Argonne National Laboratory

CONSTITUTION OF THE URANIUM-RICH U-Nb AND U-Nb-Zr SYSTEMS

by

A.E. Dwight and M.H. Mueller

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ARGONNE NATIONAL LABORATORY
P. O. Box 299
Lemont, Illinois

CONSTITUTION OF THE URANIUM-RICH U-Nb
AND U-Nb-Zr SYSTEMS

by
A. E. Dwight and M. H. Mueller

Final Report - Metallurgy Program 3.1.5

October, 1957

Portions of the material in this report have appeared in
the following Metallurgy Division Quarterly Reports:

<u>ANL NUMBER</u>	<u>PAGE</u>	<u>DATE</u>
ANL-5423	67	Dec. 31, 1954
ANL-5439	32	March 31, 1955
ANL-5465	49, 50	June 30, 1955
ANL-5489	50-52	Sept. 30, 1955
ANL-5541	33, 34	Dec. 31, 1955
ANL-5563	45, 47-49	March 31, 1956
ANL-5623	62, 64-67	June 30, 1956

Operated by The University of Chicago
under
Contract W-31-109-eng-38

TABLE OF CONTENTS

	<u>Page</u>
LIST OF TABLES	3
LIST OF FIGURES	4-6
ABSTRACT	7
INTRODUCTION	7
EXPERIMENTAL TECHNIQUE	8
Preparation of Specimens	8
Heat Treatment	8
Metallography	9
Resistivity	9
X-Ray Diffraction	9
LIMITING BINARY SYSTEMS	10
Uranium-Niobium System Up to 10.5 w/o Nb	10
The Uranium-Zirconium Binary System	23
The Zirconium-Niobium Binary System	23
THE TERNARY EQUILIBRIUM DIAGRAM	23
Isometric Model	23
Isothermal Sections	27
Vertical Sections	38
The Gamma Phases	38
The $\beta + \gamma$ Region	52
The $\alpha + \gamma$ Region	54
The Δ or UZr_3 Phase	61
RELATION OF IRRADIATION DATA TO PHASE DIAGRAM	63
URANIUM ALLOY THEORY	70
The Uranium-Zirconium-Niobium Ternary Solid Solution	70
Breakdown of One Gamma into Two Gamma Phases	71
ACKNOWLEDGEMENTS	72
APPENDIX I: Chemical Compositions of Experimental Alloys	73
BIBLIOGRAPHY	74

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
I.	Microstructural Features of Specimens Isothermally Transformed between 619°C and 638°C	58
II.	X-Ray Diffraction Data for Isothermally Transformed Specimens Lying Close to the δ UZr ₃ Phase Region	62

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1	Electrical Resistivity Circuit	10
2	Uranium-Niobium Phase Diagram to 10.5 w/o Nb.	12
3	Uranium-Niobium Phase Diagram	13
4	Microstructure of U-Nb Alloys Near $\beta + \gamma$ Region	14
5	Microstructure of U-Nb Alloys Near the $\gamma/\alpha + \gamma$ Line	16
6	Microstructure of U-Nb Alloys Near the $\alpha + \gamma/\beta + \gamma$ Region	17
7	Microstructure of U-Nb Alloys Near the $\alpha + \gamma/\beta + \gamma$ Region	18
8	Microstructure of U-Nb Alloys Near the Eutectoid	19
9	Pearlitic Nodule in Metastable Gamma Phase	20
10	Diffraction Pattern of the Body-Centered Tetragonal Gamma Phase in the U-Nb System	22
11	Uranium-Zirconium Phase Diagram	24
12	Zirconium-Niobium Phase Diagram	25
13	Three Dimensional Space Model of the U-Zr-Nb System	26
14	Isothermal Section at 700°C	28
15	Isothermal Section at 680°C	28
16	Isothermal Section at 660°C	29
17	Isothermal Section at 640°C	29
18	Isothermal Section at 630°C - 632°C	30
19	Isothermal Section at 626°C	30
20	Microstructures after 19 days at 626°C, w.q.	31-33
21	Isothermal Section at 621°C	34
22	Microstructures after 65 hours at 621°C, w.q.	35-36
23	Isothermal Section at 600°C	37
24	Location of Vertical Sections through the Ternary Diagram	39
25	Vertical Section at 1 w/o Nb.	39
26	Vertical Section at 2 w/o Nb.	40
27	Vertical Section at 7 w/o Nb.	40

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
28	Vertical Section at 25 w/o Nb	41
29	Vertical Section at 2 w/o Zr	41
30	Vertical Section at 4 w/o Zr	42
31	Vertical Section at 6 w/o Zr	42
32	Vertical Section at 20 w/o Zr	43
33	Vertical Section with Zr: Nb ratio of 5: $1\frac{1}{2}$	43
34	Projection of Monotectoid Valleys and Isothermal Lines onto the Base Plane	44
35	X-Ray Diffraction Patterns of Three Gamma Phase Specimens.	46
36	Microstructures of the Control Specimens for Figure 35	47
37	X-Ray Diffraction Patterns Showing Effect of Nb on Retention of Metastable Gamma	48
38	Microstructure of Four Alloys Quenched from the Gamma Range	50
39	Lines of Constant Lattice Parameter of the Gamma Phase in the U-Nb-Zr System	51
40	Range of Existence of the Body Centered Tetragonal γ Phase after Quenching from 900°C	51
41	Microstructures of Four Alloys Quenched from the $\beta + \gamma$ Range.	53
42	Vertical Section at 20 w/o Zr	55
43	Microstructures of Six Specimens on the 20 w/o Zr Vertical Section.	56
44	Electrical Resistivity at Room Temperature vs Isothermal Transformation Temperature	59
45	Isothermal Transformation Temperature vs Per Cent Equilibrium Gamma Phase.	60
46	Isothermal Section at 500°C	62
47	Hardness vs Transformation Temperature for Swaged 5 w/o Zr - $1\frac{1}{2}$ w/o Nb Specimens Continuously Cooled from the Gamma Range.	64
48	Time-Temperature Relations for Isothermal Transformation of 5 w/o Zr - $1\frac{1}{2}$ w/o Nb Alloy.	65

