the properties of the alloys. A very brief consensus of the findings of other investigators is given below.

A. In 1952, B. Blumenthal reported angular carbide particles and an unfamiliar fine network phase.¹ The network phase was attributed to fine particles of U(C,N,O) and to small amounts of aluminum, iron, and silicon.

B. In 1955, C. D. Matthews reported a Widmanstätten form of the network and labeled it an "incipient precipitate" forming on subgrain and former gamma grain boundaries.²

C. In 1959, A. Robillard studied the fine networks and proposed that they were produced by "polygonization", the forming of subboundaries composed of dislocations with attached impurity atoms.³

D. In 1959, B. Blumenthal investigated the uranium-rich side of the uranium-carbon phase diagram and found a network subsequently identified as a eutectoid precipitate of uranium-uranium carbide.⁴

E. In 1962, metallurgists at the National Lead Company of Ohio reported on the growth of angular carbides,⁵ and studied the network phases in uranium.⁶

F. In 1963, C. L. Angerman reported that alloying elements as well as impurity atoms segregated into a network of "incipient precipitates" revealed by specific etching conditions.⁷

G. At an informal meeting of metallographers from AEC sites, held at National Lead Company of Ohio in 1963, tentative agreement was reached that there were two types of networks: (1) a coarse network formed by secondary precipitates, and (2) a fine network formed on dislocation structures.

A review of this literature indicates that the presence of finely dispersed particles in uranium fuel cores may show a restraining effect on the irradiation swelling of the elements. The fine particles may serve to pin fission gas bubbles as they move through the uranium matrix, preventing their coalescence and growth. Observations made in post-irradiation annealing studies indicate that the "halo" of gas porosity surrounding fine uranium carbide particles is much finer than the area of porosity a few microns distant from the particle.⁸ These fine particles also

appear to refine the grain structure and strengthen the element. When the carbon content is increased (within the range of 200 to 750 ppm) by 400 ppm, the grain size of beta-heated water-quenched metal has been found to decrease approximately 10%.⁹ Increased strength should enable the fuel core to better resist "tearing" at higher irradiation temperatures.

Although finely dispersed uranium carbides are considered beneficial to the irradiation performance of fuel elements, coarse carbides are detrimental to fuel core processing for two reasons. First, the carbides, in combination with other inclusions, form seams and striations on the surface of the core that interfere with proper bonding of the core with its aluminum jacket. Second, the primary carbides act internally as stress raisers.⁹

It should be clear from this brief discussion that the role of carbon as an alloying agent in uranium is regarded with concern, both here and at other sites. Hence this study of the uranium-base dilute carbon system was undertaken, using both optical and electron microscopy. Information was obtained on the identification, formation, growth, and solid-state reactions of uranium carbides in the as-cast, heat-treated, and fabricated states. The results are presented in this report.

2. SUMMARY

Carbon, when alloyed with uranium in a nominal range of 50 to 900 ppm, showed dispersions of coarse and fine particles arranged in networks. These fine networks, visible in both as-cast and heat-treated uranium, were of two different forms. First and most predominant was the "colony" form of precipitate. The particles in the colonies were of submicron (0.1 to 0.25 micron) size, and precipitated on dislocation structures. The second was the "Widmanstätten" form of precipitate. These particles were also submicron (0.1 to 0.25) in size. The Widmanstätten network appeared to have a definite orientation. Diffraction patterns showed that in all cases the alpha orientation in relation to the particles was (100) alpha, and the direction of alignment was close to the [111] alpha. This caused a speculation that the (100) alpha-[111] alpha plane and direction have a closely paralleling habit plane and direction in either the beta or gamma phases upon which the particles precipitated.

The size of these particles prevents their identification by selected area diffraction. Identification was therefore based on similar diffraction contrasts between primary particles and submicron particles, the primary particles being those particles which were optically resolvable. Both the primary particles and submicron particles showed a change of contrast from very dark to very light when the foil was tilted slightly. Electron diffraction patterns of the primary particles showed them to be uranium carbide. Thus it was reasoned that submicron particles showing the same contrast effects were also composed of uranium carbide.

The formation of the primary carbides was found to follow the kinetics of dendritic growth by a "point diffusion effect". These dendrites were formed within the liquid + UC phase field and grew in a manner prescribed by time and saturation.

Uranium samples with carbon contents of 40, 140, and 270 ppm showed progressive increases in network particle density. Approximately 80% of the sample surface was composed of network phase at 270 ppm carbon content. The formation of primary carbide particles was found to begin when the carbon content was between 140 and 270 ppm. However, a few primary carbides were visible in samples containing less than 140 ppm carbon, and these were attributed to melt-cruci-

ble interactions. As the carbon content was increased to 860 ppm, the network phase decreased progressively while the primary carbides increased in number. Melting studies on the uranium samples containing 270 ppm and 700 ppm carbon showed the solidus isotherm occurring at $1137^{\circ}\text{C} \pm 2^{\circ}\text{C}$. By comparison, high-purity uranium samples (<120 ppm total impurities, including 4 ppm carbon) melted at $1130^{\circ}\text{C} \pm 2^{\circ}\text{C}$.

A tentative peritectic phase diagram is proposed which more fully agrees with the experimental data than does a eutectic diagram. The ratio of network phase to primary carbide particle phase fixed the peritectic at approximately 200 ppm carbon, and the melting studies placed the peritectic isotherm at 1137°C . The diagram incorporates the gamma and beta phase carbon solubilities by Blumenthal, since we observed no particular disagreement with these data in our examinations.

