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**A STUDY OF THE TIME-TEMPERATURE TRANSFORMATION
BEHAVIOR OF A URANIUM-7.5 WEIGHT PER CENT
NIOBIUM-2.5 WEIGHT PER CENT ZIRCONIUM ALLOY**

C. W. Dean

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE Y-12 PLANT

operated for the **ATOMIC ENERGY COMMISSION** under **U. S. GOVERNMENT** Contract W-7405 eng 26

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OAK RIDGE Y-12 PLANT
P. O. Box Y
OAK RIDGE, TENNESSEE 37830

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UNION CARBIDE CORPORATION
Nuclear Division

Y-12 PLANT

Contract W-7405-eng-26
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A STUDY OF THE TIME-TEMPERATURE TRANSFORMATION BEHAVIOR
OF A URANIUM-7.5 WEIGHT PER CENT NIOBIUM-2.5
WEIGHT PER CENT ZIRCONIUM ALLOY

C. W. Dean

This report is based on a study by the author as partial fulfillment of requirements for the degree of Master of Science in Metallurgical Engineering from The University of Tennessee.

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ABSTRACT

The time-temperature transformation behavior of the γ phase of a uranium-7.5 weight per cent niobium-2.5 weight per cent zirconium alloy was determined for the temperature range from 200 - 800° C. Metallography, microhardness, and X-ray diffraction techniques were used to determine a time-temperature transformation diagram. The diagram was found to consist of two overlapping C curves. The morphology of the transformation was: a lamellar structure above the upper nose, a fine precipitation of α -uranium platelets below this nose, and a Widmanstatten pattern which has its time-temperature relationship defined by the lower nose.

The critical temperature was determined to be 650° C. Above this temperature the body-centered cubic γ phase was stable. Upon water quenching to room temperature, a transition phase, γ^s , was formed in which the body-centered atoms are slightly shifted. Upon aging, this phase transformed to γ^o , which is tetragonal. Further aging produced α'' which has a monoclinic crystal structure and is observed metallographically as a Widmanstatten pattern. The hardness of the α'' phase varied from 250 to over 600 DPH when the material was completely transformed. Aging samples in water-saturated gases was found to significantly retard the beginning of the γ -phase decomposition. Under certain conditions, a substructure was found to be visible.

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CHAPTER I

INTRODUCTION

Uranium is a necessary metal for many engineering applications because of its unique nuclear properties. However, as an engineering material, uranium possesses many undesirable properties. Several of the most restrictive properties are: (1) the inability to resist corrosion, (2) relatively low tensile and compressive yield strengths, (3) extreme softness and a pronounced tendency to work harden, (4) inability to have its mechanical properties enhanced by heat treatments, and (5) lack of dimensional stability.

Alloying is the only effective means available to enhance the properties of uranium. A desirable solution to the problem, then, is to develop an alloy that is: (1) rich in uranium for nuclear properties, (2) corrosion resistant, (3) resistant to stress-corrosion cracking, (4) capable of having mechanical properties enhanced by heat treatments, and (5) dimensionally stable. Realization of these characteristics depends to a large extent on stabilizing the γ phase to a lower temperature at the expense of the β and/or α phases.

In recent years a considerable amount of work has been done on uranium-alloy development. The first alloys considered were binary systems that exhibited a high degree of solubility in the γ region. Uranium-molybdenum, uranium-niobium, and uranium-zirconium have been the most widely studied systems, because the metastable γ -phase alloys in these systems have been of interest as possible fuel

elements.⁽¹⁾ However, each of these binary alloys possesses some undesirable properties with respect to engineering applications. The γ uranium-niobium alloys, for instance, have low yield strengths, causing them to creep or rupture under high loads; the γ uranium-molybdenum alloys fail in a brittle manner under static or low-strain-rate loading in environments containing oxygen; and the γ uranium-zirconium alloys transform to very strong, hard alloys but they lack ductility at room temperature.⁽²⁾

Due to the above-mentioned problems, ternary alloy systems which would possibly combine the desirable characteristics of two binary systems have been under development. Ternary systems of interest have generally been uranium-molybdenum-titanium, uranium-molybdenum-zirconium, uranium-molybdenum-niobium, and uranium-niobium-zirconium. Data available from studies of the isothermal γ -phase reactions of the uranium-niobium and uranium-zirconium binary alloys^(3, 4) and from work on the ternary equilibrium diagram of uranium-niobium-zirconium⁽¹⁾ have stimulated a detailed examination of alloys in the uranium-rich corner of this ternary system. From these studies, a ternary γ -phase alloy with a nominal composition of uranium-7.5 weight per cent niobium-2.5 weight per cent zirconium has been developed. This alloy appears to provide a good balance of strength, stability, and corrosion resistance in the γ phase at room temperature.

The objective of this present investigation has been to determine a time-temperature transformation diagram for the uranium-7.5 weight per cent niobium-2.5 weight per cent zirconium alloy in the temperature range from 200 to 800° C. This diagram was determined by characterizing the microstructure and crystal structure

of isothermally transformed specimens for this system. Characterization of these isothermally transformed specimens included the following specific areas of study:

1. Metallographic examination to determine the appearance and distribution of the phases in the microstructure.
2. Microhardness measurements to correlate changes in hardness with changes in the microstructure and to determine if changes in hardness occur prior to changes which are visible in the microstructure.
3. X-ray diffraction to determine the crystal structure and lattice parameters of the phases present.
4. Electron microprobe scans to assist in the identification of phases and chemical inhomogeneity.

CHAPTER II

LITERATURE SURVEY

I. TYPES OF URANIUM-BASE ALLOY SYSTEMS

Numerous studies of the alloying behavior and transformation characteristics of uranium-base alloys have appeared in the unclassified literature in recent years. Most of this work has been devoted to the search for a uranium alloy that is suitable for engineering applications.

Uranium obeys most of the rules of alloying behavior that are followed by other metals. Uranium alloys may be categorized into four types of systems: (1) compound-free systems, (2) highly γ -miscible systems, (3) low-miscibility systems that form intermetallic compounds, and (4) uranium-nonmetal systems.

The compound-free category includes systems of very low miscibility, as well as some having somewhat higher miscibility and form eutectics. Elements such as magnesium, calcium, silver, tungsten, and cerium fall in the first category, while the latter category includes chromium and vanadium. The highly γ -miscible alloys include elements soluble in γ uranium to the extent of ten atomic per cent or more. These alloys include niobium, hafnium, zirconium, molybdenum, and titanium. These systems tend to form intermediate phases which are sufficiently metallic and ductile so that they are not generally considered as intermetallic compounds. The low-miscibility systems are characterized by very limited solid solubility in each

of the terminal phases. This group includes aluminum, silicon, iron, manganese, and others. The uranium-nonmetal systems include such nonmetallics as carbon, hydrogen, nitrogen, and oxygen. At residual concentrations, these elements tend to form interstitial alloys; but, at higher concentrations, they form compounds with definite crystallographic structures.⁽⁵⁾

Uranium has three distinct crystalline forms: α , up to 660°C ; β , from 660 to 770°C ; and γ , from 770°C to the melting point.⁽⁶⁾ The α phase has an orthorhombic crystal structure, the β phase has a tetragonal structure, and the γ phase has a body-centered cubic structure.

Because of the isotropy of the body-centered cubic γ structure and the absence of the highly corrodible α -uranium phase, the γ alloys generally exhibit increased high-temperature strength, improved resistance to dimensional changes on thermal cycling and irradiation, and improved resistance to corrosion.⁽⁷⁾ Thus, the γ phase is desirable for certain engineering applications.

II. BINARY SYSTEMS

To date, the major development effort has been devoted to binary alloys of uranium with either molybdenum or niobium. These alloys exhibited promise as engineering materials because of the sluggishness with which the metastable γ phase transforms at low temperatures. While transformation of the γ phase occurs very rapidly in the uranium-zirconium binary system, this alloy is still of interest because the γ phase can be retained on quenching.⁽⁸⁾

The uranium-niobium binary system,⁽⁹⁾ which is shown in Figure 1, exhibits complete solid solubility above 1,050° C. At lower temperatures, a miscibility gap exists, containing a niobium-rich and a uranium-rich body-centered cubic phase. A monotectoid transformation occurs at 634° C. The β -uranium phase is restricted by niobium and disappears at four weight per cent niobium. Below 634° C, α uranium and the niobium-rich γ phase coexist.

The uranium-zirconium binary diagram⁽⁹⁾ shown in Figure 2 is the second limiting binary diagram of interest. This diagram reveals that, with the addition of zirconium to uranium, the high-temperature body-centered cubic phase becomes stabilized to lower temperatures. This system also exhibits complete solid solubility at higher temperatures.

