METALLOGRAPHY OF URANIUM CONTAINING SMALL ADDITIONS OF IRON, SILICON, OR ALUMINUM*

by

JUL 22 1963

TID-18998

C. L. Angerman

and

M. R. Louthan, Jr.

Savannah River Laboratory
E. I. du Pont de Nemours and Co.
Aiken, South Carolina

MASTER

ABSTRACT

In uranium with alloying additions of up to 400 ppm Fe and up to 800 ppm of either Si or Al, the various U-containing phases were examined with the electron microscope. These phases were also extracted chemically and identified by electron diffraction. During γ-phase heat treatments, the alloying additions, as well as impurity atoms, segregate into networks of "incipient" precipitates that can be seen only after certain etching treatments.

Facsimile Price $ 1.60
Microfilm Price $ .80

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

---

*The information contained in this article was developed during the course of work under contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

METALLOGRAPHY OF URANIUM
CONTAINING SMALL ADDITIONS OF IRON, SILICON, OR ALUMINUM*

by

C. L. Angerman and M. R. Louthan, Jr.

INTRODUCTION

Additions of up to 400 ppm iron and up to 800 ppm of either silicon or aluminum are used to promote grain refinement during beta transformation(1) and to improve irradiation stability(2) of uranium fuel. Characterization of the phases that are produced by these additions and the effects of heat treatments on their distributions is necessary for a complete understanding of the properties of the alloys. Existing phase diagrams indicate the compounds that might be expected in binary systems, but data on the ternary and quaternary systems are not available.

This paper describes the metallographic appearance and the identification of the phases present and the effects of heat treatment on a few of the possible ternary and quaternary alloys. Since the intermetallic particles were small, electron microscopy was used extensively in the examinations of the structures. Typical heat treatments were either 30 minutes at 830°C or 10 minutes at 720°C followed by quenching in either water or oil. Annealing after quenching was done at 550°C for 30 minutes. Some samples were alpha annealed at these same conditions prior to the beta treatment.

---

*The information contained in this article was developed during the course of work under contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

SUMMARY

In each alloy, the additions were dissolved completely at gamma-phase temperature. The solubility limits at beta-phase temperatures were greater than 400 ppm Fe and 800 ppm Si, but the limit for Al was between 150 and 250 ppm. Annealing at alpha-phase temperatures after quenching from the beta or gamma phases precipitated U_6Fe, U_3Si, or UAl_2, either singly or in combinations, depending on the alloy. However, Si was soluble in both U_6Fe and UAl_2 and caused a decrease in the c/a ratio of U_6Fe of 0.014 and a decrease in the a_0 value of UAl_2 of about 0.05 to 0.12Å. Metallographic examination indicated that Fe was also soluble in UAl_2, but no change in the lattice parameter was detected within the accuracy of the measurements.

Although no discrete precipitates were observed after quenching from the gamma phase, indicating that the alloying additions were dissolved completely, networks of "incipient" precipitates were revealed by certain etchants. These incipient precipitates are believed to be the result of a segregation of the solute atoms to the grain and subgrain boundaries of the beta phase that existed during cooling. As the cooling rate increased, the degree of segregation to the boundaries decreased, and a more severe etch was required to reveal the networks.

DISCUSSION

METALLOGRAPHIC TECHNIQUES

The minor phases resulting from the alloying additions were distinguishable after electropolishing in the standard phosphoric acid-ethylene glycol-ethyl alcohol solution. For examination with the electron microscope, "Formvar" replicas were dry-stripped from the electropolished surface and shadowed with uranium at an angle of 18 degrees. The electropolish left the intermetallic phases in relief, but attacked the nonmetallic compounds, such as UC, UN, UH_3, and UO_2.

An extraction replica technique was employed to identify the intermetallic phases. Samples were electropolished in the same manner as previously described. A "Formvar" film was cast on the surface and scribed to form squares suitable for insertion into the electron microscope. Prolonged electropolishing (approximately 20 minutes) through this "Formvar" film freed the film in which the particles were imbedded.