Gamma solutionizing and subsequent aging treatments showed that dilute-carbon alloys of uranium were not suitable for dispersion hardening processes. The increase and subsequent decrease in hardness and, hence, strength during aging is caused more by stress relief of the quenched structure than by matrix precipitation. The as-quenched structure showed many loops (prismatic) and a considerable number of "superjogs," which increased the hardness over that of the as-cast structures. Aging for 3 minutes at 600°C showed an increase in hardness, indicated by the interactions of glide dislocations and loops. Aging for 7 minutes showed maximum hardness, indicated by partial entanglement of dislocations during interaction with the loop structure. Thereafter, aging caused a decrease in hardness indicated by the climb of dislocations into subboundaries. Precipitation occurred on these subboundaries within 15 minutes. Complete stress removal occurred in samples aged for 11 minutes at 600°C . Matrix precipitation occurred after approximately 2 hours and increased the hardness slightly.

3. SAMPLE PREPARATION

3.1 ALLOY PREPARATION

Dingot uranium containing 40 ppm carbon was melted in a laboratory vacuum induction furnace. The desired amounts of carbon were added during melting, and the alloys were cast into ingots 3 inches in diameter by 18 inches long. Samples were cut from top, middle, and bottom of each ingot and were submitted for chemical analyses to determine the composition and the amount of segregation. Chemical compositions of top samples and of a high-purity uranium control sample are shown in Table I.

TABLE I Chemical Analysis of Uranium Alloy and Control Samples

Sample	Element (ppm)					
	C	N ₂	O ₂	Fe	Si	Al
B66	41	27	23	53	25	12
B75	140	37	13	57	54	13
B79	271	21	20	58	33	13
B78	615	28	34	68	40	6
B76	640	9	15	76	34	<6
B81	707	18	30	55	44	<6
B77	860	25	29	74	20	<6
Control*	4	15	10	14	10	7

* Total Impurity Content <120 ppm.

3.2 METALLOGRAPHIC PREPARATION

Standard metallographic procedures were employed to prepare the samples for optical microscopy. Samples, 1 by ½ by ½ inches, were cut from the top of the special test ingots. The samples were ground successively with 60, 400 and 600 grit silicon carbide papers. Subsequent polishing with 6, 3, and 1 micron diamond paste on toweling produced a surface suitable for electropolishing.

The samples were electropolished to bring out the primary UC phase. Polishing parameters were: 30 seconds at 20 volts and 6 amperes in a bath composed of 25 g CrO₃, 25 cc H₂O, and 133 cc glacial acetic acid. To reveal the network phase, samples were electroetched in a 1:1 aqueous-concentrated nitric acid solution for 15 to 30 seconds at 0.6 ampere.

3.3 ELECTRON MICROSCOPY TECHNIQUES

Two types of samples were examined, replicas and thin-foil transmission samples. The techniques developed for their preparation are given in the appendix.

3.4 SPECIAL MELTING STUDY

The solidus isotherm for samples containing 270 ppm and 700 ppm carbon contents was investigated. Because of the highly reactive nature of uranium with crucible and thermocouple materials, special methods had to be used. They were as follows:

A small rectangular sample of uranium containing one of the aforementioned carbon contents and a control sample of high-purity uranium (4 ppm carbon) having the same dimensions were mounted beam fashion in a ceramic boat. An NBS standardized chromel-alumel thermocouple was placed very close to the samples. This assembly was placed in a quartz tube, and the tube was evacuated to 10^{-6} Torr. A tube furnace was utilized for heating with the heating rate controlled by a variable autotransformer. The samples could be observed through a mirror assembly from the outside. The temperatures were measured using an L & N precision potentiometer; allowances for ambient room temperatures were made using automatic compensators.

The samples were heated to 1100°C and held for 3 hours to effect equilibrium. The samples were then heated from 1100°C to 1130°C in 5° increments allowing 30 minutes before each increase; above 1130°C, 1 to 2° increases were used to the melting point. Since the samples were mounted beam fashion, they would sag suddenly when their melting temperatures were reached. When a sample sagged, its temperature was recorded, and the power was turned off. A total of 15 runs were made with the samples in alternate order of carbon content.

4. HEAT TREATMENT

4.1 HOMOGENIZATION

All of the samples except those from the special melting study, were homogenized in a laboratory vacuum resistance furnace at 880°C for 63 hours, and then were cooled very slowly to room temperature prior to any studies.

4.2 GAMMA SOLUTION TREATMENT

The samples were held in a Vycor tube at 950°C under argon atmosphere for 3 hours and then quenched in an ice-brine bath held at -20°C. Quenching was accomplished by upending the Vycor tube, which allowed the samples to plunge into the quenching bath within 2 seconds.

4.3 BETA SOLUTION TREATMENT

The samples were held at 745°C under argon for 3 hours and were quenched in an ice-brine solution held at -20°C.

4.4 ALPHA ANNEAL

The gamma heat-treated samples were annealed in a tube furnace at 600°C and quenched in water at room temperature. For optical microscopy, the samples were annealed 2, 6, 70, and 135 hours. For electron microscopy, the samples were annealed 3, 7, 11, 15, 120, and 360 minutes.

5. RESULTS: AS-CAST STRUCTURES

5.1 SECOND-PHASE STRUCTURES

Three main forms of primary carbides* were noted in the as-polished state. These were: (1) angular, (2) dendritic, and (3) acicular. The angular and acicular forms are visible in Figure 1a while the dendritic form is visible in Figure 1b.

FIGURE 1 Three Principal Forms of Primary Uranium Carbides; (a) Angular and Acicular (100X), (b) Dendritic (300X).

*The term "primary carbide" is used to describe those carbides, angular or otherwise, which are resolvable by optical microscopy at 100X to 1500X magnifications.

Etching these samples electrolytically in 1:1 aqueous -concentrated nitric acid solution darkened the primary carbide phase for identification and delineated the network phase. The network phase showed two forms: (1) "colony", and (2) "Widmanstätten". The colony type of structure is shown in Figure 2a and consists mainly of colonies of fine network structure with interconnecting, discontinuous boundaries. Examination by electron microscopy of a replica of a colony network disclosed that it consisted of both pits and particles (Figure 2b). A transmission electron micrograph of a thin foil of uranium is presented in Figure 2c. This shows that the colony structure is composed of particles 0.25 micron in diameter or smaller. The lines connecting these particles are dislocation lines slightly out of contrast. The indistinct matrix-particle interface is also caused by dislocation structure. Figure 3 shows the interconnecting boundary of particles that were associated with this particular colony.