The third limiting binary system of interest is the niobium-zirconium system.⁽⁹⁾ This diagram is shown in Figure 3. As may be seen from the diagram, this system also exhibits complete solid solubility at high temperatures. At lower temperatures, a separation of one body-centered cubic phase into two body-centered cubic phases occurs.

III. URANIUM-NIOBIUM-ZIRCONIUM TERNARY SYSTEM

The behavior of the binary uranium-niobium and uranium-zirconium alloys inspired an interest in the ternary uranium-niobium-zirconium system. A desirable alloy should combine a sufficient amount of niobium for stabilizing the γ phase with a sufficient amount of zirconium for strengthening. The alloy system should also retain, as much as possible, the ductility which is characteristic of the binary

FIGURE 1

URANIUM-NIOBIUM BINARY COMPOSITION DIAGRAM
 (HANSEN, P.; "CONSTITUTION OF BINARY ALLOYS,"
 P. 1021, MCGRAW-HILL BOOK COMPANY, INCOR-
 PORATED, NEW YORK, NEW YORK (1958))

FIGURE 2

URANIUM-ZIRCONIUM BINARY COMPOSITION DIAGRAM
 (HANSEN, P.; "CONSTITUTION OF BINARY ALLOYS,"
 P. 1023, MCGRAW-HILL BOOK COMPANY, INCOR-
 PORATED, NEW YORK, NEW YORK (1958))

FIGURE 3

NIOBIUM-ZIRCONIUM BINARY COMPOSITION DIAGRAM
 (HANSEN, P.; "CONSTITUTION OF BINARY ALLOYS,"
 P. 1251, MCGRAW-HILL BOOK COMPANY, INCOR-
 PORATED, NEW YORK, NEW YORK (1958))

uranium-niobium alloys. This uranium-niobium-zirconium ternary system exhibits a complete solid solution of γ uranium over a wide composition range at high temperatures.⁽¹⁾ Addition of both niobium and zirconium stabilizes the body-centered cubic γ phase to a lower temperature. Indeed, when the atomic percentages of zirconium plus niobium are in the range of 50 to 80, the γ solid solution is very stable down to temperatures of 500° C.⁽³⁾

The sequence of phase transformations in a ternary system can best be shown by a series of isothermal sections through the ternary space model. The 660, 640, 630, and 621° C isothermal sections⁽³⁾ for the uranium-niobium-zirconium ternary systems are shown in Figures 4 through 7, respectively.

A feature of those γ alloys having complete γ miscibility is the miscibility gap containing two different γ compositions. This gap occurs, for example, in the uranium-titanium, uranium-zirconium, and uranium-niobium systems on cooling certain compositions of the homogeneous γ phase. From the isothermal sections mentioned above, we see that relatively small amounts of the third element merge the two γ 's in each binary system into a single γ . The addition of less than 15 per cent zirconium merges the uranium-niobium miscibility gap, and as little as two per cent niobium can close the uranium-zirconium miscibility gap which is relatively small.⁽⁵⁾

Most of the phases observed in the uranium-niobium-zirconium alloys are metastable or transition phases, rather than stable phases. Metastable phases are defined as phases which temporarily maintain their existence although they have a

FIGURE 4

ISOTHERMAL SECTION THROUGH A TERNARY
SPACE DIAGRAM AT 660° C

FIGURE 5

ISOTHERMAL SECTION THROUGH A TERNARY
SPACE DIAGRAM AT 640° C

FIGURE 6

ISOTHERMAL SECTION THROUGH A TERNARY
SPACE DIAGRAM AT 631° C

FIGURE 7

ISOTHERMAL SECTION THROUGH A TERNARY
SPACE DIAGRAM AT 621° C

higher Gibbs free energy than the equilibrium phase. A transition phase has a lower free energy than the initial phase but a higher free energy than the stable form.⁽¹⁰⁾ For instance, the γ phase is metastable as it will slowly decompose at low temperatures and rapidly decompose at slightly higher temperatures. The γ -s phase, which transforms to γ -0' then to α'' , is a transition phase. These transition phases form because of favorable kinetic factors.

The nomenclature of phases in the ternary system have been derived from the limiting binary systems. In the case of the γ phases, a new nomenclature is necessary. At temperatures above 1,050° C, a single γ phase extends over the entire uranium-niobium-zirconium system. An isometric view of the uranium-niobium-zirconium phase diagram⁽³⁾ is given in Figure 8. The notation used in the ternary diagram and the uranium-zirconium binary diagram are inconsistent. In the uranium-zirconium system, the γ breaks down into two γ 's, called γ_1 and γ_2 ; γ_1 is uranium rich and γ_2 is zirconium rich. Similarly, the uranium-niobium system decomposes into γ_1 and γ_2 ; γ_1 is uranium rich and γ_2 is enriched in niobium. The uranium-rich γ of the uranium-niobium system exhibits complete solid solubility with the uranium-rich γ of the uranium-zirconium system. Thus, the term γ_1 can be applied to the uranium-rich γ of both the uranium-niobium and uranium-zirconium systems. The niobium-rich γ , being separated from γ_1 by a two-phase field, required a distinctive name and is designated γ_3 . Thus, in the uranium-zirconium binary, the miscibility gap contains γ_1 and γ_2 ; in the uranium-niobium binary, the miscibility gap contains γ_1 and γ_3 . For the convenience of the reader, these γ -phase nomenclatures are

FIGURE 8

THREE-DIMENSIONAL SPACE DIAGRAM OF THE
URANIUM-NIOBIUM-ZIRCONIUM SYSTEM

listed in Table I. Other phases present in the ternary system are α and β uranium and the compound corresponding to UZr_3 , which is designated as δ .

In addition to true α , β , and γ , there are four or perhaps more types of low-alloy or medium-alloy phases retainable at room temperature: γ_0 , γ_s , α' , and α'' . These phases differ in their crystal structures and parameters as well as in properties and composition.

The superscript "prime," as in α' , denotes a relative change of lattice parameters producing a tetragonal structure; "double prime," as in α'' , denotes a relative lattice parameter change to a monoclinic cell. Some authors⁽⁵⁾ introduce an α^0 phase which is generally used to indicate ordering, but also indicates an orthorhombic superlattice, perhaps a modification of tetragonal γ . The reader should refer to Table II for the nomenclature of the most common phases in the uranium-7.5 niobium-2.5 zirconium system.

Several major features of the ternary system can be noted from the space diagram in Figure 8 and the isothermal sections⁽³⁾ in Figures 4 through 7, Pages 11 through 14. The ternary sections are not entirely consistent with phase relationships as predicted by the phase rule. Additions of zirconium and niobium both lower the temperature at which γ is stable as a single phase, but niobium is far more potent than is zirconium. Secondly, four weight per cent or more of niobium eliminates the β phase, so that the transformation on cooling is from γ to α . Third, each monotectoid valley approaches a critical point several degrees centigrade below the binary monotectoid temperature; and, at the critical point, the two γ phases merge into one. (The transformation is called monotectoid because of its close resemblance

TABLE I
NOMENCLATURE OF GAMMA PHASES IN U-Nb,
U-Zr, AND U-Nb-Zr SYSTEMS

	U Rich γ	Nb Rich γ	Zr Rich γ
U-Nb	γ_1	γ_2	
U-Zr	γ_1		γ_2
U-Nb-Zr	γ_1	γ_3	γ_2

TABLE II
NOMENCLATURE OF PHASES IN THE
U-Nb-Zr SYSTEM

Name of Phase	Type of Crystal Structure	
α	Orthorhombic	Stable phase.
α'	Tetragonal	Transition α phase.
α''	Monoclinic	Transition α phase precipitated by aging γ^0 .
γ^s	Cubic	Water-quenched γ phase having body-centered atoms slightly shifted.
γ^0	Tetragonal	Transition γ phase produced by aging γ^s .

to a monotectic, which involves two liquids and a solid. The monotectoid is defined as a reaction between two solids having similar crystal structures and a third solid having a different structure.) Fourth, one of the γ phases, γ_3 , occurs as an equilibrium phase throughout most of the ternary system. Lastly, the δ phase, based on UZr_3 , is eliminated by seven weight per cent niobium and occurs in only a small portion of the ternary system.⁽³⁾

In the search for an explanation as to why the γ structure can exist at higher uranium concentrations in the ternary than in either of the binaries, Dwight and Mueller⁽³⁾ investigated the nature of the isothermal line joining the limiting γ compositions of the uranium-niobium and uranium-zirconium binary systems. They applied Hume-Rothary's observation that a straight line (for ternary alloys based on copper and silver) is the result of a constant electron/atom ratio, when that is the dominant factor, but that deviation from a straight line results from lattice distortions introduced by the solute atoms.