IDENTIFICATION OF PHASES

Three phases, U_6Fe, UAl_2, and U_3Si, that were extracted in the manner described above, were identified by selected area electron diffraction. The lattice constants calculated from these patterns indicated that Si was soluble in both U_6Fe and UAl_2. The c/a ratio for U_6Fe decreased from 0.500 for an alloy containing 30 ppm Si to 0.486 for an alloy containing 330 ppm Si. The value of a_o for UAl_2 decreased from 7.74 Å for an alloy with 30 ppm Si to 7.69 and 7.62 Å for alloys containing 310 and 340 ppm Si, respectively. Iron had no significant effect on the lattice parameter of UAl_2. However, the metallographic examinations showed that some Fe was soluble in UAl_2. No changes were observed in the lattice parameter of U_3Si when either Fe or Al was present in the alloy.

Each phase had a characteristic appearance after electropolishing that permitted a tentative identification on the basis of metallographic appearance (see Figure 1). The U_6Fe [or $U_6(Fe,Si)$] particles were in relief with somewhat rounded interfaces. Frequently they were elliptical when the particle lay in a grain boundary, or triangular when the particle was at an intersection of three grains. Although the UAl_2 [or $U(Al,Si)_2$] particles were also in relief, they had a more rounded shape than the U_6Fe and had more vertical interfaces. Additionally, the UAl_2 particles were smaller than the

U_6Fe particles. The U_3Si had a characteristically striated surface that made identification relatively easy.

EFFECT OF HEAT TREATMENT

In the as-cast condition all the alloys contained an eutectoid structure, as illustrated in Figure 2. The eutectoid was composed of a mixture of either U_6Fe, U_3Si, UAl_2, or a phase tentatively identified as UC; the relative amounts of each phase depended upon the composition and the cooling rate during solidification.

Gamma Treatment

At least 400 ppm of Fe and 800 ppm each of Si and Al were soluble in the gamma phase. The standard electropolish did not reveal any minor phases in small samples that were water quenched after 30 minutes at 830°C. Trace amounts of UAl_2 were observed in more massive pieces of alloy (240 or 800 ppm Al) that were oil quenched.

In contrast, electrolytic etching in a 50 vol % HNO_3 solution at 1 v (open circuit) for 15 to 30 seconds revealed a network structure in all of the gamma-quenched alloys, as illustrated in Figure 3. Examination of this structure with the electron microscope indicated that the lines were rows of shallow pits. These line are believed to be the result of segregation of some alloying or impurity atoms to the grain and subgrain boundaries of the beta phase during cooling and are called incipient precipitates. The white bands are believed to be "ghosts" of the gamma grain boundaries. These hypotheses are supported by the similarities in sizes of the beta and gamma grains, as observed by hot-stage metallography,(3) and the sizes of the networks formed by the black lines and the white bands, respectively. Similar structures were observed with the same etch by Mathews(4) and with a chromic-acetic acid etch by Robillard.(5) Althaus and Cook(6) also observed these structures, but concluded they were artifacts after a study of the etching conditions.

The nature of the particles comprising these networks and the ability to reveal the networks with etchants other than the HNO_3 etch were dependent on the cooling rate from the gamma phase. Samples of unalloyed ingot uranium were annealed 30 minutes at 950°C to dissolve some of the carbon, then air cooled or quenched in either water at 22°C, brine at -2°C, or a 50% $CaCl_2$ solution at -50°C. The networks in the air cooled sample were composed of discrete precipitates of UC that could be revealed by electropolishing (Figure 4, a and b). In contrast, the networks in the quenched samples were composed of incipient precipitates that could be revealed only by a "pitting" type etch (Figure 4, c and d). As the cooling rate increased a more severe etch was required to reveal the networks, as indicated in the Table. The exact nature of the incipient precipitates is not known at this time.

TABLE I

CONDITIONS FOR REVEALING NETWORKS

	Networks revealed by		
Cooling Conditions	HNO_3 Etch	Chromic-Acetic Etch	H_3PO_4 Electropolish
Air cool	Yes	Yes	Yes
Water quench	Yes	Yes	No
Brine quench	Yes	No	No
$CaCl_2$ quench	Yes	No	No

Any segregation of the solute atoms to the beta grain boundaries should increase the chemical reactivity in the localized area in proportion to the degree of segregation. When only a portion of the solute atoms were segregated, as in a rapid quench, a more reactive etchant was required to reveal these areas. When more, or essentially all of the atoms, as in the case of a discrete precipitate, were segregated, the less severe etchants or polishes could be used.