The second form of network structure, as shown in Figure 4a, is the Widmanstätten. Replication of this particular network (Figure 4b) showed that it consisted of more-or-less evenly spaced particles within the matrix. Thin-foil study (Figure 4c) showed that the particles of the Widmanstätten structure were 0.25 micron or less in diameter. Interactions between dislocations and the particles were notably absent. The results of etching the foil in 1:1 aqueous-nitric acid is shown in Figure 4d. Electron diffraction analysis of these areas showed the plane of the foil to be the (100) alpha and that the particles were aligned close to the [111] alpha direction. The small size of these particles made their identification by selected area diffraction impossible.

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8

(a)

(b)

FIGURE 2 "Colony" Form of Network Structure; (a) Etched in 1:1 HNO_3 (100X), (b) Positive Replica of "Colony" and Large Carbide Particle, (c) Thin-foil Specimen Showing "Colony" Network Particles.

(c)

FIGURE 3 Interconnecting Boundary for Colony Network Structure Shown in Figure 2c. Thin-Foil.

In one instance selected area diffraction was attempted on a group of particles. The results showed a uranium carbide pattern superimposed on a uranium pattern; however, this was an isolated occurrence.

In the course of the thin-foil studies, both the massive primary carbide particles and the network particles showed peculiar diffraction contrast effects. Figures 5a and 5b are examples of this phenomenon. Tilting the primary carbide resulted in a change of contrast from dark to light in the core of the particle as shown. The core of this particle and other particles showing this effect were determined by electron diffraction to be uranium carbide. An identical type of diffraction contrast was seen in the network particles (Figure 6).

The high purity uranium sample (4 ppm carbon), when etched with the standard nitric acid solution, also showed a network (Figure 7a). Thin-foil studies on this sample did not reveal any precipitates, but the etched foils did show a series of large pits along dislocation structures (Figure 7b).

5.2 PHASE DISTRIBUTION AND INTERACTIONS

The samples showed an increase in network phase as the carbon content increased from 4 to 270 ppm carbon. Samples containing 615 ppm carbon or more showed less network phase than did the samples with lower carbon contents (see Figure 8); however, the exact point of decrease

in network was not determined. The primary carbide particle density was observed to increase as the amount of network phase decreased.

For those samples below 200 ppm carbon content, the colony form of network phase was predominant. Above 200 ppm carbon content, the Widmanstätten form of network phase predominated.

A possible interaction between primary carbides and the network phase was suggested by micrographs showing the primary carbide surrounded by a zone devoid of network. Figure 9 shows a sample with 270 ppm carbon which was homogenized at 880°C for 63 hours and from which successive layers 0.001 inch thick were removed. The micrographs show the structure at the sample surface and at 0.002- and 0.005-inch depths. Two clear areas surrounded by network phase are encircled on each micrograph. Investigating this area to a depth of 0.005 inches shows a change in structure and relationship between the primary carbides and network. Note that as the primary carbides appear, the network structure decreases in particle density.

In the colony form of network structure, discontinuities in network boundaries were caused frequently by the growth of small particles within the boundaries (Figure 10). The angular particles, in this case, were identified as UC by their etching characteristics in nitric acid.

FIGURE 4 "Widmanstätten" Form of Network Structure; (a) Etched in 1:1 HNO₃ (100X), (b) Positive Replica, (c) Thin-Foil Study. Plane of Foil is (100) α , (d) Thin-Foil Etched in 1:1 HNO₃.

(FIGURE 4 CONTINUED)

233

239

(c)

(d)

198

199

(a)

(b)

FIGURE 5 Primary Carbide Particle Showing Diffraction Contrast Effects Within the Core;
(a) Before Tilting the Foil, (b) After Tilting the Foil. Core Identified as UC.

(a)

(b)

FIGURE 6 Submicron Network Particles Showing Same Diffraction Contrast Effects Seen in Figure 5; (a) Before Tilting the Foil, (b) After Tilting the Foil.

(a)

(b)

FIGURE 7 Structure of High-Purity Uranium; (a) Etched in Standard Nitric Acid Solution (100X), (b) Thin-Foil Similarly Etched.

FIGURE 8 Relationship Between Carbon Content and Network Phase in Uranium-Carbon Alloys (Determined by Optical Microscopy)

(b)

(a)

(c)

FIGURE 9 Sample Containing 270 ppm Carbon from which Successive Layers Have Been Removed to Show the Interaction Between the Network Structure and Primary Carbides: (a) Original Surface, (b) 0.002 Inches Removed, and (c) 0.005 Inches Removed (All Taken at 100X). Sample Was Homogenized at 880°C for 63 Hours and Furnace Cooled.

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FIGURE 10 Primary Carbide Particle Growth on Network Phase (1500X).

6. RESULTS: HEAT-TREATED STRUCTURES

6.1 HOMOGENIZATION (880°C For 63 Hours, Then Furnace Cooled)

Several changes were apparent within the structure after the homogenization treatment, both in the primary carbides and in the network. The Widmanstätten form of network was changed to the colony form. This change was seen, regardless of carbon content, for all homogenized samples that had originally showed Widmanstätten networks. Along with the structural change in the network phase, an increase in the particle density of the network was observed coupled with a corresponding decrease in the density of primary carbides. Also, those primary carbides that remained were seen to have undergone a rounding off of their corners. In some cases, there was a complete spheroidization of the angular carbides. The change in particle density was particularly noticeable in areas having large quantities of acicular carbide particles in the as-cast structures. Here, there was an almost complete dissolution of the acicular particles and a large increase in the network particle density. This may be seen in Figure 11, which shows the same approximate area before and after homogenization. The denuded zones surrounding the primary carbides are also evident.