In the uranium-niobium-zirconium system, the $(\beta + \gamma)/\gamma$ line at 700°C is concave toward the solvent (convex toward the uranium corner), which is γ uranium.⁽³⁾ (See the plot in Figure 9.) This concavity is attributable to lattice distortion. Niobium decreases the lattice parameter and zirconium slightly increases the lattice parameter of γ uranium. One solute, therefore, helps to relieve the distortion introduced by the other. Because of this compensation, the γ structure in the ternary can exist at higher uranium concentrations than is possible with either binary. Other uranium-base ternary alloys also exhibit this characteristic.

FIGURE 9

ISOTHERMAL 700° C SECTION OF THE URANIUM-
 NIOBIUM-ZIRCONIUM SYSTEM EXHIBITING
 HUME-ROTHARY OBSERVATION

IV. THE URANIUM-7.5 NIOBIUM-2.5 ZIRCONIUM TERNARY SYSTEM

According to Yakel,⁽¹¹⁾ a true body-centered cubic structure is not retained upon quenching the uranium-7.5 niobium-2.5 zirconium alloy in water. Rather, a transition structure, called γ^s , is formed. This structure is described as eight unit cells of the γ structure in which the body-centered atoms have been displaced slightly in correlated $\langle 100 \rangle$ directions. This structure has a unit cell parameter about twice that of the true γ phase.

Upon aging for short times at 150 or 350° C, the γ^s transition structure changes to another transition structure which is called γ^o . This structure is tetragonal and is produced by further atom shifts which are correlated along a particular [001] direction. Some authors have reported this structure as being chemically ordered, but Yakel could find no evidence of chemical ordering.

The engineering properties including fabricability, corrosion resistance, and dimensional stability and integrity under thermal cycling and irradiation are related to the microstructure and the phases comprising it, and thus to the hardness. The remainder of this report is concerned with the characterization of the metallographic structure, hardness, and crystal structure of the uranium-7.5 per cent niobium-2.5 per cent zirconium alloy.

CHAPTER III

EXPERIMENTAL PROCEDURE

I. MATERIAL PREPARATION

The material used in this investigation was prepared by double arc melting, hot forging, homogenizing, and hot rolling to a 0.250-inch-thick plate. The gross chemical and impurity analysis of the material used is reported in Table III.

The plate was cut into samples which were one inch long, one-half inch wide, and one-fourth inch thick. Four hundred of these samples were produced with no effort being made to preserve the identity of the individual samples. This procedure permitted samples to be selected for isothermal transformation on a purely random basis with respect to any inhomogeneity that might be present in the plate.

II. ISOTHERMAL TREATMENT OF SPECIMENS

Individual samples were solution heat treated in a tube furnace for one hour at 800° C and rapidly transferred to a lead-bismuth bath or another tube furnace for isothermal transformation. For temperatures of 500° C and below, isothermal heating was conducted in a tube furnace to prevent oxygen contamination of the samples in the molten lead. Argon gas at approximately 20 liters per hour was flowing through the tube furnaces to prevent oxidation of the samples.

TABLE III

GROSS CHEMICAL AND IMPURITY ANALYSIS OF THE
NOMINAL U-7.5 WEIGHT PER CENT Nb-2.5
WEIGHT PER CENT Zr ALLOY USED IN
THIS INVESTIGATION^a

Uranium	89.85 wt. %
Niobium	7.66 wt. %
Zirconium	2.58 wt. %
Carbon	63
Oxygen	48
Hydrogen	2
Nitrogen	3
Chromium	< 10
Vanadium	< 1
Aluminum	< 2
Manganese	6
Tungsten	< 60
Copper	6
Molybdenum	< 10
Phosphorus	< 100
Iron	50
Lead	4
Silicon	25
Nickel	6

^aAll values in p.p.m., except where noted.

The lead bath was heated on a hot plate controlled by a variable transformer. The temperature was found to vary not more than $\pm 2^{\circ}$ C from the temperature setting. The volume of the bath was sufficiently large so that the temperature was not changed by the insertion of the samples. The tube furnaces were also controlled to $\pm 2^{\circ}$ C. After being isothermally transformed, the samples were water quenched to room temperature. The combination of aging times and temperatures evaluated in this investigation are listed in Table IV.

III. METALLOGRAPHY AND HARDNESS MEASUREMENTS

After isothermal transformation, the samples were examined metallographically. The specimens were mounted in epoxy, ground through 600-grit silicon carbide paper, and polished on a Syntron using Linde A with five per cent chromic acid on met-cloth and finally Linde B with five per cent chromic acid on microcloth. Etching was done electrolytically in a solution that varied from two to five per cent oxalic acid in water. An open-circuit voltage ranging from two to four volts was required. Etching time varied from ten seconds to three minutes.

Room-temperature hardness values were determined on all the isothermally transformed metallography specimens. Diamond pyramid hardness values were attained using a 1,000-gram load on a Tukon microhardness tester. Fifteen readings were taken per sample, and the hardness value was taken as the mathematical average of these readings if no significant variation occurred among the individual readings. In samples where more than one phase was detected, an average hardness value was determined for each phase.

TABLE IV
COMBINATIONS OF TIMES AND TEMPERATURES STUDIED IN THIS INVESTIGATION

Temperature (° C)	Time (minutes)															
	1	2	5	10	15	30	60	120	180	300	480	720	1,440	2,880	4,320	5,760
775			X	X	X	X	X	X	X	X	X	X	X	X	X	X
750			X	X	X	X	X	X	X	X	X	X	X	X	X	X
725			X	X	X	X	X	X	X	X	X	X	X	X	X	X
700			X	X	X	X	X	X	X	X	X	X	X	X	X	X
675			X	X	X	X	X	X	X	X	X	X	X	X	X	X
650			X	X	X	X	X	X	X	X	X	X	X	X	X	X
625			X	X	X	X	X	X	X	X	X	X	X	X	X	X
600			X	X	X	X	X	X	X	X	X	X	X	X	X	X
575	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
550	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
525	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
500	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
475	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
450	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
425	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
400	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
375	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
350	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
325	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
300	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
275	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
250	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
225	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
200	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X

IV. PHASE IDENTIFICATION AND CRYSTAL STRUCTURE

A rod of the alloy was swaged to 0.032 inch in diameter. The swaging was done at room temperature, and the rod was given intermediate anneals for one hour at 800° C after every 20 per cent reduction of the cross-sectional area. This wire was cut into one-half-inch-long pieces, and each piece was tapered to have a conically shaped point of less than 0.002 inch diameter on one end. The needles were wrapped in tantalum foil, and a needle was heat treated with each large specimen as mentioned above. These needle-shaped samples were then mounted in a two-radian powder camera, and a Debye Scherrer pattern was made from each. Patterns were made using nickel-filtered copper $K\alpha$ radiation. An excitation potential of 35 kilovolts using 30 milliamperes produced the best patterns. Exposure times of greater than 12 hours were required to produce patterns having sufficient intensity. Investigation revealed that polycrystalline material did not produce satisfactory X-ray diffraction patterns. Lines were broad and diffuse, and background interference lines were numerous. To minimize these problems, single crystals are normally required for precise studies.

An attempt was made to grow single crystals by zone-refining and strain-anneal techniques. Both of these techniques were unsuccessful. By heating specimens of this material at 1,200° C for 48 hours, grains ranging from 1/16 to 1/4 inch in diameter were produced. By judicious sectioning, rod-shaped samples having a single grain on one end were cut from these specimens. These rods were then tapered to a 0.001-inch-diameter point on one end. Patterns produced from these specimens were much superior to those produced from polycrystalline material.

Extensive use was made of the electron microprobe for identification of phases, inclusions, and chemical inhomogeneity. Linear scans were made across distances of up to 200 microns of material to detect chemical inhomogeneity. Linear scans and static-beam quantitative counting were used in phase identification. Comparison of unknowns against calibrated standards produced quantitative analysis data that were interpreted as being reliable.

Treatment of Data

The metallographic and hardness data were correlated and plotted to determine a time-temperature transformation diagram. The beginning of transformation was taken as the point at which the hardness began to increase appreciably. In most instances an initial hardness increase occurred before any transformation product could be detected in the microstructure.

CHAPTER IV

RESULTS AND DISCUSSION

I. HOMOGENIZATION OF MATERIAL

Initially, data were taken from material which had been homogenized for four hours at 900°C , but these data were found to be very erratic. Hardness numbers varied considerably within a single sample and the microstructures were found to be severely banded. In addition, the grain size was extremely fine (ASTM 7-8) and no structure could be resolved within the grains. A typically banded microstructure is shown in Figures 10 and 11. This sample was isothermally transformed for 30 minutes at 350°C .

Investigation with the electron microprobe revealed that the above-mentioned inconsistencies were caused by chemical inhomogeneity. The light-colored bands are rich in niobium and the darker bands are depleted in niobium. The niobium typically varies from a high of 9.0 weight per cent to a low of 6.0 weight per cent. Upon isothermal heating, the niobium depleted areas start to transform first and are more rapidly attacked by the etchant, thus producing the dark-pitted bands.