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
49	Irradiation Growth of 5 w/o Zr - $1\frac{1}{2}$ w/o Nb Alloy	65
50	Microstructures of Isothermally Transferred 5 w/o Zr - $1\frac{1}{2}$ w/o Nb Alloy	67
51	Metastable Gamma Retention in Quenched Specimens	69
52	$\gamma/\gamma + \beta$ Line at 700°C	71

CONSTITUTION OF THE URANIUM-RICH U-Nb AND U-Nb-Zr SYSTEMS

by
A. E. Dwight and M. H. Mueller

ABSTRACT

The uranium-niobium binary system exhibits a continuous series of solid solutions above 850°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 4 w/o Nb. Below 634°C α uranium and the niobium-rich gamma co-exist.

The uranium-niobium-zirconium ternary system exhibits a continuous series of solid solutions at high temperatures. Miscibility gaps in the uranium-niobium and uranium-zirconium binary systems close with addition of the third element. Addition of both zirconium and niobium stabilizes the body-centered cubic gamma phase to lower temperatures. The β -uranium phase is eliminated in ternary alloys of 4 w/o Nb or more. The δ phase of the uranium-zirconium binary system extends into the ternary system to no more than 10 w/o Nb. Over the major portion of the uranium-rich corner of the ternary system the equilibrium phases are α -U and γ solid solution. The uranium-niobium binary system is the more dominant of the limiting systems. No new ternary phases were found. The relation of microstructures to irradiation stability is discussed. The relation of lattice strain to limits of solid solubility is also discussed.

INTRODUCTION

The investigation of the uranium-zirconium-niobium phase diagram was undertaken as the system was of interest because of favorable properties. It has been known for several years that additions of niobium to uranium greatly increased the corrosion resistance in the gamma-quenched condition. It was found somewhat later that additions of zirconium to uranium improved the stability of the metal when subjected to thermal cycling or to neutron irradiation. It was a logical step to combine niobium and zirconium into a ternary alloy in an attempt to obtain both corrosion resistance and irradiation stability. A further consideration in selection of alloying elements was the absorption cross section for thermal neutrons. Because

zirconium has a low absorption cross section, it is particularly desirable as an alloying element. From these considerations there evolved the fuel alloy containing $1\frac{1}{2}$ w/o niobium and 5 w/o zirconium, which has undergone intensive study.

It was apparent that the useful properties of uranium-niobium-zirconium alloys could be best interpreted and improved if a ternary equilibrium diagram were available. Therefore a major effort has been made to determine the phase relationships in the system up to 40 w/o Zr and 10 w/o Nb. The data so obtained are presented in this report.

EXPERIMENTAL TECHNIQUE

Preparation of Specimens

Of the 49 alloy compositions used in this investigation, 17 were purchased from Battelle Memorial Institute and 32 were prepared at Argonne National Laboratory. The Battelle alloys were arc melted in approximately 200-gm lots and hot rolled to $3/8$ in. rod. Seventeen of the alloys prepared at Argonne were centrifugally cast under vacuum. Melting was done in high-purity magnesia crucibles and the molten alloy centrifugally cast into massive copper molds rotating at an angular velocity of 360 rpm. Pouring temperatures ranged around 1500°C . The cast slugs were swaged at 800°C down to approximately 0.2 in. diameter.

In the latter stages of the phase diagram investigation, an arc-melting furnace was set up and 13 alloys were prepared. Roughly 20-gm buttons were made by remelting the charge three times under a partial pressure of argon. No hot working was attempted on the cast buttons.

Chemical analyses were done on the Battelle alloys and on the centrifugally cast and swaged alloys. Carbon analyses generally ranged from 40 to 170 ppm, nitrogen analyses generally ranged from 10 to 150 ppm, and oxygen from 100 to 800 ppm. Niobium and zirconium analyses held closely to the nominal compositions.

Heat Treatment

Specimens were wrapped in 0.003 in. tantalum foil and sealed in evacuated Vycor capsules. The customary procedure was to hold the capsule at 800° or 900°C for one hour to obtain all gamma phase, then quickly transfer to a second furnace which was at the desired transformation temperature. After transformation times varying from 24 hours to 19 days, the capsule was broken under water. Heat treating was done in vertical tube resistance furnaces, with voltage regulated by a Variac and controlled by a Micromax recorder. In some regions of the phase

diagram the slight slope of the $\gamma/(\alpha + \gamma)$ surface made close temperature control necessary. The technique which was developed was to seal up to 12 different alloy specimens into a single capsule and place the capsule inside a massive stainless steel heat sink which fitted closely into the furnace tube. A calibrated Pt-Pt 10% Rh thermocouple was inserted into a second hole in the heat sink and the temperature read on a precision potentiometer with external galvanometer. The heat sink served to smooth out the fluctuations which normally result from the off-on operation of the Micromax recorder. Temperatures obtained by this method are estimated to be accurate to within $\pm 1^\circ\text{C}$.