6.2 GAMMA SOLUTION TREATMENT (950°C For 3 Hours, Then Quenched In Ice-Brine At -20°C)

Solution treatment of samples with carbon contents of 4 (high purity), 40, 270, and 700 ppm gave structures of the type shown in the optical micrograph, Figure 12a. A high magnification micrograph, Figure 12b, of a sample containing 270 ppm carbon shows the general polygonal bounda-

ries and mottled matrix caused by rapid quenching. No fine precipitate structure could be found by electron microscopy in these quenched samples. The quenched samples were slightly harder than the as-cast samples.

As the carbon content increased, the matrix of these samples became more mottled, and the dislocation lines and loop densities increased. (See Figure 13, which shows uranium samples containing 4, 40, 270, and 700 ppm carbon.) Loops were also found to be associated with dislocation structures, as shown in Figure 14. The dislocation lines within these structures are composed of "superjogs" and large irregular loops as seen in Figure 14a. In other structures, the dislocation lines tend toward large spiral or helix formations (Figure 14b). Note the zone surrounding these structures containing no loops or precipitates.

The prismatic loops were identified by using the tilting stage of the electron microscope. The loops show an average diameter of less than 200 angstroms. Tilting these samples revealed either black spot contrasts within a few of the loops or strain fields around the loop which could not be attributed to the strain field of the loop itself. Black spot contrast within the loop could indicate stacking faults, in which case the loop would be sessile. Strain fields around the loop could indicate solute atom atmospheres. Further tilting experiments indicated that not all of the loops had the same Burger's vectors.

In the same quenched structures, the results of interactions between glide dislocations, vacancies, and loops were observed. The interaction of glide dislocations and vacancies, which hinders loop formation, is shown in Figure 15. In this figure, area A-A is almost completely void of loops and at area B-B one can see two glide dislocations C which have apparently swept out vacancies in a small area to leave a band void of loops. Figure 13d shows the interaction of long glide dislocations and loops to form "superjogs".

6.3 BETA SOLUTION TREATMENT (745°C For 3 Hours, Then Quenched In Ice-Brine At -20°C)

A sample containing 270 ppm carbon was given a beta treatment, and its structure was compared with those of the gamma-treated samples. Very few small loops were formed, but some of the substructures showed large irregular loops (Figure 16a). The submicron particles of the network phase in the as-cast structures were still visible (Figure 16b). The beta-quenched samples in Figure 16 also show a lower dislocation line density than that of the gamma-quenched samples.

6.4 ALPHA ANNEAL (600°C For 3 Minutes To 135 Hours, Then Quenched In Water At Room Temperature)

The gamma-quenched samples containing 270 ppm carbon were annealed for 3, 7, 11, 15, 120, and 360 minutes and examined by electron microscopy. Another group of samples of the same type was annealed for 70 and 135 hours and was examined by optical, as well as electron microscopy. The results were as follows, in order of increasing annealing time:

FIGURE 11 Dissolution of Acicular Carbides and Concomitant Increase in Network Phase in Sample Containing 670 ppm Carbon. (a) As-Cast Structure, (100X), (b) Same General Area of Sample After Homogenization (880°C for 63 Hours, Then Furnace Cooled) (100X).

FIGURE 12 Sample Containing 270 ppm Carbon Gamma Solution Treated (950°C for 3 Hours, Then Quenched at -20°C). (a) Structure at 100X, (b) Polygonal Boundaries at 1500X.

489

261

(a)

(b)

296

370

(c)

(d)

FIGURE 13 Samples Having Varied Carbon Contents Quenched at -20°C from 950°C After 3 Hours. Carbon Levels of the Four Samples Shown Are; (a) 4 ppm, (b) 40 ppm, (c) 270 ppm, and (d) 700 ppm.

6.4.1 Three Minutes

A general increase in the size of the loops and a decrease in their number was observed. There was also a tendency for glide dislocations to be pinned at existing loop structures causing loose entanglements and deep cusps (Figure 17a). Some superjogging is still evident; however, the dislocation lines have started to straighten indicating a climb mechanism at work. No precipitation was in evidence at this time.

6.4.2 Seven Minutes

A decrease in the number of small loops was observed. Along with this decrease was an increase in dislocation tangling and further straightening of dislocation lines by climb (Figure 17b). Figure 17b also shows some large irregular loops and jogging. Electron diffraction indicated no coherent zones of precipitation.

6.4.3 Eleven Minutes

The dislocations now have the appearance of as-cast structures. Precipitates can be seen forming on the dislocation tangles (Figure 17c) which form the subboundaries in the alpha phase. These particles are much less than 0.25 micron in diameter.

FIGURE 14 Loop Structures in Material Quenched at -20°C from 950°C After 3 Hours; (a) Prismatic Loops and "Superjogs", Note Void Zone, (b) Prismatic Loops and Dislocation Structure, Note Climb of Dislocations to Form Partial Helices.

6.4.4 Fifteen Minutes

Further precipitation along substructures can be observed (Figure 17d); most of the particles are rod shaped. Figure 17d also shows the growth of some of the particles over those of the 11 minute anneal. The dislocation structure in Figure 17d was tilted out of contrast.

6.4.5 Two Hours

The polygonal boundaries of the gamma-treated material (Figure 12) have started to coalesce (Figure 18a). Electron micrographs show that the rod-like precipitates along the substructures have shown some growth (Figure 17e). Figure 17e, (2), taken after the foil was etched in nitric acid, shows the boundaries being outlined by precipitates. Neither optical nor electron microscopy revealed any evidence of matrix precipitation.