No metallographic or etching technique used in this investigation was capable of resolving the structure in the banded material. Figure 12 shows a specimen which was isothermally heated for three hours at 500°C . This sample was etched in a five per cent oxalic acid solution and the photomicrograph made using bright-field

FIGURE 10

MICROSTRUCTURE OF THE URANIUM ALLOY EXHIBITING
BANDING AFTER BEING ISOTHERMALLY TRANSFORMED
FOR 30 MINUTES AT 350° C. LIGHT-COLORED AREAS
ARE NIOBIUM ENRICHED AND DARK AREAS ARE
NIOBIUM DEPLETED. (100X; ETCHANT: 5%
OXALIC ACID SOLUTION)

FIGURE 11

MICROSTRUCTURE OF THE URANIUM ALLOY EXHIBITING
BANDING AFTER BEING ISOTHERMALLY TRANSFORMED
FOR 30 MINUTES AT 350° C. LIGHT-COLORED AREAS
ARE NIOBIUM ENRICHED AND DARK AREAS ARE
NIOBIUM DEPLETED. (500X; ETCHANT: 5%
OXALIC ACID SOLUTION)

FIGURE 12

MICROSTRUCTURE OF THE URANIUM ALLOY AFTER BEING ISOTHERMALLY TRANSFORMED FOR THREE HOURS AT 500° C. BANDING IS CAUSED BY INSUFFICIENT HOMOGENIZATION OF CHEMICAL CONSTITUENTS. (BRIGHT-FIELD ILLUMINATION; 250X; ETCHANT: 5% OXALIC ACID SOLUTION)

illumination at a magnification of 250X. Figure 13 shows the same sample photographed under polarized light at a magnification of 250X; Figure 14 shows the same sample photographed using sensitive-tint illumination at 1,000X. Figure 15 shows this same sample after it has been repolished and cathodically etched. This photomicrograph was made at 250X using oblique bright-field illumination.

A correlative investigation was conducted to determine optimum times and temperatures for the homogenization of this material to eliminate or minimize chemical inhomogeneity. Samples were heat treated for varying times at different temperatures and were subsequently examined with the electron microprobe. A homogenization treatment of eight hours at $1,000^{\circ}\text{C}$ was found to be adequate to reduce the chemical variation to acceptable levels. This heat treatment also increased the grain size from ASTM 7-8 to ASTM 3-4.

II. GAMMA SOLUTION TREATMENT

Before phase transformation studies can be conducted, samples must be held in the γ solution treating temperature region for a sufficient length of time to insure that the samples are completely transformed to the γ phase. After one hour at 800°C , the alloy is completely transformed to the γ phase. The γ phase is body-centered cubic with a lattice parameter of 3.464 ± 0.003 angstroms. In the γ -treated, as-water-quenched condition, hardness varies from a diamond pyramid hardness (DPH) value of 190 - 200. No significant differences are detected in samples which are solution treated at temperatures higher than 800°C . A sample which has been water quenched to room temperature from 800°C is shown in Figure 16.

FIGURE 13

MICROSTRUCTURE OF THE URANIUM ALLOY AFTER
BEING ISOTHERMALLY TRANSFORMED FOR THREE
HOURS AT 500° C. LIGHT-COLORED MATERIAL
IN BANDS IS α URANIUM. NIOBIUM DEPLETED
MATERIAL STARTS TO TRANSFORM FIRST.
(POLARIZED LIGHT; 250X; ETCHANT:
5% OXALIC ACID SOLUTION)

FIGURE 14

MICROSTRUCTURE OF INSUFFICIENTLY HOMOGENIZED
URANIUM-7.5 WEIGHT PER CENT NIOBIUM-2.5
WEIGHT PER CENT ZIRCONIUM ALLOY AFTER
ISOTHERMAL TRANSFORMATION FOR THREE
HOURS AT 500° C. (SENSITIVE-TINT IL-
LUMINATION; 1,000X; ETCHANT: 5%
OXALIC ACID SOLUTION)

FIGURE 15

MICROSTRUCTURE OF INSUFFICIENTLY HOMOGENIZED
URANIUM-7.5 WEIGHT PER CENT NIOBIUM-2.5
WEIGHT PER CENT ZIRCONIUM ALLOY AFTER
ISOTHERMAL TRANSFORMATION FOR THREE
HOURS AT 500° C. (OBLIQUE BRIGHT-
FIELD ILLUMINATION; 250X;
CATHODICALLY ETCHED)

FIGURE 16

MICROSTRUCTURE OF THE URANIUM ALLOY AFTER
BEING GAMMA SOLUTION TREATED FOR ONE
HOUR AT 800° C AND WATER QUENCHED TO
ROOM TEMPERATURE. (250X; ETCHANT:
5% OXALIC ACID SOLUTION)

III. TRANSFORMATION STRUCTURES

The transformation microstructures in this alloy system are of three distinct types: (1) a lamellar structure at the higher temperature, (2) a fine intergranular and intragranular α -uranium precipitation at intermediate temperatures, and (3) a Widmanstätten pattern at low temperatures. The time-temperature transformation diagram, as determined by metallography and hardness, is presented in Figure 17.

The rate of phase decompositions is controlled by processes of nucleation and growth. At temperatures slightly below the critical temperature, nucleation is the controlling mechanism. Few nuclei are available at these higher temperatures; therefore, long times are required to initiate transformations. As the temperature is considerably decreased, the number of nuclei available is drastically increased, but growth becomes very slow due to lower atom mobility. Under these conditions, long times are again required to begin transformations. However, between these two extremes a position is reached where optimum nucleation and growth rates occur. At this position, transformation begins in the shortest possible time. This fact accounts for the "nose" on a time-temperature transformation diagram.

In the case of the uranium-7.5 weight per cent niobium-2.5 weight per cent zirconium alloy, the monotectoid decomposition results in a lamellar structure at the higher temperatures. With decreasing temperatures, the interlamellar spacing becomes smaller and smaller until a point is reached below the nose of the upper curve where the lamellar structure no longer exists. The lamellar structure is replaced by a fine precipitation of α -uranium platelets.

FIGURE 17

TIME-TEMPERATURE TRANSFORMATION DIAGRAM FOR A
 URANIUM-7.5 WEIGHT PER CENT NIOBIUM-2.5
 WEIGHT PER CENT ZIRCONIUM ALLOY AS
 DETERMINED BY METALLOGRAPHY
 AND HARDNESS

Lamellar Structure

The critical temperature, or the highest temperature at which any phase transformation reaction could be detected by either metallographic or hardness measurement techniques, was 650°C for times up to 120 hours. This reaction became optically visible in the form of a lamellar-type structure at the grain boundaries.

This lamellar structure is nucleated at the grain boundaries and, with increasing transformation times, proceeds further into the center of the grains until the grain is entirely transformed. Figure 18 shows a sample which has been transformed for two hours at 625°C . In this sample, the lamellar structure is just beginning to form at the grain boundaries. Figure 19 shows a sample which has been transformed for three hours at 625°C . In this sample, the percentage of lamellar structure present has increased by nucleation and growth of new structure at different sites along the grain boundaries, and by growth of the structure already present. Figure 20 shows a sample which has been transformed for five hours at 625°C . In this sample, transformation is approximately 20 per cent complete. Figure 21 shows a sample which has been transformed for 24 hours at 625°C . In this sample, transformation is approximately 80 per cent complete. After 48 hours at 625°C , transformation is 98 per cent complete. This 625°C series is typical of any series of samples which is taken along any isotherm within the limits of the upper nose of the time-temperature transformation diagram.

In samples that are down quenched; i.e., heated to the solution treating temperature and transferred to the isothermal heating furnace while still hot, the lamellar structure is very fine. This fine structure cannot be resolved by optical metallography,

FIGURE 18

MICROSTRUCTURE OF THE URANIUM ALLOY AFTER
BEING ISOTHERMALLY TRANSFORMED FOR TWO
HOURS AT 625° C. NOTICE EXTREMELY FINE
LAMELLAR STRUCTURE WHICH IS BEING
FORMED AT THE GRAIN BOUNDARIES.
(250X; ETCHANT: 2% OXALIC
ACID SOLUTION)

FIGURE 19

MICROSTRUCTURE OF THE URANIUM ALLOY AFTER
BEING ISOTHERMALLY TRANSFORMED FOR THREE
HOURS AT 625° C. (250X; ETCHANT: 2%
OXALIC ACID SOLUTION)

FIGURE 20

MICROSTRUCTURE OF THE URANIUM ALLOY AFTER
BEING ISOTHERMALLY TRANSFORMED FOR FIVE
HOURS AT 625° C. (250X; ETCHANT: 2%
OXALIC ACID SOLUTION)

FIGURE 21

MICROSTRUCTURE OF THE URANIUM ALLOY AFTER
BEING ISOTHERMALLY TRANSFORMED FOR 24
HOURS AT 625° C. TRANSFORMATION IS
APPROXIMATELY 80 PER CENT COM-
PLETE. (250X; ETCHANT: 2%
OXALIC ACID SOLUTION)

but must be resolved by electron microscopy. An electron microscope photomicrograph of a sample down quenched to 550°C and held for one hour is shown in Figure 22. The average width of each lamella is approximately 0.04 micron. Samples that are quenched to room temperature from the solution-treating operation and then reheated to the isothermal-treating temperature, exhibit a much coarser structure, and the average width of each lamella is approximately 0.3 micron. A typical up-quenched structure is seen in Figure 23 for a sample heated for 19 hours at 600°C .