Metallography

The standard technique for metallographic examination was as follows. Specimens were mounted in Bakelite or Lucite, usually with three to ten specimens to a mount. The mounted specimens were ground on water wheels with 80 through 600 papers, then polished on cloth covered wheels with #14 through #1 diamond paste. Etching was done electrolytically, by immersing the mounted specimens and touching each in turn with a platinum anode. The electrolyte used for the martensitic and two phase alloys was the following: eight parts phosphoric acid, five parts ethylene glycol, five parts ethyl alcohol. For specimens containing all metastable gamma phase, an aqueous oxalic acid solution was used. In a few instances a bath of ten parts acetic acid, one part perchloric acid was used. All photomicrographs, with one exception, were taken at 500X, bright field illumination.

Resistivity

Resistivity measurements were taken at room temperature after the specimen had been isothermally transformed at some temperature between 590° and 720°C . The specimens were centerless ground to 0.210 in. diameter and had leads of chromel spot welded to them before heat treatment. The specimen and the shorted leads were heat treated in evacuated Vycor capsules. After quenching, longer leads were attached by spot welding onto the short leads. Resistivity was measured by use of the circuit shown in Figure 1, which is the customary potential drop method.

X-Ray Diffraction

For the most part, samples used for the X-ray diffraction study consisted of solid needle-shaped specimens, approximately $1/32$ in. diameter and $3/8 - 1/2$ in. in length and tapered at one end. These specimens were usually cut from the cast button or rolled rod, given a prescribed heat treatment, water quenched, and then cleaned up electrolytically by polishing for several seconds in a perchloric-acetic acid bath. In many cases a small piece was cut from the larger end of the needle, mounted and polished in order to correlate the metallography with the X-ray results.

Figure 1. Electrical Resistivity Circuit

The X-ray diffraction patterns were obtained with a 114.6-mm diameter camera using filtered $\text{CuK-}\alpha$ radiation. In all cases where the pattern of the cubic phase was sufficiently sharp, its lattice parameter was obtained by a modified Cohen least squares method or by extrapolation.

The high-temperature pattern of the $\text{U} - 7\frac{1}{2} \text{ w/o Nb}$ alloy was obtained with a resistance-type vacuum high-temperature camera.

LIMITING BINARY SYSTEMS

Uranium-Niobium System Up to 10.5 w/o Nb

Earlier work, summarized in BMI 1000,⁽¹⁾ had established the general type of diagram. However, a more accurate binary diagram was needed to serve as a base for the investigation of the ternary uranium-niobium-zirconium system. The attempt was made to establish the binary uranium-niobium system with as high a degree of precision as was consistent with the quality of the available alloys.

In general the method was to bracket the boundary of a phase field within increasingly narrow limits of temperature, until eventually a $\pm 2^\circ$ bracket was obtained. The uranium-niobium system has a continuous series of solid solutions above 800°C , which greatly simplifies the method of temperature brackets. All specimens were held at 800° or 900°C to obtain the gamma solid solution. Then in most cases the specimen was

transferred quickly to another furnace at the desired transformation temperature, held there until transformation was complete, and water quenched. The time required to complete transformation varied with temperature, but the practice was followed of transforming at various times from 24 hours to one week. If, for example, the structure of a 24-hour specimen was identical to that of a 48-hour specimen at the same temperature, it was assumed that both were completely transformed, but the 48-hour specimen was photographed. As a check, some specimens were quenched from the gamma range, and quickly reheated to the transformation temperature. Both treatments led to the same temperature brackets for a given alloy.

The number of specimens which were studied is best shown in Figure 2, which shows the phase diagram as determined by this investigation. In this and all other phase diagrams, single-phase regions are denoted by $\odot$ and two-phase regions by $\ominus$, regardless of their nature of composition. Figure 3 shows the probable diagram to 100% Nb. All compositions listed in this paper are in weight per cent, all temperatures in degrees Centigrade. The major differences between this diagram and the original diagram reported by B. Sawyer,⁽²⁾ are that the eutectoid is now established at $634 \pm 2^\circ\text{C}$ and $8.1 \pm 0.2\%$ Nb, a lower temperature and higher niobium content than originally reported, and that a body-centered tetragonal form of gamma exists near the eutectoid. The term γ_3 in Figure 2 was adopted for the Nb-rich gamma phase to avoid confusion with the γ_2 of the uranium-zirconium system.

Phase identification is one of the more interesting problems involved in the determination of a phase diagram by metallographic examination. For example, at 680°C , the sequence of phases, with increasing niobium content, is beta uranium, beta + gamma, then gamma. Figure 4 exhibits the microstructure at the 680°C level. In the first three photomicrographs, it is apparent that the dark phase increases in quantity as the niobium content increases. It is therefore the gamma phase, and the white phase was beta at the transformation temperature, though at room temperature is probably alpha. In the fourth photomicrograph of the series, the structure is all gamma, as shown by the equiaxed grains and the longer etching time required. The dispersed particles are unidentified inclusions which do not respond to heat treatment.