6.4.6 Six Hours

Further growth or coalescence of precipitates along the boundaries can be seen in the optical micrograph, Figure 18b, and the electron micrograph, Figure 17f. These particles now show the same diffraction contrast mechanism that was evident in the submicron particles of the network phase in the as-cast materials. Figures 18b and 17f showed that precipitation within the matrix has been initiated. The size of the particles indicate that precipitation began just after the 2-hour anneal.

FIGURE 15 Interaction of Vacancies and Glide Dislocations to Form Loop-Free Zones; Area A-A is Large Area Free of Loops, Area B-B is Narrow Band Swept Free of Loops, Probably by the Two Glide Dislocations C, C.

Figure 19 gives an indication of the interaction between boundary precipitates and dislocations. The irregular dislocation line at A has become straightened near the boundary. The dislocation line at B has also been straightened. The straightening mechanism is a result of solute atoms being "piped" along the dislocation structures into the boundary.

6.4.7 Seventy Hours and One Hundred Thirty-Five Hours

Further coalescence of particles in the boundaries can be seen at 70 hours (Figure 18c). There is no apparent change in structure at the 135-hour anneal (Figure 18d).

6.4.8 Hardness versus Annealing Time

The hardness (Rockwell A) of these gamma quenched and annealed samples was measured after annealing times as long as 15 minutes. The results are plotted in Figure 20. Hardness measurements made after the 15 minute anneal are not plotted, since hardness increased only slightly with longer annealing times.

FIGURE 16 Material Containing 270 ppm Carbon Held at 745°C for 3 Hours and Quenched at -20°C. (a) General Structure with Large Irregular Loops and a Few Very Small Loops, (b) Stable Precipitates.

568

(1)

567

(2)

(a) Three-Minute Anneal; (1) Interaction Between Glide Dislocations and Loops, (2) Some Entanglement of Dislocation Structure.

581

(1)

596

(2)

(b) Seven-Minute Anneal; (1) Formation of Large Irregular Loops and Increased Entanglement, (2) Heavy Entanglement of Dislocation Structure to Form Alpha-phase Subboundaries.

FIGURE 17 Sample Containing 270 ppm Carbon Gamma-Treated and Alpha-Annealed at 600°C for Various Lengths of Time.

(c) Eleven-Minute Anneal; Precipitation on Subboundaries.

(d) Fifteen-Minute Anneal; Growth of Precipitates on Subboundaries.

(1)

(2)

(e) Two-Hour Anneal; (1) Slight Growth of Particles on Subboundaries. Particles Show Same Diffraction Contrast Effect as Noted in Figure 6, (2) Thin-Foil Etched in Nitric Acid.

(FIGURE 17 CONTINUED)

460

(1)

466

(2)

(f) Six-Hour Anneal; (1) Further Growth of Particles Within the Boundaries, Note Diffraction Contrast Effects, (2) Precipitation of Particles on Dislocation Structure Within the Matrix.

91A - 29

(a)

91A - 38

(b)

FIGURE 18 Sample Containing 270 ppm Carbon, Gamma-Treated and Alpha-Annealed at 600°C; (a) 2-Hour Anneal, (b) 6-Hour Anneal, (c) 70-Hour Anneal, (d) 135-Hour Anneal (All 1500X). All Samples Etched in Nitric Acid.

(FIGURE 18 CONTINUED)

91A-59

91A-34

(c)

(d)

465

FIGURE 19 "Pipe" Diffusion Effect of Dislocation Structures;
Sample Alpha - Annealed 3 Hours at 600°C.

FIGURE 20 Hardness versus Annealing Time for Sample with 270 ppm Carbon; Annealing Temperature: 600°C.

7. DISCUSSION

7.1 AS-CAST STRUCTURES

7.1.1 Identification

The identification of primary carbides was relatively easy. Etching in 1:1 aqueous-nitric acid darkens the carbon-rich uranium carbides, making them easily distinguishable from the nitrogen-rich $U(C, N)$ compounds, which do not darken. The network phases were also delineated by the above etchant but could not be identified visually. Hence other methods had to be used in this study to determine the composition of the networks.

Both optical and electron microscopy revealed that the fine network phases in the uranium-carbon alloys were composed of small particles. These particles were so small (generally considerably less than a micron in diameter) that selected area diffraction could not be used for their identification. Therefore, the identification of the submicron particles was based on the following two points:

7.1.1.1 The relative quantity of phases present (Figure 8). Optical microscopy showed that as the carbon content increased there was an increase in the amount of network phase up to 270 ppm carbon. At that point there appeared to be an increase in the amount of primary carbide. Alloys with lower carbon content also showed some primary carbides, and these were attributed to either the graphite crucible or the derby feed stock.

7.1.1.2 The nature of diffraction contrast effects between the primary carbides and the network-phase particles. The diffraction contrast effect, in this case, was thought to be related to a mass-thickness mechanism both for the primary particle centers and the submicron network phase particles. Since the primary particle centers showing this effect were identified as uranium carbide through electron diffraction, it was reasoned that the submicron particles, which showed the same effect, were also uranium carbide.

7.1.2 Etching Characteristics of High-Purity Samples

Observations of the carbon-alloyed samples and high-purity samples showed a difference in types of structures when etched in a 1:1 aqueous-nitric acid solution. Incoherent precipitate structure was notably absent in the high-purity sample, (Figure 7b). (Prior studies on pure aluminum showed that it was a necessary criterion for impurity atoms to be associated with dislocations before the structure would show attack.¹⁰ The same study also showed that if the impurity was present as a precipitated particle on either a microscopic or submicroscopic scale, there was no etching on dislocation structure. From this and our own studies, it was concluded that high-purity uranium etched in nitric acid tends to be attacked at dislocation structures having associated, condensed, solute atom atmospheres.)