Beta Treatment

The examination of samples containing up to 400 ppm Fe, 800 ppm Si, and 800 ppm Al in the beta-quenched condition indicated that the solubility limit in beta uranium was greater than 400 ppm for iron, greater than 800 ppm for Si, and between 150 and 250 ppm for Al. In general, U_6Fe or U_3Si precipitates were observed in alloys containing up to 400 ppm Fe or 800 ppm Si. UAl_2 was not observable in alloys containing approximately 25 ppm Al but was present in trace amounts in a sample containing 110 ppm Al and was readily observable in samples containing 250 ppm Al or more. The alloys containing more than 700 ppm Al contained a network of UAl_2 precipitates similar to the networks of incipient precipitates observed in the gamma-quenched samples.

In some instances trace amounts of U_6Fe and U_3Si were observed after beta quenching. This slight precipitation may have resulted from local nonuniformities during cooling or to incomplete dissolution of any pre-existing particles. The U_3Si was observed in only one of 25 samples examined, while $U_6(Fe,Si)$ was present in five samples. The alloy content appeared to have little or no effect on whether or not U_6Fe was precipitated since trace amounts of precipitation were observable in a sample with 63 ppm Fe and no precipitation was observable in a sample with 400 ppm Fe.

Alpha Annealing

The structures produced by alpha annealing at 550°C after either beta or gamma quenching corroborated the interactions indicated in the diffraction patterns. This treatment precipitated U_6Fe, U_3Si, and UAl_2, depending upon the composition. The U_6Fe precipitated as networks in alloys containing 25 ppm Al and as random precipitates in alloys containing greater than 250 ppm Al (Figure 5). The U_3Si was always present as random precipitates regardless of Al content. U_3Si was not observed in samples containing up to 350 ppm Si if Fe was present in at least equal concentrations. In samples containing two to three times more Si than Fe, the concentrations of U_3Si and U_6Fe were approximately equal. These observations corroborate the selected area diffraction work, showing that Si was highly soluble in U_6Fe. Alloys with 800 ppm Al in addition to the Fe and Si contained less U_6Fe and U_3Si than corresponding alloys with 25 ppm Al, indicating that Fe and Si were soluble in UAl_2.

One alloy, containing 250 ppm Fe and 25 ppm Si, had a microstructure radically different from any of the other alloys examined. Networks of U_6Fe precipitates were present after beta quenching, and alpha annealing caused additional precipitation of U_6Fe in a Widmanstätten pattern (Figure 6). No explanation can be given for this unusual behavior since the chemical analyses did not indicate an abnormally high Fe content.

REFERENCES

1. Boland, J. F., H. C. Kloepper, Jr., and N. F. Neumann. "The Alloying Influence of Iron and Silicon on the Grain Size of Beta Heat-Treated Dingot Uranium". Process Development Quarterly Progress Report. MCW-1465 (August 1961).

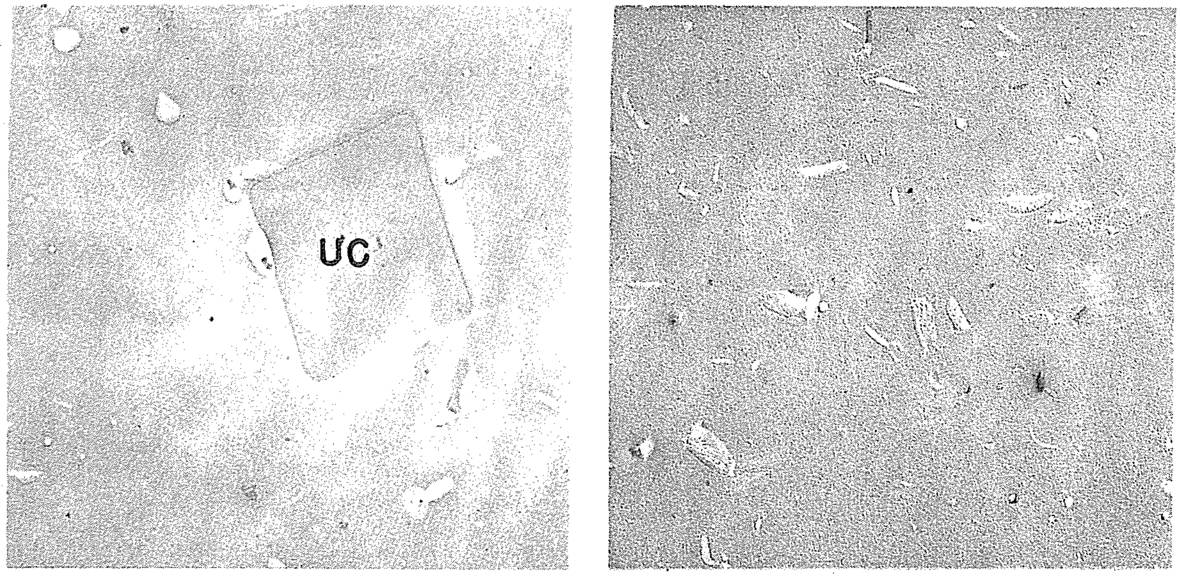
2. Bellamy, R. G. "The Swelling of Alpha-Uranium under Neutron Irradiation to 0.7 at. % Burnup". Symposium on Uranium and Graphite. Institute of Metals. (1962).