An electron microprobe investigation of this lamellar structure reveals that alternate lamellae are depleted in niobium and zirconium and are enriched in uranium. Thus, adjacent lamellae are enriched in niobium and zirconium. Typical analysis data shows alternate lamellae to be 20 per cent niobium, 3.3 per cent zirconium, and 75 per cent uranium; adjacent lamellae show three per cent niobium, 1.1 per cent zirconium, and 95 per cent uranium. A true chemical analysis of each component of this structure is difficult to attain because the microprobe beam can be focused to a spot no smaller than one micron in diameter. The coarsest lamellae are less than one micron in width; thus, some overlapping of the beam onto adjacent lamellae is inevitable.

A microhardness examination of the samples isothermally treated at 625°C reveals that the average hardness of the samples increases as a function of the transformation time. (See the plot of DPH values versus heating time at 625°C in Figure 24.) These hardness numbers are the average of 15 readings taken at random across the specimen without regard to phase distribution. The DPH readings were

FIGURE 22

TRANSMISSION ELECTRON MICROGRAPH OF THE URANIUM ALLOY WHICH HAS BEEN DOWN QUENCHED AND ISOTHERMALLY TRANSFORMED FOR ONE HOUR AT 550° C. AVERAGE INTERLAMELLAR SPACING IS APPROXIMATELY 0.04 MICRON. (60,000X)

FIGURE 23

MICROSTRUCTURE OF THE URANIUM ALLOY AFTER
BEING UP QUENCHED AND ISOTHERMALLY
TRANSFORMED FOR 19 HOURS AT 600° C.
AVERAGE INTERLAMELLAR SPACING IS
APPROXIMATELY 0.3 MICRON.
(2,000X; ETCHANT: 2% OX-
ALIC ACID SOLUTION)

FIGURE 24

PLOT OF DPH VALUES VERSUS ISOTHERMAL TRANSFORMATION TIME AT 625° C FOR A URANIUM-7.5 WEIGHT PER CENT NIOBIUM-2.5 WEIGHT PER CENT ZIRCONIUM ALLOY. EACH POINT IS THE AVERAGE OF 15 READINGS.

verified against Rockwell A readings and the agreement was excellent. The true DPH of the transformed structure is 500, whereas the hardness of the untransformed structure is 200. All samples taken on any isotherm within the boundaries of the upper nose show a similar increase in hardness with increasing aging time.

Precipitation of Fine α -Uranium Particles

The lowest temperature at which any lamellar structure could be observed is 530°C . Immediately below this temperature the γ -phase decomposition occurs via an intragranular precipitation of extremely fine α -uranium platelets. For short times, this precipitation is distributed randomly among the grains and along the grain boundaries. With increasing times, a larger amount of precipitation occurs at the grain boundaries. Figure 25 shows a sample which was isothermally transformed for two hours at 525°C . Notice the considerable amount of precipitation in the grains and the small amount in the grain boundaries. Figure 26 shows a sample which was heated for 12 hours at 500°C . Notice the increased amount of precipitation at the grain boundaries. An electron micrograph exhibiting the platelet nature of this structure is shown in Figure 27.

This intragranular and grain boundary type α precipitation occurs in the temperature range from 525°C down to 400°C . At 525°C , this structure appears in 20 minutes; at 425°C it appears in one hour. On the time-temperature transformation diagram in Figure 17, Page 39, this phase appears as the lower part of the upper nose on the diagram. This nose is shown as two dotted C curves since the mode by which the lamellar structure decomposes into this fine platelet structure is

FIGURE 25

MICROSTRUCTURE OF THE URANIUM ALLOY AFTER
BEING ISOTHERMALLY TRANSFORMED FOR TWO
HOURS AT 525° C. THE PRECIPITATION IN
THE GRAINS IS α -URANIUM PLATELETS.
(BRIGHT-FIELD ILLUMINATION;
250X; ETCHANT: 1% OX-
ALIC ACID SOLUTION)

FIGURE 26

MICROSTRUCTURE OF THE URANIUM ALLOY AFTER
BEING ISOTHERMALLY TRANSFORMED FOR 12
HOURS AT 500° C. (POLARIZED LIGHT;
250X; ETCHANT: 1% OXALIC
ACID SOLUTION)

FIGURE 27

TRANSMISSION ELECTRON MICROGRAPH OF THE URANIUM ALLOY AFTER
BEING ISOTHERMALLY TRANSFORMED FOR 12 HOURS AT 500° C.
NOTICE PLATELET-SHAPED α -URANIUM
PARTICLES. (120,000X)

not known. The lower boundary for this phase is an approximately horizontal line for times up to 96 hours.

Widmanstatten Pattern

With increasing aging times at and below 400° C, a Widmanstatten pattern becomes visible. The time dependance of the initial formation of this structure is exhibited as the lower "nose" on the time-temperature transformation diagram. The structure becomes optically visible in samples heated for less than ten minutes at 400° C, but is not visible in samples heated for 96 hours at 410° C. Thus, the upper limit of this phase separation is a horizontal line occurring between 400 and 410° C. The minimum time of appearance, which is three minutes, occurs at 350° C. At 200° C, the phase appears after six hours. This phase, called α'' , after aging one hour at 350° C has a monoclinic crystal structure with lattice parameters of: $a = 2.89 \pm 0.01$ angstroms, $b = 5.68 \pm 0.02$ angstroms, $c = 4.99 \pm 0.02$ angstroms, and γ (the angle between a and b) = 91.0 ± 0.3 degrees.⁽¹¹⁾ It appears that the structural parameters change very slightly with temperature and time.

The alloy increases in hardness from DPH 250 when α'' first becomes visible in the microstructure to over 600 DPH when the material is completely transformed. A plot of DPH as a function of the transformation time at 325° C is given in Figure 28. The hardness numbers along any isotherm within the phase boundary increase with increasing time in a fashion similar to those in Figure 28. Since the hardness is still increasing for times up to 120 hours, and X-ray diffraction reveals

FIGURE 28

PLOT OF DPH VALUES VERSUS ISOTHERMAL TRANSFORMATION TIME AT 325° C FOR A URANIUM-7.5 WEIGHT PER CENT NIOBIUM-2.5 WEIGHT PER CENT ZIRCONIUM ALLOY. EACH POINT IS THE AVERAGE OF 15 READINGS.

that structural parameters are slightly changing, no end of transformation is plotted for the lower C curve.

Figures 29 through 37 show photomicrographs of samples taken along the 325°C isotherm after being aged for 10 minutes to 48 hours. The Widmanstatten pattern is oriented along the (110) habit planes. A transmission electron micrograph showing the Widmanstatten pattern in a sample aged for 30 minutes at 325°C is presented in Figure 38.

Once the Widmanstatten pattern appears, the attack of the etchant shifts from the grain boundaries to the grains. This mode of attack leaves the grain boundaries standing in relief. A phase contrast metallography photograph of the Widmanstatten pattern showing the raised grain boundaries can be seen in Figure 39. A scanning electron microscope photograph of a sample aged for 30 minutes at 325°C is shown in Figure 40.

Substructure

As may be seen from the photomicrographs in Figures 41 through 45, a considerable amount of substructure is visible in samples which have been isothermally transformed for various combinations of time and temperature. This substructure is not visible in the initial samples which have been water quenched to room temperature from the γ solution treating temperature.

Figures 41 through 43 show samples which were isothermally treated at 325°C for times of one, two, and five minutes, respectively. The sample in Figure 41, which was heated for one minute, shows a moderate amount of substructure.