7.1.3 Formation of Structures

Melting studies on uranium samples containing 270 ppm and 700 ppm carbon showed the solidus isotherm occurs at $1137^{\circ}\text{C} \pm 2^{\circ}\text{C}$. By comparison, the high-purity uranium samples melted at $1130^{\circ}\text{C} \pm 2^{\circ}\text{C}$. (These temperatures have been corrected for thermocouple errors.) Further liquid-phase study showed that the angular primary carbides and network phase in samples containing 270 ppm carbon dissolved at 1300°C , since cooling from that temperature produced the fine dendritic form of the primary carbides (Figure 21) with very little network phase. Holding samples of the same carbon content at approximately 1200°C and slow cooling showed partial dissolution of the primary carbides and enlargement of network phase with visible particles (Figure 22).

In another study of these alloys, melting points were determined by melting samples in a Knudsen cell. The temperatures determined closely approximated the above temperatures, thereby adding more weight to the prediction of a peritectic system for uranium-base dilute carbon alloys.¹¹

The equilibrium diagram for the uranium-uranium carbide system was proposed by Blumenthal as a eutectic system, with the eutectic at 500 ppm carbon.⁴ Such a diagram does not agree with the metallographic and melting point observations made during this study; therefore an alternate, peritectic phase diagram is proposed (Figure 23). The peritectic point is located at approximately 200 ppm and the peritectic isotherm at 1137°C . This diagram includes the gamma- and beta-phase carbon solubilities reported by Blumenthal, since no particular change could be seen in the

FIGURE 21 Sample Containing 270 ppm Carbon Held at 1300°C for 10 Minutes and Quenched. (100X)

FIGURE 22 Closer Approach to Equilibrium of the Peritectic System: Sample Containing 270 ppm Carbon Held at 1200°C for 30 Minutes and Slow Cooled. (100X)

metallographic data of this investigation. Further support of this proposed peritectic system is found in the study of peritectic reactions by Uhlmann & Chadwick.¹² They found that dendrites of the higher melting phase are found in a matrix of lower melting phases within the range of peritectic compositions, which is also found in the metallographic study of the U-UC phase diagram.

Metallographic observations of samples with carbon contents of 40, 140, and 270 ppm carbon showed a progressive increase in network particle density. At 270 ppm carbon the principal beginning of primary carbide formation occurred. This indicated that the carbon content had exceeded the peritectic point. The relationship of carbon content to the amount of network phase (Figure 8) contradicts a eutectic at 500 ppm carbon since sample B78, containing 615 ppm carbon, would have had to be at a maximum of network and decrease as B77 (860 ppm carbon) is approached. Sample B81 (700 ppm carbon), stood in contradiction to the rest of the samples in that general range of carbon content. Its behavior was probably due to cooling at a faster rate.

As the molten alloys are cooled through the UC + liquid phase, primary UC particles will precipitate and grow. The length of time in the UC + liquid phase will determine the size and shape of the carbide. The time spent in the UC + liquid phase is dependent upon the separation of the liquidus and solidus phase boundaries and the rate of cooling through this phase region. Since

FIGURE 23 Proposed Peritectic Phase Diagram for the Uranium-Uranium Carbide System.

the temperature difference separating the liquidus and solidus phase boundaries is greater for higher carbon contents, those alloys with greater than 200 ppm carbon content will show an increase in the primary carbides and a relative decrease in network phase. The effect of rates of cooling through the UC + liquid phase is illustrated by comparing Figures 22 and 24.

The samples with 40 and 140 ppm carbon contents revealed a colony form of network, while the samples containing 270 ppm carbon or more had a Widmanstätten network. Both the colony and Widmanstätten forms of network are formed by precipitation in the solid state. The colony network particles in samples with 40 and 140 ppm carbon precipitate on dislocation structures, and the formation of these particles produces stresses that cause dislocations at the particle-matrix interface. The colony network appears to precipitate at somewhat higher temperatures than does the Widmanstätten network. This can be seen by comparing the size of the colony network particles (Figure 2a) with the Widmanstätten network particles (Figure 4a). The rate of precipitation is controlled by the rate of diffusion, which is enhanced by the dislocation structure. The Widmanstätten network appeared to have a definite orientation relationship. Diffraction patterns showed that in all cases the alpha orientation in relation to the particles was (100) alpha and the direction of alignment was close to the [111] alpha. This causes a speculation that the (100) alpha-[111] alpha, plane and direction, have a closely paralleling habit plane and direction in either the beta or gamma phases upon which the particles precipitated. The precipitation of the Widmanstätten particles does not cause the formation of dislocations as did the colony particles.

FIGURE 24 Structure of Chill-Cast Ingot with 250 ppm Carbon.
(100X)

7.1.4 Growth Characteristics of UC in the UC + Liquid Phase

Samples of uranium containing more than 200 ppm carbon, either in the as-cast and slow-cooled or as-cast and quenched state, have shown the angular primary carbide particles in dendritic forms. These carbides were so similar to salts precipitated from supersaturated aqueous solutions by A. Papapetrou that his conclusions may be held applicable to primary uranium carbide formations.¹³ Papapetrou stated that dendrites started from an "idiomorphic" form and preferentially grew dendritic arms from the corners of the idiomorph. This growth is illustrated schematically in Figure 25a and is shown in micrographs of actual uranium carbide particles in Figure 1 and Figure 26a. An electron micrograph of a carbide particle in Figure 26b also showed the "point diffusion effect" postulated by Papapetrou in the core of the particle. This core was identified as UC by electron diffraction and the enveloping material was thought to be $U(C,N,O)$.

Mathematical expressions for crystal growth indicate that dendritic growth and spacing are directly proportional to the diffusion coefficient and/or heat dissipation in the solution. Also, dendritic crystal growth is inversely proportional to the cooling rate or rate of increasing supersaturation. A high diffusion rate in the solution would slow down preferential corner growth, since the concentration differences surrounding the corners and that adjacent to the crystal

FIGURE 25 Growth of Primary Carbides Within UC + Liquid Phase Region; (a) Schematic of Growth by "Point Diffusion Effect", (b) Variations in Dendritic Growth with Time and Velocity by "Point Diffusion Effect".