A second method of phase identification is available. The phases which were alpha and beta at transformation temperature will stain rapidly in air, whereas gamma is unaffected. Therefore in cases where a sequence of specimens is not available it is only necessary to compare a freshly etched structure with the structure after several hours exposure to air. The fact that beta is light in the first three microphotographs is peculiar only to a freshly etched specimen and by itself is not a means of phase identification.

Figure 4. Microstructure of U-Nb Alloys in the $\beta + \gamma$ Region

0.5 w/o Nb

 $\beta + \gamma_1$

16,747

500X

1.0 w/o Nb

 $\beta + \gamma_1$

16,748

500X

800° C

680° C

w.q.

1.9 w/o Nb

 $\beta + \gamma_1$

16,749

500X

4.1 w/o Nb

 γ_1

17,923

500X

Referring again to Figure 2, the evidence for locating the gamma/(alpha + gamma) line is presented in the form of microstructures above and below the line. The upper three photomicrographs in Figure 5 exhibit retained gamma plus the usual inclusions. The three alloys shown have different fabrication histories, which account for the difference in the gamma grain sizes. The lower three photomicrographs exhibit alpha particles in a gamma matrix for the same three alloys at temperatures from 3 to 7°C below the corresponding gamma structures. Other specimens of the same three alloys, not shown here, permit bracketing the gamma/(alpha + gamma) line within $\pm 2^\circ\text{C}$. As the established points could be fitted by a straight line, the line was extrapolated to meet the eutectoid line at 8.1 w/o Nb. As extrapolation is often uncertain, the eutectoid composition is placed at 8.1 ± 0.2 w/o Nb.

Referring again to Figure 2, the line dividing the gamma and beta + gamma fields was determined by the same method. The difference between gamma alloys and beta plus gamma alloys is readily apparent, though with lower niobium contents the gamma cannot be retained by ordinary water quenching. The study of a sequence of several alloys at one temperature readily permits identification of the phases which existed at the transformation temperature.

It is now apparent that the lines forming the lower limit of the gamma field are not continuous; i.e., a change of slope exists at the alpha to beta transformation. The data can best be fitted by locating the change of slope at 668°C . A considerable effort was made to locate the alpha to beta transformation by metallographic examination of low niobium alloys. As shown in Figures 6 and 7, identical structures are obtained by transforming at 664° and 667°C , in alloys up to 2 w/o Nb. Other specimens transformed at 653° , 660° , and 670°C showed similar structures, leading to the conclusion that the alpha to beta transformation, in the presence of gamma, cannot be definitely located by metallographic examination. It is considered that high-temperature X-ray work is needed to locate definitely the temperature of alpha to beta transformation. The diagram as drawn requires a peritectoid rather than a eutectoid at the uranium end, which has been a controversial point among the other investigators of the system.

Referring again to Figure 2, the eutectoid line was also investigated. Three alloys were used, two of which were hypo and one hyper eutectoid. The higher niobium content and lowered temperatures required longer transformation times; in most cases, 72 to 96 hours were adequate to complete the transformation. The metallographic evidence for the location of the eutectoid temperature at $634^\circ\text{C} \pm 2$ is presented in Figure 8. Here again three alloys are shown, at temperatures above and below the eutectoid. Above the eutectoid line, the two hypo eutectoid alloys exhibit an alpha plus gamma structure; the third alloy is all retained gamma. Below the eutectoid, a pearlitic structure is exhibited. The pearlite lamellae become

Figure 5. Microstructure of U-Nb Alloys near the $\gamma/\alpha + \gamma$ Line

4.1 w/o Nb γ_1 667°C

17,908 500X

4.9 w/o Nb γ_1 664°C

17,899 500X

6.0 w/o Nb γ_1 652°C

17,914 500X

4.1 w/o Nb $\alpha + \gamma_1$ 664°C

17,904 500X

4.9 w/o Nb $\alpha + \gamma_1$ 658°C

17,900 500X

6.0 w/o Nb $\alpha + \gamma_1$ 645°C

17,915 500X

γ soak

w.q.

Figure 6. Microstructure of U-Nb Alloys near the $\alpha + \gamma/\beta + \gamma$ Line

0.5 w/o Nb

$\alpha + \gamma_1$

17,905

500X

1.0 w/o Nb

$\alpha + \gamma_1$

17,902

500X

γ soak

667°C

w.q.

0.5 w/o Nb

$\alpha + \gamma_1$

17,901

500X

1.0 w/o Nb

$\alpha + \gamma_1$

17,906

500X

γ soak

664°C

w.q.

Figure 7. Microstructure of U-Nb Alloys near the $\alpha + \gamma/\beta + \gamma$ Line

1.9 w/o Nb

$\alpha + \gamma_1$

17,907

500X

4.1 w/o Nb

γ_1

17,908

500X

1.9 w/o Nb

$\alpha + \gamma_1$

17,903

500X

4.1 w/o Nb

$\alpha + \gamma_1$

17,904

500X

Figure 8. Microstructure of U-Nb Alloys near the Eutectoid

17,917

500X

17,910

500X

17,911

500X

17,912

500X

17,913

500X

17,916

500X

γ Soak

w.q.

more perfectly formed with increasing niobium content, but some tendency to form pearlite is noticeable in the 4.9 w/o alloy. Other specimens not shown here permit the eutectoid to be established at $634^{\circ}\text{C} \pm 2$. The phase diagram requires two gamma phases above 634°C and beyond 8 w/o Nb.