3. Angerman, C. L. "High-Temperature Metallography of Uranium". Presented at the 15th Meeting of the AEC Metallography Group. E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, S. C. (1961).

4. Mathews, C. O. "The Precipitation of Impurities in Commercial and High-Purity Uranium". Technical Papers of the Tenth Metallographic Group Meeting Held at Knolls Atomic Power Laboratory, October 24, 1955. TID-7523 (Pt. 2) (declassified September 30, 1960).

5. Robillard, A. Influence of Heat Treatment in β and γ Phases on the Microscopic Structure of Uranium. Commissariat à l'Energie Atomique, Paris, France. CEA-1057 (1959).

6. Althaus, W. A. and M. M. Cook. "An Anomalous Structure Produced by Etching Polished Uranium Surfaces with 1:1 Nitric Acid". Summary Technical Report for the Period April 1, 1962 to June 30, 1962. NLCO-855 (1962).

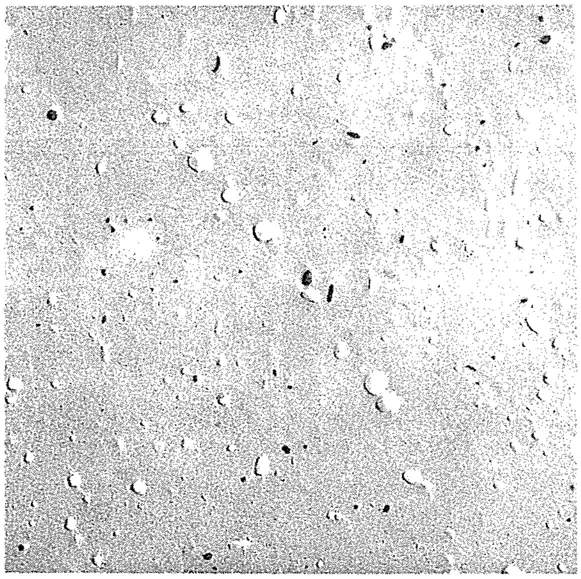


Neg. 1268A 4000X

a. U_6Fe particles. Both triangular and round shapes, rounded interfaces.

Neg. 1090A 7800X

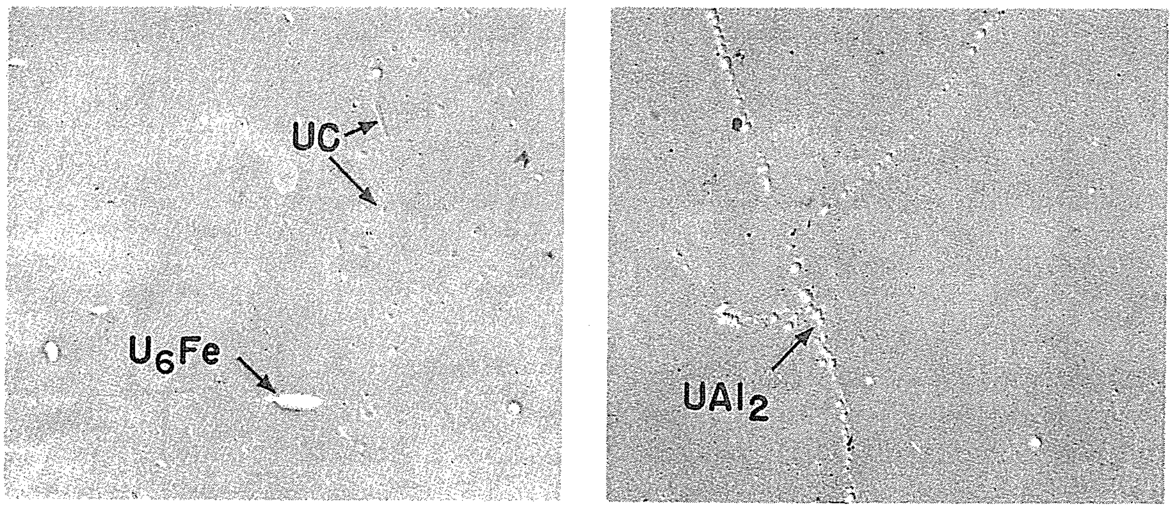
b. U_3Si particles. Striated surface.