FIGURE 26 Primary Carbide Particles Representative of the Growth Forms Shown Schematically in Figure 25; (a) Optical Micrograph (1500X), (b) Electron Micrograph of Thin-Foil, Core Identified as Uranium Carbide. Surrounding Material is $U(C,N,O)$.

faces would be equalized. Conversely, a low diffusion rate would promote the dendritic type of formation. The geometric shape of the particle is also a function of time.¹⁴ This is shown schematically in Figure 25b. Figure 27 shows the primary carbide dendritic growth as predicted above.

The growth of primary uranium carbide particles by "point diffusion effect" is by no means the only mechanism; however, it is the predominant one. Others include the heterogeneous nucleation of uranium carbide on foreign particles and further growth on the crystal faces. The rate of diffusion of carbon in the $UC + liquid$ phase appears to be intermediate, and this rate promotes the corner growth of uranium carbide.

7.1.5 Changes Produced in As-Cast Structures During Fabrication

Earlier work on production ingots showed the presence of uranium carbide forms similar to those reported in this study. These carbides are fractured during alpha-phase rolling of the ingot to rod form, and become elongated, as shown in Figure 28. The dendritic UC formation present in the ingot (Figure 28a) is transformed during the first rolling into the form shown in Figure 28b. On further rolling to final rod size, the broken-up dendrites form stringers as shown in Figure 28c.

FIGURE 27 Sample Containing 400 ppm Carbon Held at 1300°C for 20 Minutes and Quenched in Liquid N₂. Dendritic Growth of Carbides Follows Figure 25b. (100X)

The acicular uranium carbide form and the network can also be traced from ingot to formed rod. The as-cast acicular carbides shown in Figure 1 are aligned during the rolling process and may appear as layers between zones of stringers (Figure 29). The network is elongated, and the individual fine carbides are somewhat aligned. These carbides form the background inclusions seen in photomicrographs.

The amount of carbide permitted in reactor-grade uranium is set by a specification limit for carbon. In rather extreme cases, heavy stringers of uranium carbide cause internal cracks. Similar formations produce seams if they occur on the surface of the core, and these seams may adversely affect the bond between the uranium fuel core and its aluminum jacket or "can". Large voids are cause for rejection of the finished reactor fuel element.

7.2 HEAT-TREATED STRUCTURES

7.2.1 Homogenization Treatments

After the homogenization anneal, samples that had previously displayed the Widmanstätten form of network changed to the colony form upon slow cooling to room temperature. This kind of change in structure means that at the annealing temperature of 950°C, the network phase was soluble in gamma uranium. This statement is further supported by the fact that this structural change occurred only in those samples heated into the gamma range (not in samples heated only into the beta range) and was reasoned to be indicative of the eutectoidal decompositions.

(a)

(b)

(c)

FIGURE 28 Breakup of Carbide Dendrites During Fabrication; (a) As-Cast Structure, (b) Billet Structure, (c) Final Rod Structure. (All 100X.)

FIGURE 29 Alternate Layers of Acicular and Angular Uranium Carbides in Rolled Rod. Compare with the As-Cast Structure Shown in Figure 1a.

Homogenization treatments cause almost complete dissolution of the acicular carbide particles to form the network phase. A tentative explanation of this phenomenon follows. Two facts are known: (1) the acicular particles do not darken as readily as the angular carbides in 1:1 nitric acid, and (2) the angular carbides do not go readily into solution. The acicular particles are not as carbon-rich and are not as stable at high temperatures as are the angular carbides. If the particles were nitrogen- or oxygen-rich, they would not show dissolution because both the uranium nitride and uranium oxide compounds are less soluble. The acicular particles are caused by the peritectic reaction. Intermetallic compounds resulting from peritectic reactions show a "coring" effect. This results in a decrease of solute (carbon) from center to edge. Slow cooling would result in the diffusion of solute atoms in an attempt by the compound to achieve equilibrium. With acicular particles of uranium carbide, this reaction would leave the particle in a non-equilibrium state. When heated into the gamma range, these acicular carbides, which would be less stable, would show a more rapid dissolution than would the angular carbides.

7.2.2 Alpha Anneal

The first results of the optical studies of uranium samples that were gamma heat-treated, quenched, and alpha annealed indicated that uranium-rich carbon alloys might be dispersion hardenable. Hardness measurements (Figure 20) on a sample containing 270 ppm carbon showed that the system had a very short hardening period. The results of electron microscopy studies on this particular alloy confirmed the data of Figure 20.

Electron microscopy showed that all of the network phase went into solution at 950°C. In solution the carbon atoms reacted with vacancies to form atom-vacancy pairs. The carbon atoms further tended to cluster causing the vacancies to collapse and form pure prismatic loops in the matrix of uranium. The high rate of clustering on the polygonized substructures was indicated by the loop-free zones surrounding the substructure boundaries. The vacancy clusters which precipitate on the dislocation substructures cause the dislocations to break away and climb, thus forming larger loops and helices. This action is analogous to that which takes place in the aluminum-magnesium alloy system.

The quench hardening is caused by the interaction of the matrix loops with glide dislocations moving through applied stresses caused by the quenching. In the first stages of annealing, the loops increase in size and pin more moving dislocation lines (the dislocation movement is caused by thermal activation). This causes the increase in hardness over that of the quench hardness.

Further annealing shows the complete disappearance of loops. The dislocation tangles are formed from the pinned dislocation lines. These dislocation lines have straightened (loss of superjogs) indicating that they have reacted with the vacancies from the loops causing climb. This mechanism causes a decrease in the hardness by relieving stresses in the crystalline lattice.