X-ray diffraction patterns taken on an alloy containing 10.5 w/o Nb, quenched from 638°C show two body-centered cubic (gamma) phases. The pattern, reproduced in Figure 35, is discussed more completely in the section on the ternary gamma phases. However, indirect metallographic proof of the two gamma phases is presented in Figure 9. This figure shows the growth of a nodule of pearlite into the metastable gamma matrix at a temperature below the eutectoid. The interface of the nodule advances into the gamma by the usual lengthwise growth of alpha platelets separated by the niobium-rich gamma solid solution. At high magnification a difference in color can be detected between the metastable gamma and the niobium-rich gamma.

Figure 9.. Pearlitic Nodule in Metastable Gamma Phase.

A previously unreported phase has been observed in the uranium-niobium binary system whose X-ray diffraction pattern can be indexed seemingly on the basis of a body-centered tetragonal unit cell. It has been found in five different alloy compositions ranging from 6 to 9 w/o Nb in the as-cast, as-cast and rolled, and annealed condition. For example, this tetragonal phase was found in the 8.0 w/o alloy in the as-cast material and in the 7.5 w/o alloy in as-cast and rolled condition. It was also observed in the 7, 7.5 and 8.0 w/o Nb alloys after annealing small needle X-ray specimens 2 hours at 900°C plus 5 days at 668°C and water quenching. With this same treatment the 9 w/o alloy showed a body-centered cubic γ_1 phase only. Similar specimens ranging in composition from 6 to 8 w/o Nb when annealed in the range of 706°-990°C and quenched, yielded either the tetragonal or the cubic γ_1 phase. It appears from these quenched specimens that the cubic to tetragonal transformation is more sluggish as the Nb content increases, as indicated below:

	w/o Nb			
	7	7.5	8	9
No. of specimens quenched from above 706°C	1	9	7	2
No. showing γ_1 cubic	0	1	4	2
No. showing tetragonal	1	8	3	0

The quenching rate is also apparently critical for the retention of the cubic γ_1 phase. For example, two of the above 8 w/o Nb needle specimens sealed in the same capsule and quenched from 990°C showed the cubic γ_1 phase in one needle specimen and the tetragonal phase in the other needle.

It was also found that if some of the above needles of the 7.5, 8 and 9 w/o Nb content, which showed the cubic γ_1 phase only, were annealed for 1 hour at 406°C they would transform to the tetragonal phase plus a slight amount of α uranium. The identification of the cubic and tetragonal phase was made in all cases by X-ray diffraction, since metallographic examination failed to distinguish between these two phases.

This tetragonal phase has not been found in the 10.5 w/o Nb alloy, although some fourteen X-ray diffraction patterns of this alloy were made in an attempt to find this phase.

This body-centered tetragonal cell may be derived from the body-centered cubic γ_1 phase by slightly distorting this latter phase, as indicated by two 8 w/o Nb specimens quenched from 900°C in which the one specimen was cubic with an $a_0 = 3.45 \text{ \AA}$ and the other specimen was tetragonal with $a_0 = 3.48 \text{ \AA}$ and $c_0 = 3.40 \text{ \AA}$. The degree of tetragonality is apparently

a function of the Nb content - the higher the Nb content, the less the tetragonality; for example, in two specimens, both annealed at 640°C, the c/a ratio for the 6 w/o Nb alloy was 0.955 whereas this ratio was 0.975 for the 8 w/o Nb alloy. The degree of tetragonality may also be a function of temperature. A typical diffraction pattern of the tetragonal phase is reproduced in Figure 10.

Figure 10. Diffraction Pattern of the Body-Centered Tetragonal Gamma Phase in the Uranium-Niobium System.

Film #5158

92.5 w/o U
7.5 w/o Nb

Although it appears that the X-ray diffraction patterns from this phase can be indexed on the basis of a tetragonal crystal structure, there are a few extra lines which appear consistently in these patterns which cannot be accounted for by this small tetragonal cell. A metallographic study of these particular specimens seems to rule out the possibility of the presence of a second phase. However, if this tetragonal phase is formed by an ordering process it may be that the true unit cell is larger or has less symmetry than the small tetragonal cell, which might account for the extra lines. Since the tetragonal structure has been observed in the 14 to 20 a/o Nb alloys, which corresponds to approximately a U_5Nb composition, ordering would also be more easily explained on the basis of a larger cell. It appears that substitution of one niobium atom in three body-centered cubic γ_1 unit cells is the critical amount for the formation of this tetragonal structure.

In addition to the X-ray evidence for the existence of this phase, a thermal arrest has been detected in certain alloys as follows:

Alloy	Arrest Point °C
U - 4.1 w/o Nb	702 to 710°C
U - 4.9 w/o Nb	705 to 725°C
U - 7.5 w/o Nb	675 to 703°C

These thermal arrests were noted at cooling rates from 16 to 110°C per second, with the lower temperature arrest being found for the faster cooling rate. It is very possible that these observations also indicate that the tetragonal structure is a result of an ordering of the cubic γ_1 and is not a true phase change; therefore, the cubic and tetragonal structures have been designated γ_1 and γ_1' , respectively, in Figure 2.