Neg. 1110B 7800X

c. UAl_2 particles. Round shape, sharp interfaces.

FIG. 1 TYPICAL APPEARANCES OF PRECIPITATE PARTICLES



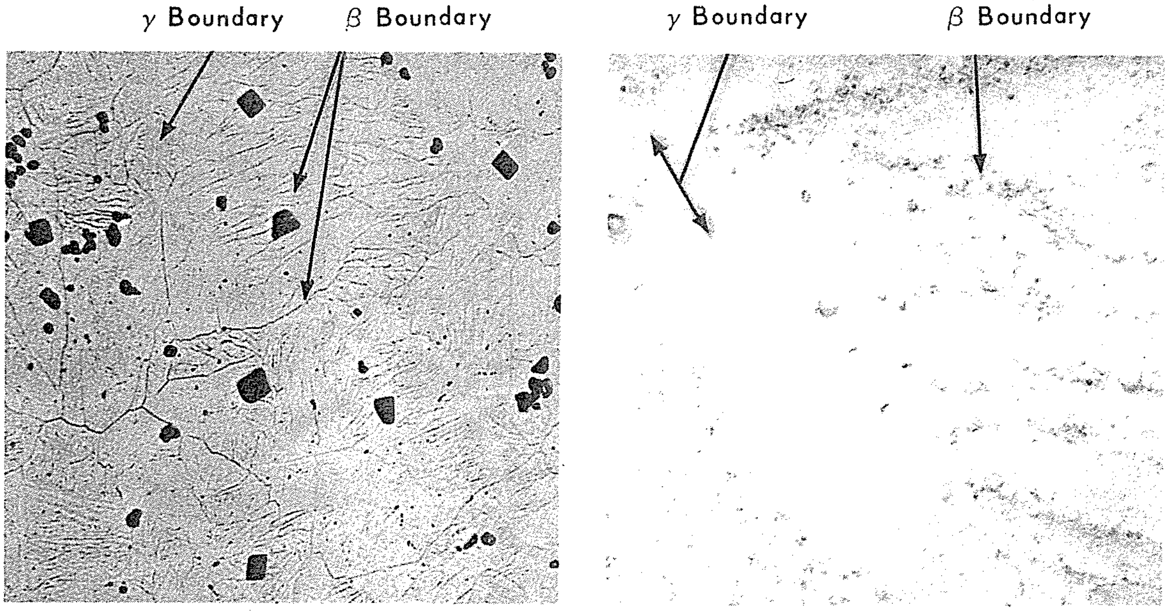
Neg. 1000A 2000X

a. Alloy: 150 ppm Fe - 100 ppm Si - 10 ppm Al

Neg. 1097D 5400X

b. Alloy: 350 ppm Fe - 30 ppm Si - 800 ppm Al

FIG. 2 EUTECTOID STRUCTURES IN AS-CAST ALLOYS



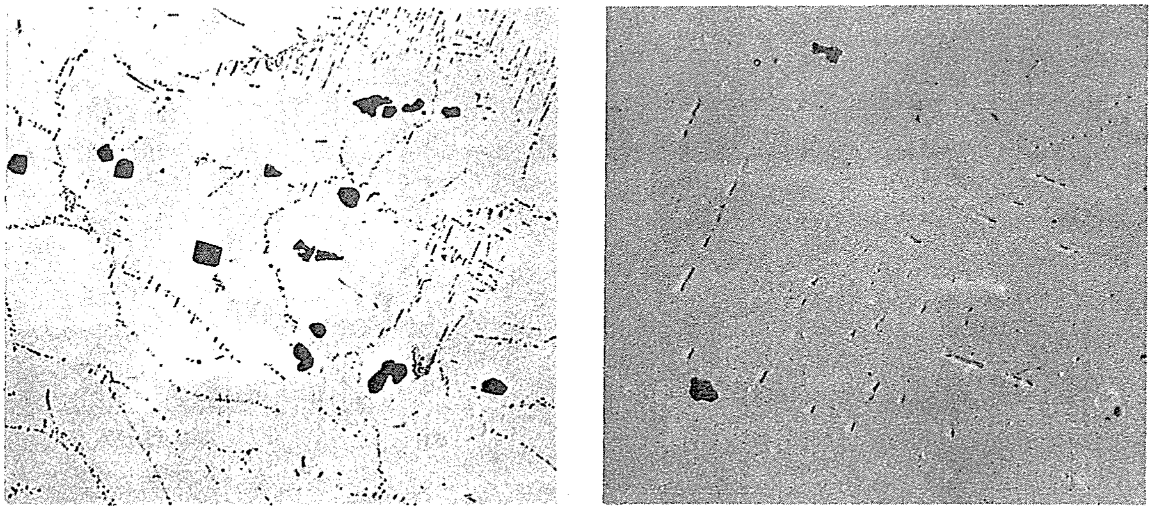