Precipitation within the subboundaries and boundaries occurred in about the same period of time that complete stress relief was taking place. The precipitate particles showed a large growth rate for an annealing time as long as 6 hours. Thereafter the growth decreased depending upon saturation conditions. Longer anneals (6 to 135 hours) showed a slight increase in hardness. The slight increase in hardness was caused by the beginning of precipitation in the matrix. This dispersion of particles in the matrix increased the hardness and strength slightly.

The greater precipitation occurred within the subboundaries and boundaries of the alpha phase. Hence, the uranium-base dilute carbon alloy system cannot be called dispersion hardenable in the strict sense of the word. Rather, the increase and subsequent decrease in hardness was caused by stresses induced by quenching and the subsequent removal of these stresses by annealing. The dispersion hardening mechanism for the alloys came only after longer annealing times and caused only a very slight increase in hardness.

The fact that a fine dispersion of particles within the matrix increases the resistance of fuel cores to swelling rules out the use of uranium-base carbon alloys which are given gamma-phase heat treatments. The overall strength of the core would be lowered by the formation of brittle precipitates in the boundaries and subboundaries. The absence of any great amount of matrix precipitation would leave very few sites for the capture of gas bubbles, and the presence of brittle intermetallic compounds in the boundaries would aid grain boundary tearing. Therefore, uranium-base dilute carbon alloys having no other alloying element should be used only in the beta heat-treated condition.

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10. APPENDIX: PREPARATION OF SAMPLES FOR ELECTRON MICROSCOPY

10.1 THIN FOILS

10.1.1 Equipment

A Buehler electropolishing cell was modified to accept a double jet assembly that would deliver a stream of electrolyte simultaneously to both sides of the sample. The polishing cell, Figure 30, consists of a magnetically driven impeller pump within the electrolytic cell, the double jet assembly, and a lamp.

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FIGURE 30 Buehler Electropolishing Cell Modified with a Double Jet Assembly; (A) Polishing Cell and Pump, (B) Double Jet Assembly, (C) Lamp, (D) Sample.

A later design of the jet assembly is shown in Figure 31. This device was fabricated from standard, stainless steel tubing and fittings. The nozzles are of $\frac{3}{16}$ -inch stainless steel tubing and are attached to a stainless steel tee with swagelock fittings. A rubber stopper serves as a reducer and connects the jet assembly to the polishing cell orifice.

10.1.2 Bulk Sample Preparation

Samples 0.050-inch thick are cut from the material under investigation using a small water-cooled cut-off wheel. Approximately 0.030 inch of the thickness is then removed by chemical attack in concentrated HCl. This reaction is rapid and must be stopped when the periphery of the sample becomes rounded. The sample is washed, dried, and attached to a holder for mechani-

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FIGURE 31 Double Jet Assembly; (A) Nozzles, (B) Tee, (C) Swagelock Fittings, (D) Electrolyte Tube, (E) Rubber Stopper.

cal grinding. The holder consists of two blocks of stainless steel, each $\frac{1}{2}$ by $\frac{1}{2}$ by 1 inch. The sample is attached to the holder by tape to facilitate changing sides of the sample during grinding.

Both sides of the sample are ground on 60 grit paper until its thickness has been reduced to 0.010 inch. Further grinding with 400 grit paper removes the rough finish left by the previous grinding while reducing the sample thickness to 0.008 inch. The sample surface is now suitable for final thinning. The sample thickness of 0.008 inch must not be reduced by further grinding. Previous experiments showed that further grinding resulted in dislocation structures not indicative of the bulk sample.

10.1.3 Final Thinning

The sample is the anode and is placed between the nozzles, which are made the cathodes. The electrolyte consists of 1330 cc glacial acetic acid, 250 cc H_2O , and 250 g CrO_2 . The electrolyte flow is regulated to a volume that gives suitable polishing conditions when 80 volts is applied across the cell. Polishing is continued until a perforation occurs. The exact moment of perforation is best determined by focusing a beam of light on one side of the sample and watching from the shadowed side.

At first appearance of light, the current is turned off, the sample is removed from the jets, washed with alcohol, and dried. The electropolished area ($\frac{1}{8}$ -inch diameter) containing the perforation is coated on both sides with a masking lacquer or fingernail polish. After drying, the sample is replaced in the jet assembly. The same electropolishing conditions are used. The attack is concentrated at the periphery of the mask, allowing the specimen to be cut out. The mask is removed in acetone; the specimen is then washed with alcohol and dried.

10.1.4 Dioxidizing Procedure

The electropolishing process leaves an oxide layer on the surface of the sample. A deoxidizing solution composed of 75% H_2SO_4 , 7% H_2O , and 18% glycerol was developed by electron microscopists at Harwell, England.¹⁵ A successful method for removing the oxide layer with this solution was developed by C. L. Angerman of Savannah River.

The deoxidizing solution is applied dropwise from a flask fitted with a platinum tube as the cathode. An open circuit potential of 10 volts is applied across the cell, while the specimen is held vertically allowing only one drop at a time to transverse the sample. The anodic layer is generally removed by 20 drops. The sample is immediately washed with alcohol, dried on filter paper, and placed in the microscope.

10.2 REPLICAS

The bulk samples were ground successively with 60, 400, and 600 grit silicon carbide papers. They were then rough-polished on wheels using diamond paste and given a final electrolytic polish in chromic-acetic acids. The samples were etched electrolytically in a 1:1 aqueous-concentrated nitric acid solution before replication.

A two-stage replication method was used. First, the etched sample was coated with a 4% collodion film. After drying the film was stripped off and shadowed with gold or uranium at an angle of 30° . Carbon was evaporated onto the film and the collodion was removed from the carbon film by immersion in acetone for 15 minutes. The carbon film and acetone were then transported to a water bath and submerged, allowing the film to uncurl and float freely on the water surface. The film was then picked up on grids, washed, dried, and placed in the microscope. This method gives a **positive** copy on the sample surface.