FIGURE 29

MICROSTRUCTURE OF THE URANIUM ALLOY AFTER
BEING ISOTHERMALLY TRANSFORMED FOR 10
MINUTES AT 325° C. (250X; ETCHANT:
5% OXALIC ACID SOLUTION)

FIGURE 30

MICROSTRUCTURE OF THE URANIUM ALLOY AFTER
BEING ISOTHERMALLY TRANSFORMED FOR 15
MINUTES AT 325° C. (250X; ETCHANT:
5% OXALIC ACID SOLUTION)

FIGURE 31

MICROSTRUCTURE OF THE URANIUM ALLOY AFTER
BEING ISOTHERMALLY TRANSFORMED FOR 30
MINUTES AT 325° C. (250X; ETCHANT:
5% OXALIC ACID SOLUTION)

FIGURE 32

MICROSTRUCTURE OF THE URANIUM ALLOY AFTER
BEING ISOTHERMALLY TRANSFORMED FOR ONE
HOUR AT 325° C. (250X; ETCHANT: 5%
OXALIC ACID SOLUTION)

FIGURE 33

MICROSTRUCTURE OF THE URANIUM ALLOY AFTER
BEING ISOTHERMALLY TRANSFORMED FOR TWO
HOURS AT 325° C. (250X; ETCHANT: 5%
OXALIC ACID SOLUTION)

FIGURE 34

MICROSTRUCTURE OF THE URANIUM ALLOY AFTER
BEING ISOTHERMALLY TRANSFORMED FOR FIVE
HOURS AT 325° C. (250X; ETCHANT: 5%
OXALIC ACID SOLUTION)

FIGURE 35

MICROSTRUCTURE OF THE URANIUM ALLOY AFTER
BEING ISOTHERMALLY TRANSFORMED FOR 16
HOURS AT 325° C. (250X; ETCHANT: 5%
OXALIC ACID SOLUTION)

FIGURE 36

MICROSTRUCTURE OF THE URANIUM ALLOY AFTER
BEING ISOTHERMALLY TRANSFORMED FOR 24
HOURS AT 325° C. (250X; ETCHANT: 5%
OXALIC ACID SOLUTION)

FIGURE 37

MICROSTRUCTURE OF THE URANIUM ALLOY AFTER
BEING ISOTHERMALLY TRANSFORMED FOR 48
HOURS AT 325° C. (250X; ETCHANT: 5%
OXALIC ACID SOLUTION)

FIGURE 38

TRANSMISSION ELECTRON MICROGRAPH OF THE URANIUM ALLOY AFTER
BEING ISOTHERMALLY TRANSFORMED FOR 30 MINUTES AT 325° C.
NOTICE "SUBSTRUCTURE" WITHIN WIDMANSTATTEN
NEEDLE. (60,000X)

FIGURE 39

PHASE-CONTRAST METALLOGRAPHY PHOTOGRAPH
OF A URANIUM-7.5 WEIGHT PER CENT NIOBIUM-
2.5 WEIGHT PER CENT ZIRCONIUM ALLOY
SAMPLE THAT WAS ISOTHERMALLY TRANS-
FORMED FOR 30 MINUTES AT 325° C.
GRAIN BOUNDARIES ARE IN RELIEF.
(250X; ETCHANT: 5% OXALIC
ACID SOLUTION)

FIGURE 40

SCANNING ELECTRON MICROSCOPE PHOTO-
GRAPH OF THE URANIUM ALLOY AFTER BEING
ISOTHERMALLY TRANSFORMED FOR 30 MIN-
UTES AT 325° C. (3,000X; ETCHANT:
5% OXALIC ACID SOLUTION)

FIGURE 41

MICROSTRUCTURE OF THE URANIUM ALLOY AFTER
BEING ISOTHERMALLY TRANSFORMED FOR ONE
MINUTE AT 325° C. (250X; ETCHANT:
5% OXALIC ACID SOLUTION)

FIGURE 42

MICROSTRUCTURE OF THE URANIUM ALLOY AFTER
BEING ISOTHERMALLY TRANSFORMED FOR TWO
MINUTES AT 325° C. (250X; ETCHANT:
5% OXALIC ACID SOLUTION)

FIGURE 43

MICROSTRUCTURE OF THE URANIUM ALLOY AFTER
BEING ISOTHERMALLY TRANSFORMED FOR FIVE
MINUTES AT 325° C. (250X; ETCHANT:
5% OXALIC ACID SOLUTION)

FIGURE 44

MICROSTRUCTURE OF THE URANIUM ALLOY AFTER
BEING ISOTHERMALLY TRANSFORMED FOR TWO
MINUTES AT 475° C. (250X; ETCHANT:
5% OXALIC ACID SOLUTION)

FIGURE 45

MICROSTRUCTURE OF THE URANIUM ALLOY AFTER
BEING ISOTHERMALLY TRANSFORMED FOR FIVE
MINUTES AT 475° C. (250X; ETCHANT:
5% OXALIC ACID SOLUTION)

The sample in Figure 42, Page 69, which was heated for two minutes, shows considerably more substructure than the one-minute sample—the maximum amount of substructure that was seen in any sample. After this maximum is reached, the amount of substructure present decreases with increasing time. Finally, after five minutes time, no substructure is present, as may be seen in Figure 43, Page 70. This series is typical of all the other temperatures at which the substructure appeared. That is, the substructure appeared after some time at temperature, became progressively more pronounced with increasing time, and then completely disappeared before evidence of a phase transformation product could be seen in the microstructure. The substructure is uniformly distributed throughout the samples and is not restricted to areas near the surfaces.

In order to pursue the effects of certain variables on the substructure, several experiments were conducted. It was especially desirable to determine why the substructure was visible under certain conditions and not visible under others. Certain gaseous impurity atoms were suspected as having decorated the subgrain boundaries, thus making the substructure visible under certain optimum conditions. The experiments which were conducted are as follows: (1) hydrogen was charged into samples at high temperatures in a carbonate salt bath, (2) samples were isothermally transformed in a vacuum-purified lead bath, (3) samples were isothermally transformed in a water-saturated argon atmosphere, (4) samples were isothermally transformed in dry atmospheres consisting of argon, nitrogen, oxygen, and argon plus five per cent hydrogen, (5) hardness traverses were made to detect any diffusion of gaseous impurities, and (6) samples were strained and isothermally

transformed to determine the effect of strain upon the occurrence of the substructure.

1. Hydrogen Charging Samples at High Temperatures. In order to investigate the effect of hydrogen charging samples at high temperatures on the substructure, samples were heated for two hours at 800°C in a salt bath composed of potassium carbonate, lithium carbonate, and sodium carbonate. After heating in the salt bath, the samples were quenched into a lead bath at 325°C and isothermally transformed for varying times. Heating the samples in the salt bath for two hours charged them with an average of 15 p.p.m. hydrogen. The hydrogen content near the sample surface varied from 15 to 20 p.p.m.; at the center, the hydrogen varied from 10 to 15 p.p.m. The samples also contained 52 p.p.m. carbon, 40 p.p.m. oxygen, and five p.p.m. nitrogen.

These samples exhibited less substructure than samples which contain considerably less hydrogen, as may be seen in Figure 46 which shows a sample that was heated in the lead bath for two minutes at 325°C after being solution treated in the salt bath. However, regions near the surfaces of these samples contained large quantities of uranium hydride platelets, as may be seen in Figure 47.

2. Heating in a Vacuum-Purified Lead Bath. To determine whether heat treatment in a vacuum would reduce the amount of substructure, samples were γ solution treated for one hour in dry argon and then quenched into a lead bath at 325°C which had been held molten in a vacuum for one hour. It was believed that this operation would purify the lead bath; and, if the substructure of the samples

FIGURE 46

MICROSTRUCTURE OF THE URANIUM ALLOY AFTER
BEING HEATED FOR TWO HOURS AT 800° C IN A
CARBONATE SALT BATH AND ISOTHERMALLY
TRANSFORMED FOR TWO MINUTES AT 325° C
IN A LEAD BATH. SAMPLE CONTAINS AP-
PROXIMATELY 15 P.P.M. HYDROGEN.
(250X; ETCHANT: 5% OXALIC
ACID SOLUTION)

FIGURE 47

URANIUM HYDRIDE PLATELETS IN A URANIUM-7.5 WEIGHT PER CENT NIOBIUM-2.5 WEIGHT PER CENT ZIRCONIUM ALLOY AFTER BEING HEATED FOR TWO HOURS AT 800° C IN A CARBONATE SALT BATH. SAMPLE CONTAINS 20 P.P.M. HYDROGEN. (500X; ETCHANT: 2% OXALIC ACID SOLUTION)

was being influenced by the gaseous-type impurities, the substructure should be less visible. However, no significant purification of the bath resulted. The oxygen content was reduced from ten p.p.m. to seven p.p.m.; but the carbon, hydrogen, and nitrogen remained constant at five p.p.m., less than one p.p.m., and two p.p.m., respectively. Figure 48 shows a sample which was treated for two minutes at 325° C in the vacuum-treated lead bath. As may be seen from the figure, the substructure does not appear to be significantly diminished in this sample.

3. Hydrogen Charging at Transformation Temperatures. Samples were γ solution treated for one hour in a tube furnace through which a dynamic purified argon atmosphere was flowing. These samples were then rapidly transferred to another tube furnace maintained at 325° C through which water-saturated argon was flowing.