Neg. 44540 250X

a. Networks revealed by electrolytic nitric acid etch.

Neg. 1156B 7800X

b. Rows of pits which form the lines shown in Fig. 3a.

FIG. 3 NETWORKS OF INCIPIENT PRECIPITATES IN GAMMA QUENCHED ALLOYS



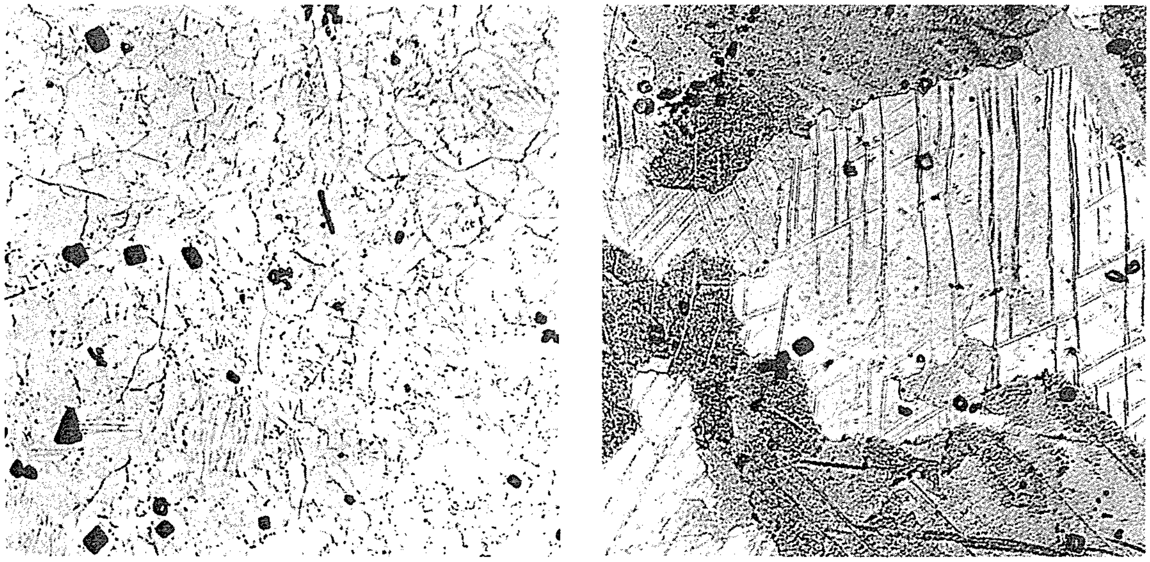
Neg. 46936 250X

a. Electrolytic nitric acid etch.

Neg. 1166A 7800X

b. Phosphoric acid electropolish.