A further diffraction study and an investigation of some of the physical properties of this tetragonal phase are necessary in order to determine its true nature.

The Uranium-Zirconium Binary System

The second limiting binary system is the uranium-zirconium system. Through the greater part of the present investigation the diagram reported by D. Summers-Smith⁽³⁾ was assumed to be correct. However, in the later phases of the present investigation, evidence of the δ phase was found in certain low Nb ternary alloys. This δ phase was found to originate in the uranium-zirconium binary system. The diagram which is assumed as the limiting binary of the ternary system is shown in Figure 11. In this diagram, the portion above 606°C is taken from the work of Summers-Smith and that below 606°C is taken from the work of Rough, Austin, Bauer and Doig.⁽⁴⁾

The Zirconium-Niobium Binary System

The third limiting binary system, Zr-Nb, has appeared in the open literature and is the work of the Ames Laboratory.⁽⁵⁾ Although certain features of the diagram were questioned in the discussion of the Ames paper, the system as reported is assumed as the third limiting binary system. The phase diagram is reproduced in Figure 12. It should be noted that all three limiting binary systems exhibit complete solubility at high temperature, and in all three a breakdown of one body-centered cubic phase into 2 body-centered cubic phases occurs at a lower temperature.

THE TERNARY EQUILIBRIUM DIAGRAM

Isometric Model

An isometric view of the three limiting binary systems and the ternary system is shown in Figure 13. The portion of these systems ranging from pure uranium to 20 w/o Nb and to 50 w/o Zr is the result of experimental work described in this report. For the portion of these systems outside of this range, data have been taken from published reports, principally those from Ames Laboratory and Battelle Memorial Institute.

FIGURE 12
ZIRCONIUM - NIOBIUM PHASE DIAGRAM

Figure 13. Three Dimensional Space Model of U-Zr-Nb System.

As there is not yet full agreement among all laboratories on the nature and extent of the δ U-Zr phase, some modification of the ternary diagram may be necessary in the region of the δ phase.

Isothermal Sections

The sequence of phase transformations in a ternary system is most readily shown by a series of isothermal sections through the ternary space model. These are shown in Figures 14 through 19 and in Figures 21 and 23. Only six phases occur in the portion of the ternary diagram covered by this investigation. The nomenclature of the ternary system was derived from the limiting binary systems as far as possible; however, in the case of the gamma phases a new nomenclature is necessary. At temperatures above 900°C only one gamma phase (body-centered cubic) extends over the entire uranium-zirconium-niobium system. In the uranium-zirconium system, the gamma breaks down into two gammas, called γ_1 and γ_2 . In the uranium-niobium system also, one gamma breaks down into two gammas, one rich in uranium and the other rich in niobium. The uranium-rich gamma exhibits complete solid solubility with the uranium-rich gamma of the uranium-zirconium system; hence the term γ_1 can be applied to the uranium rich gamma of both the uranium-zirconium and uranium-niobium systems. The niobium-rich gamma, 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 .

Other phases present in the ternary system are α and β uranium and the compound corresponding to UZr_3 now designated as δ .

Several major features of the ternary system can be noted from the isothermal sections. First, 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, 4 w/o 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 gamma phases merge into one. (The term monotectoid follows the terminology used by Summers-Smith for the uranium-zirconium system. The transformation is called monotectoid because of its close resemblance 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 gamma 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 7 w/o Nb and occurs in only a small portion of the ternary system.

Figures 20 and 22 show microstructures upon which the isothermal sections at 626°C and 621°C, respectively, are based.

Figure 20. Microstructure after 19 days at 626°C, w.q.
(Letters refer to positions on Figure 19)

G

7.5 w/o Nb

19,668

500X

A

25 w/o Nb, 1.5 w/o Zr

19,663

500X

B

25 w/o Nb, 4.5 w/o Zr

19,664

500X

C

25 w/o Nb, 7.5 w/o Zr

19,665

500X

Figure 20. Continued

D

10.5 w/o Nb

19,660

500X

E

10.5 w/o Nb, 2 w/o Zr

19,661

500X

F

10.5 w/o Nb, 4 w/o Zr

19,662

500X

G

7 w/o Nb, 10 w/o Zr

19,671

500X

Figure 20. Continued

K 6 w/o Nb, 2 w/o Zr

19,666

500X

L 6 w/o Nb, 4 w/o Zr

19,667

500X

H 8 w/o Nb, 2 w/o Zr

19,669

500X

J 8 w/o Nb, 4 w/o Zr

19,670

500X

FIGURE 21
ISOTHERMAL SECTION AT 621 °C.

Figure 22. Microstructures after 65 Hours at 621°C, w.q.
(Letters refer to positions on Figure 21)

Figure 22. Continued

Vertical Sections

For demonstrating the sequence of phase changes in any given alloy a vertical section through the ternary space model is most useful. Figure 24 shows the position of the vertical sections through the space model, and the vertical sections are shown in Figures 25 through 33. The strong effect of niobium in depressing the temperature at which gamma is stable is particularly evident from the vertical sections at constant zirconium content. Figure 33 is a specialized vertical section, drawn so that the alloy content is always in the ratio of five parts by weight zirconium to $1\frac{1}{2}$ parts niobium. The fact that this vertical section originates at the pure uranium corner, where solid solubility in α and β uranium is negligible, and passes through a two-phase region, means that the section lies on a conode. Therefore, the law of levers can be applied in Figure 33 in order to calculate the quantity and composition of the alpha and gamma phases. Of course the law of levers may not be applied to any of the other vertical sections, as the others do not lie on conodes. The 20 w/o Zr vertical section and the photomicrographs which verify it are given in the section on $\beta + \gamma$ phases.