Samples treated in this fashion were unaffected by isothermal heating for times up to five hours. Samples heated for short times in the "wet" argon exhibited considerably less substructure than samples which were heated in the lead bath. (See Figures 49 and 50 for photomicrographs of samples which were aged for one minute and two minutes, respectively, at 325° C.)

4. Aging in Dry Atmospheres of Argon, Oxygen, Nitrogen, and Argon Plus Five Per Cent Hydrogen. Samples aged in dynamic dry atmospheres of argon, oxygen, nitrogen, and argon plus five per cent hydrogen at 325° C were not significantly different from samples heated in a lead bath. The short-time samples showed a little less substructure.

FIGURE 48

MICROSTRUCTURE OF THE URANIUM ALLOY
AFTER BEING ISOTHERMALLY TRANSFORM-
ED FOR TWO MINUTES AT 325° C IN A
VACUUM-PURIFIED LEAD BATH. (250X;
ETCHANT: 2% OXALIC
ACID SOLUTION)

FIGURE 49

MICROSTRUCTURE OF THE URANIUM ALLOY
AFTER BEING ISOTHERMALLY TRANSFORM-
ED FOR ONE MINUTE AT 325° C IN
WATER-SATURATED ARGON. (250X;
ETCHANT: 5% OXALIC
ACID SOLUTION)

FIGURE 50

MICROSTRUCTURE OF THE URANIUM ALLOY
AFTER BEING ISOTHERMALLY TRANSFORM-
ED FOR TWO MINUTES AT 325° C IN
WATER-SATURATED ARGON. (250X;
ETCHANT: 5% OXALIC
ACID SOLUTION)

5. Diffusion of Gaseous Impurities. In an effort to determine whether the diffusion of some gaseous impurity element was having an influence on the substructure, microhardness traverses were made perpendicular to the edges of several samples. These hardness traverses were made along lines that were parallel to the rolled surfaces of the plate. This treatment was necessary since gross segregation of niobium occurs from the edge to the center of the plate, the niobium being higher at the center.

Two possibilities exist for the diffusion of gaseous impurities. The impurities could diffuse either from the samples into the lead bath or from the lead bath into the samples. Assuming either of these to be the case, a hardness gradient should exist from the edge to the center of the samples for times less than those required for equilibrium to be reached.

Hardness traverses were run on nine samples which had been aged at 325° C in the lead bath, dry argon, and wet argon for times of one, five, and 30 minutes. In all cases, the hardness numbers were relatively constant, and no evidence of a hardness gradient was found. This result shows that either no diffusion of impurity atoms occurs, or that diffusion occurs very rapidly and equilibrium is reached in times less than one minute, or impurities do not affect the hardness.

6. Effect of Strain on Substructure. To determine the effect of strain on the substructure formation, tensile bars were machined from well-homogenized material that was taken from the same billet used in the other parts of this investigation. After being machined, the tensile bars were γ solution treated for one hour at 800° C

and water quenched to room temperature. These tensile bars were then strained to produce a one per cent plastic deformation.

After deformation, samples were cut from these strained bars and isothermally heated in a lead bath for varying times at 325°C . The deformation produced twinning in the microstructure and a DPH value of 220. No substructure was observed in samples aged at 325°C for times up to 30 minutes. Figures 51 through 56 show a series of samples aged for times of one minute to 30 minutes at 325°C .

Formation of Lamellar Structure from Widmanstatten Structure

As previously mentioned on Page 40, the lamellar structure is considerably coarser in samples which are quenched to room temperature and reheated than in samples which are quenched to transformation temperature and held. This difference was believed to be caused by the different types of crystal structure from which the lamellar structure was formed. On down quenching, the lamellar structure was formed from a body-centered cubic crystal structure; but, on up quenching, it was formed from a combination of tetragonal and monoclinic structures.

To determine the effect of the monoclinic crystal structure on the morphology of a lamellar structure formed from it, samples were aged for times of from one to 60 hours at 350°C , then each was subsequently aged for two hours at 550°C . Each sample revealed the formation of a lamellar structure at the grain boundaries. The interlamellar spacing width of this structure was essentially constant for all aging times, and was the same as that for samples which were quenched to room temperature and rapidly reheated. A sample which was initially aged for two hours at

FIGURE 51

MICROSTRUCTURE OF THE URANIUM ALLOY
AFTER HAVING BEEN GIVEN ONE PER CENT
PLASTIC DEFORMATION AND SUBSEQUENT-
LY AGED FOR ONE MINUTE AT 325° C.
(250X; ETCHANT: 5% OXALIC
ACID SOLUTION)

FIGURE 52

MICROSTRUCTURE OF THE URANIUM ALLOY
AFTER HAVING BEEN GIVEN ONE PER CENT
PLASTIC DEFORMATION AND SUBSEQUENT-
LY AGED FOR TWO MINUTES AT 325° C.
(250X; ETCHANT: 5% OXALIC
ACID SOLUTION)

FIGURE 53

MICROSTRUCTURE OF THE URANIUM ALLOY AFTER
HAVING BEEN GIVEN ONE PER CENT PLASTIC
DEFORMATION AND SUBSEQUENTLY AGED
FOR FIVE MINUTES AT 325° C. (250X;
ETCHANT: 5% OXALIC
ACID SOLUTION)

FIGURE 54

MICROSTRUCTURE OF THE URANIUM ALLOY AFTER
HAVING BEEN GIVEN ONE PER CENT PLASTIC
DEFORMATION AND SUBSEQUENTLY AGED
FOR 10 MINUTES AT 325° C. (250X;
ETCHANT: 5% OXALIC
ACID SOLUTION)

FIGURE 55

MICROSTRUCTURE OF THE URANIUM ALLOY AFTER
HAVING BEEN GIVEN ONE PER CENT PLASTIC
DEFORMATION AND SUBSEQUENTLY AGED
FOR 15 MINUTES AT 325° C. (250X;
ETCHANT: 5% OXALIC
ACID SOLUTION)

FIGURE 56

MICROSTRUCTURE OF THE URANIUM ALLOY AFTER
HAVING BEEN GIVEN ONE PER CENT PLASTIC
DEFORMATION AND SUBSEQUENTLY AGED
FOR 30 MINUTES AT 325° C. (250X;
ETCHANT: 5% OXALIC
ACID SOLUTION)

350° C and subsequently aged for two hours at 550° C is shown in Figure 57. A higher magnification photomicrograph of this same sample is given in Figure 58.

Effect of Certain Treatments on the Transformation Kinetics

Several experiments were conducted to determine the effect of certain treatments upon the alloy transformation kinetics. These tests included: (1) hydrogen charging samples at transformation temperatures in water-saturated argon, (2) hydrogen charging samples at elevated temperatures in a salt bath, (3) isothermally transforming samples in atmospheres of various dry gases, (4) determining the effect of strain, and (5) hydrogen charging at transformation temperatures and removal at higher temperatures.

1. Hydrogen Charging at Transformation Temperatures. Aging individual samples at 325° C in water-saturated argon retards the beginning of phase decomposition for significant periods of time. After heating for four hours at 325° C, the hardness of the samples was approximately 200 DPH, which is no increase over the as-quenched hardness. No effect of the heat treatments could be observed in the microstructure. After a 24-hour isothermal transformation time at 325° C, a slight amount of the Widmanstatten pattern could be observed in the microstructure of all the samples. These samples all had a hardness of approximately 290 DPH, significantly lower than a 480 DPH for a sample aged for 24 hours at 320° C in a lead bath. The hardness increased to 450 DPH after 48 hours and 500 DPH after 72 hours at 325° C in these "wet" atmospheres. No increase in the impurity analysis could be detected by conventional methods.

FIGURE 57

MICROSTRUCTURE OF A URANIUM-7.5 WEIGHT PER CENT NIOBIUM-2.5 WEIGHT PER CENT ZIRCONIUM ALLOY AFTER BEING INITIALLY AGED FOR TWO HOURS AT 325° C AND SUBSEQUENTLY AGED FOR TWO HOURS AT 550° C. STRUCTURE AROUND GRAIN BOUNDARIES HAS A LAMELLAR MORPHOLOGY. (250X; ETCHANT: 5% OXALIC ACID SOLUTION)

FIGURE 58

MICROSTRUCTURE OF A URANIUM-7.5 WEIGHT
PER CENT NIOBIUM-2.5 WEIGHT PER CENT
ZIRCONIUM ALLOY AFTER BEING INITIAL-
LY AGED FOR TWO HOURS AT 325° C
AND SUBSEQUENTLY AGED FOR TWO
HOURS AT 550° C. (1,500X;
ETCHANT: 5% OXALIC
ACID SOLUTION)

2. Hydrogen Charging at Elevated Temperatures. To determine the effect of high-temperature hydrogen charging on the transformation kinetics, samples were charged with known amounts of hydrogen ranging from 10 to 100 p.p.m. by heating in a carbonate salt bath at 800°C . No difference could be detected in the γ -to- α'' phase transformation rates at 325°C in any of the samples. However, most of the hydrogen is probably present as uranium hydride, as may be seen in Figure 47, Page 76.