Figures 4a and 4b show networks of discrete UC precipitates formed during air cooling.



Neg. 50982 250X

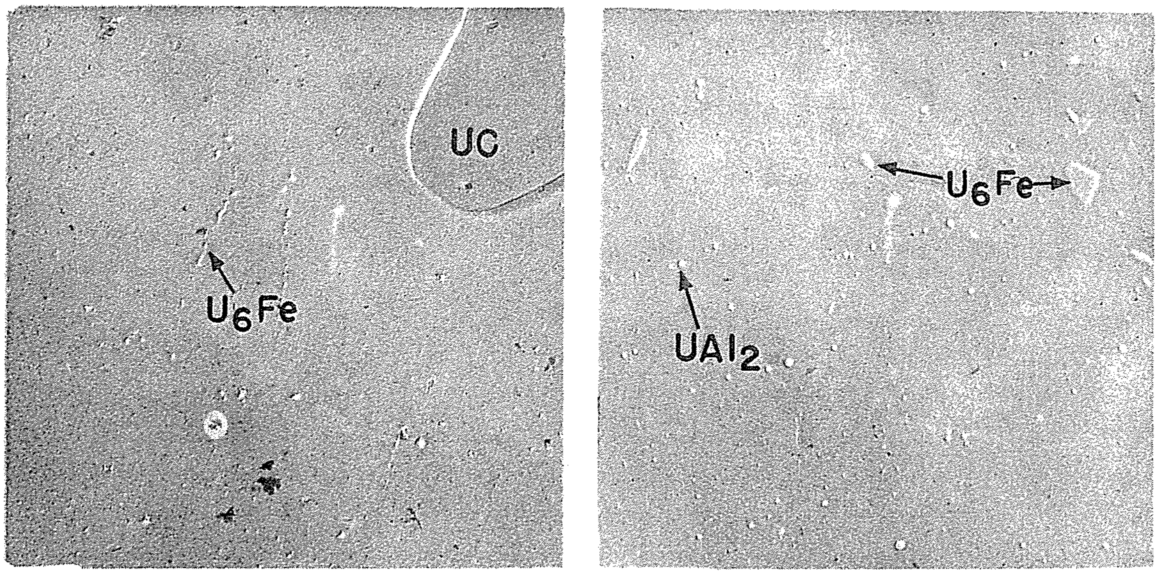
c. Electrolytic nitric acid etch.

Neg. 51020 250X

d. Chromic-acetic acid etch.

Comparison of Figures 4c and 4d shows the necessity for more severe nitric acid etch to reveal incipient precipitates in samples quenched in 50% $CaCl_2$ at –50°C. Structure in Fig. 4d was etched more severely than in Fig. 4c to insure that if networks were present they would be revealed.

FIG. 4 EFFECT OF COOLING RATE FROM GAMMA TEMPERATURES ON NETWORK STRUCTURES



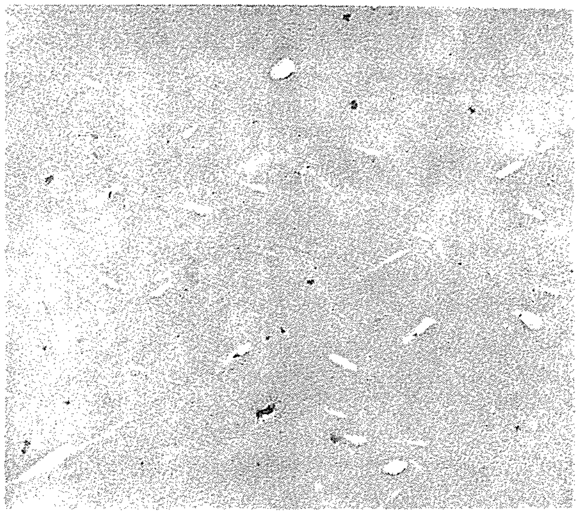
Neg. 1238C 7800X

a. U_6Fe precipitated in networks.

Neg. 1235C 4000X

b. U_6Fe precipitated randomly.

FIG. 5 U_6Fe DISTRIBUTIONS PRODUCED BY ALPHA ANNEALING



Neg. 1268B 4000X

This pattern was observed in only one sample.

FIG. 6 U_6Fe PRECIPITATED IN A WIDMANSTÄTTEN PATTERN