The Gamma Phases

Miscibility gaps. By gamma phases are meant both the unbroken series of solid body-centered cubic solutions existing at high temperatures, and the γ_1 , γ_2 , and γ_3 phases existing within the miscibility gaps. The various gamma phases vary widely in their ability to be retained, i.e., in the critical transformation rate. All appear quite similar metallographically, and are all cubic with the exception of a narrow composition range in which a tetragonal structure appears.

The $\gamma_1 + \gamma_2$ miscibility gap closes with addition of niobium until a critical point is reached. The line leading from γ_1 and γ_2 to the critical point is designated a monotectoid valley and is not isothermal. The projection of the monotectoid valleys, both for $\gamma_1 + \gamma_2$ and $\gamma_1 + \gamma_3$, onto the base plane is shown in Figure 34.

The lower bounding surface of the single γ region is shown by a series of isothermal lines in Figure 34. At 610°C the gamma surface was still descending with increasing amounts of zirconium and niobium. It is assumed that the gamma which is stable at 610°C (20 w/o Zr, 10 w/o Nb) forms a continuous series of solid solutions with the niobium-rich gamma which is stable at room temperature; that is to say, addition of sufficient niobium stabilizes the gamma phase in much of the ternary system to room temperature or below.

The existence of the monotectoid valley near the uranium-niobium binary system is shown by X-ray diffraction and metallography. Specimens of the 10.5 w/o Nb, 10 w/o Nb + 2 w/o Zr, and 10 w/o Nb + 4 w/o Zr alloys

Figure 24 Location Of Vertical Sections Through The Ternary Diagram

Figure 25 Vertical Section at 1 w/o Nb

Figure 26 Vertical Section at 2 w/o Nb

Figure 27 Vertical Section at 7 w/o Nb

Figure 28 Vertical Section at 25 w/o Nb

Figure 29 Vertical Section at 2 w/o Zr

Figure 30 Vertical Section at 4 w/o Zr

Figure 31 Vertical Section at 6 w/o Zr

Figure 32 Vertical Section at 20 w/o Zr

Figure 33 Vertical Section with Zr: Nb ratio of 5:1½

were prepared by interrupting the quench from 800°C at 639°C for 26 hours. The X-ray diffraction patterns reproduced in Figure 35 show two body-centered cubic gamma phases in the 10.5 w/o Nb alloy. The stronger pattern is that of the uranium-rich γ_1 with a lattice parameter of 3.446 Å. The weaker pattern is that of the niobium-rich γ_3 , with a lattice parameter of 3.35 Å. At room temperature γ_3 is stable and γ_1 is metastable. The transformation of γ_1 to its equilibrium products, $\alpha + \gamma_3$, is so sluggish in the 10.5 w/o Nb alloy that a mild quench will retain the γ_1 in a metastable condition for room-temperature examination.

The diffraction patterns of the 10 w/o Nb + 2 w/o Zr and 10 w/o Nb + 4 w/o Zr alloys show only the uranium-rich γ_1 ; there is no trace of γ_3 . From these data it is concluded that the monotectoid valley which originates at 634°C passes between the 10.5 w/o Nb and the 10 w/o Nb + 2 w/o Zr alloys at 638°C. The course of the monotectoid valley can also be derived from the course of the $(\alpha + \gamma)/\gamma$ line, which is discussed in some detail in the section on $\alpha + \gamma$ phases.

The microstructure of the control specimens which accompanied the three X-ray specimens discussed above, is shown in Figure 36. Only one gamma phase is visible in the two ternary alloys. The structure of the 10.5 w/o Nb binary alloy, while difficult to interpret, appears to be two-phase.

A monotectoid valley also originates in the uranium-zirconium system at 693°C and descends toward a critical point. Evidence for such a construction is largely metallographic, due to inability to retain the uranium-rich γ_1 at room temperature for examination by X-ray diffraction. According to Summers-Smith⁽³⁾ the γ_1 cannot be retained but undergoes a transformation on quenching, while the zirconium-rich γ_2 can be retained in a metastable state by a drastic quench. In the present investigation, numerous specimens were quenched from the range 700° to 710°C, which should be within the $\gamma_1 + \gamma_2$ region. Metallographic evidence of $\gamma_1 + \gamma_2$ was found only in the 80 w/o U + 20 w/o Zr binary alloy and in the 20 w/o Zr + 0.4 w/o Nb + 79.6 w/o U ternary alloy. Ternary alloys containing 20 w/o Zr with 0.8 w/o and 1.5 w/o Nb, respectively, appeared to consist of one gamma phase.

X-ray diffraction patterns from needles quenched from 708°C show a mixed $\gamma + \alpha$ U pattern in the 20 w/o Zr binary and the 20 w/o Zr + 0.8 w/o Nb, 20 w/o Zr + 1.5 w/o Nb ternary alloys, but a clear γ pattern in an alloy of 20 w/o Zr + 4 w/o Nb. In the patterns showing both γ and α U, the γ lines were too fuzzy to permit an accurate parameter calculation, which in turn would have led to identification of the pattern as either γ_1 or γ_2 . Diffraction patterns for the above four alloys are reproduced in Figure 37.