3. Aging in Dry Atmospheres of Argon, Oxygen, Nitrogen, and Argon Plus Five Per Cent Hydrogen. Samples aged in dry atmospheres of argon, oxygen, nitrogen, and argon plus five per cent hydrogen appeared to experience the same γ -to- α'' transformation rate at 325°C as samples which were aged in a lead bath.

4. Effect of Strain on the Transformation Kinetics. Samples, taken from tensile bars which had been strained to produce a one-per cent plastic deformation, were isothermally transformed for varying times at 325°C . This amount of strain appeared to accelerate the beginning of the γ -phase decomposition. In relatively strain-free samples, the Widmanstätten pattern did not become clearly defined until after a ten-minute aging time at 325°C . However, the Widmanstätten pattern was clearly visible in the strained samples after a five-minute aging time, as may be seen in Figure 53, Page 85. A plot of DPH as a function of the aging time for strained samples is given in Figure 59.

5. Hydrogen Charging at Transformation Temperatures and Removal at Elevated Temperatures. Samples which are aged for two hours at 325°C in water-

FIGURE 59

PLOT OF DPH VALUES VERSUS AGING TIME AT 325°C FOR A
URANIUM-7.5 WEIGHT PER CENT NIOBIUM-2.5 WEIGHT
PER CENT ZIRCONIUM ALLOY THAT HAD PREVIOUSLY
BEEN PLASTICALLY DEFORMED ONE PER CENT

saturated argon exhibit no transformation product in the microstructure. However, if these samples are subsequently given an 800° C heat treatment for one hour, and then reaged at 325° C in dry argon or a lead bath, they transform in the same fashion as samples that have never been treated in wet argon. Thus, the impediment to transformation (presumably hydrogen) is removed by a γ -solution treatment.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

This investigation was concerned with a study of the time-temperature transformation behavior of the γ phase of a uranium-7.5 weight per cent niobium-2.5 weight per cent zirconium alloy system. A summation of the more important conclusions and recommendations for related investigations follows.

The transformation microstructures in this system consist of three distinct types: (1) a lamellar structure at the higher temperatures ($650 - 525^{\circ}\text{C}$), (2) a fine α -uranium precipitation at intermediate temperatures ($525 - 410^{\circ}\text{C}$), and (3) a Widmanstätten pattern at low temperatures ($< 410^{\circ}\text{C}$). The time-temperature transformation diagram consists of two C-shaped curves. The nose of the upper curve occurs at 525°C , with reaction starting in 20 minutes; the lower nose occurs at 350°C , with three minutes to initiate reaction. In as much as the transformation kinetics are influenced by impurities and chemical segregation, the time-temperature transformation behavior observed should be considered accurate only for the material used in this investigation; otherwise, the transformation diagram will probably be slightly different.

The upper C curve, which is asymptotic to an upper limit of 650°C , may actually result from two nearly overlapping C curves because the morphology of the transformation is a lamellar structure above the upper nose ($525 - 650^{\circ}\text{C}$) but is a

fine precipitate of α uranium below the nose ($410 - 525^{\circ}\text{C}$). The lower C curve gives the time-temperature relationships for the initiation of a Widmanstatten transformation. This C curve is asymptotic to an upper limit of 410°C .

The γ phase, which is stable above 650°C , is body-centered cubic with a lattice parameter of 3.464 ± 0.003 angstroms. Upon water quenching, this phase is not retained, but rather a transition phase, called γ^s , is formed whose crystal structure may be described as eight γ -phase unit cells in which the body-centered atoms have shifted along correlated $\langle 100 \rangle$ directions. The as-quenched hardness of the γ^s phase is DPH 190 - 200. Upon aging, this γ^s phase transforms to another transition phase called γ^o , which has a tetragonal crystal structure and is formed by further atom shifts correlated along a particular $[001]$ direction.

Upon further aging, the γ^o phase transforms to another phase called α'' which has a monoclinic crystal structure with lattice parameters of $a = 2.89 \pm 0.01$ angstroms, $b = 5.68 \pm 0.02$ angstroms, $c = 4.99 \pm 0.02$ angstroms, and γ (the angle between a and b) = 91.0 ± 0.3 degrees. This phase is exhibited in the microstructure as the Widmanstatten pattern. It increases in hardness from DPH 250 when first visible to DPH 600 when the material is completely transformed.

By aging samples in certain water-saturated atmospheres, the α'' phase formation may be retarded for times in excess of four hours. The impediment to transformation is suspected to be nascent hydrogen which is charged from the decomposition of the water. A subsequent γ -solution treatment will remove this impediment to the transformation. Samples which are hydrogen charged by other means do not experience this retardation of transformation.

Under certain conditions, a substructure is visible in samples which have been aged. The reason for this substructure being visible was not completely determined in this investigation. Several possibilities have been evaluated, but none of these has given conclusive proof that it is responsible. More work should be done to determine what is decorating this substructure.

This investigation should be repeated using material that is perturbed on both the high side and low side of the niobium content. The transformation kinetics appear to be very sensitive to the niobium content, thus the effect of small alloy variations should be determined.

A time-temperature transformation curve should be determined for the beginning of the γ^0 phase formation. Also, the effect of gaseous impurities on the phase transformation kinetics should be determined.

LIST OF REFERENCES

LIST OF REFERENCES

- (1) Peterson, C. A. W. and R. R. Vandervoot; "The Properties of a Metastable Gamma-Phase Uranium-Base Alloy: U-7.5 Nb-2.5 Zr," p. 1, UCRL-7869, Lawrence Radiation Laboratory, University of California, Livermore, California, May, 1964.
- (2) Peterson, C. A. W.; "A Study of the Isothermal Transformations of Some Binary-Uranium-Base Alloys Between 400° C and 650° C," UCRL 7824, Lawrence Radiation Laboratory, University of California, Livermore, California, May, 1965.
- (3) Dwight, A. E. and M. H. Mueller; Constitution of the Uranium-Rich U-Nb and U-Nb-Zr Systems, ANL 5581, Argonne National Laboratory, Argonne, Illinois, October, 1957.
- (4) Peterson, C. A. W. and W. J. Steele; "A Study of the Effect of Alloying on the Gamma-Phase Stability of Uranium Using Vacuum Differential Thermal Analysis," UCRL 7595, Lawrence Radiation Laboratory, University of California, Livermore, California, March, 1963.
- (5) Wilkinson, W. D.; "Uranium Metallurgy," pp. 859-860, Interscience Publishers, New York, New York (1962).
- (6) Harrington, Charles D. and Archie E. Ruekle; "Uranium Production Technology," p. 3, D. Van Nostrand Company, Incorporated, Princeton, New Jersey (1959).
- (7) Repas, R. E., R. H. Goodenov, and R. F. Hehemann; "An Investigation of Transformation Characteristics of Three Uranium Base Alloys," Technical Report AMRA CR 63-02/1 (F), p. 4, The Department of Metallurgy, Case Institute of Technology, January, 1963.
- (8) Storhok, V. M., A. A. Bauer, and R. F. Dickerson; "Survey of Ternary and Quaternary Metastable Gamma-Phase Uranium Alloys," p. 2, BMI 1278, Battelle Memorial Institute, Columbus, Ohio, July, 1958.
- (9) Hansen, P.; "Constitution of Binary Alloys," pp. 1021, 1023, and 1251, McGraw-Hill Book Company, Incorporated, New York, New York (1958).
- (10) VanVlack, L. H.; "Elements of Materials Science," pp. 288-289, Addison Wesley Publishing Company, Reading, Massachusetts (1964).

- (11) Yakel, H. L.; "Crystal Structures of Transition Phases Formed in U-16.60 At % Nb-5.64 At % Zr Alloys," Not Published, Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

VITA

Charles William Dean was born in Dixiana, Alabama, on May 7, 1938. He attended Pinson Elementary and Junior High Schools and was graduated from Tarrant High School in 1956. In January 1959, he entered the University of Alabama, and in January 1963 received a Bachelor of Science degree in Metallurgical Engineering. Immediately thereafter, he accepted employment with Republic Steel Corporation.

He accepted employment with the Oak Ridge National Laboratory in October 1966; and, simultaneously, began part-time graduate studies at The University of Tennessee. In August 1968 he transferred to the Development Division of the Oak Ridge Y-12 Plant.

Mr. Dean resides at 116 Jellico Lane, Oak Ridge, Tennessee, with his wife, Faye, and two daughters, Lisa and Laura, ages six and four, respectively.