Figure 35. X-Ray Diffraction Patterns of Three Gamma Phase Specimens

<u>Pattern</u>	<u>Specimen</u>	<u>Heat Treatment</u>
a	U - 10.5 w/o Nb	1-1/2 hours 800°C + 26 hours 638°C, w.q.
b	U - 10.5 w/o Nb, 2 w/o Zr	Same
c	U - 10.5 w/o Nb, 4 w/o Zr	2 hours 800°C + 72 hours 642°C, w.q.

Figure 36. Microstructures of the Control Specimens For Fig. 35

Figure 37. X-Ray Diffraction Patterns Showing Effect of Niobium on Retention of Metastable Gamma

It is concluded from the above evidence that the $\gamma_1 + \gamma_2$ region is small and is merged into a single gamma with amounts of niobium between 0.4 and 0.8 w/o.

Microstructure. Microstructures of four typical gamma alloys are shown in Figure 38. The martensitic structure shown for the 2 w/o Nb + 2 w/o Zr alloy is a result of a diffusionless transformation which occurs during the quench.⁽¹⁰⁾ A very similar structure has been reported in a uranium-titanium alloy containing 10 w/o Ti⁽⁶⁾ and also in the indium-thallium system.⁽⁷⁾ Unpublished work on the uranium-molybdenum system demonstrates the presence of the martensitic structure in uranium-rich alloys.⁽⁸⁾ In the present investigation, the martensitic structure was found both in binary uranium-niobium and uranium-zirconium alloys as well as in many ternary uranium-niobium-zirconium alloys. It is concluded that the martensitic structure is to be expected in any uranium alloy in which the gamma phase can dissolve sufficient solute to slow down its critical transformation rate, but which does not contain enough solute to permit retention of metastable gamma. An example of the latter structure is also shown in Figure 38 for an alloy of 40 w/o Zr + 10 w/o Nb. The remaining two photomicrographs of Figure 38 show alloys within the $\gamma_1 + \gamma_2$ and $\gamma_1 + \gamma_3$ miscibility gaps. In the $\gamma_1 + \gamma_2$ miscibility gap both gamma phases appear to be retained, but X-ray diffraction shows that one, probably γ_1 , has transformed to alpha uranium.

Lattice parameters of the gamma phases. The lattice parameters of the uranium-niobium-zirconium ternary system are shown in Figure 39. The lattice parameters of the uranium-niobium and niobium-zirconium systems are taken from published reports^(5,9) by the Ames Laboratory. The lattice parameters of the uranium-zirconium system are taken from unpublished work at Argonne National Laboratory.

In the present investigation various ternary alloy specimens were quenched from 800°C for parameter measurements. The measured values are shown on Figure 39, as well as a family of isoparametric lines drawn to conform to the data. These isoparametric lines are of particular usefulness in identifying the two gamma phases which occur in the $\gamma_1 + \gamma_3$ miscibility gap, originating in the uranium-niobium binary system.

It should be noted that the effect of each of the two solutes, zirconium and niobium, counteracts that of the other on the lattice parameter of gamma uranium. The theoretical significance of this fact is described in Section VI.

Body-centered tetragonal gamma phase. The body-centered tetragonal structure which was reported in Section III for the uranium-niobium binary system (6 to 9 w/o Nb) was also found in four ternary uranium-niobium-zirconium alloys with the following compositions: 4 w/o Nb-6 w/o Zr, 6 w/o Nb-2 w/o Zr, 6 w/o Nb-4 w/o Zr and 7 w/o Nb-10 w/o Zr.

Figure 38. Microstructure of Four Alloys Quenched from the Gamma Range

FIGURE 39
LINES OF CONSTANT LATTICE
PARAMETER OF THE GAMMA
PHASE IN THE U-Zr-Nb SYSTEM

FIGURE 40
RANGE OF EXISTENCE OF THE
BODY CENTERED TETRAGONAL
GAMMA PHASE AFTER QUENCHING
FROM 900°C

As shown in Figure 40, these compositions lie in a band which parallels the borderline between those compositions in which metastable gamma can be retained and those in which a martensitic-type transformation prevails. The body-centered tetragonal structure may be explained as an ordered structure based upon the 7.5 w/o Nb binary alloy, and permitting substitution of zirconium atoms for uranium up to approximately 10 w/o (24 a/o) Zr. It is known that increasing amounts of niobium greatly retard the transformation of the gamma phase. It may be that on quenching alloys with increasing niobium content, there is first a range of compositions in which the martensitic transformation may occur; secondly, a range in which the Nb atoms may assume preferred positions on the body-centered cubic lattice; and thirdly, a range where atom movement is too slow for any change to occur. The body-centered tetragonal structure would then be the product of lattice strain caused by the presence of the smaller niobium atoms in some ordered lattice site.

It was also noted that all four of the ternary alloys in which the tetragonal structure was found were quenched from a temperature 13°C or less above that temperature at which the $\gamma \rightarrow \alpha + \gamma$ transformation would have started.

The $\beta + \gamma$ Region

The $\beta + \gamma$ region is one of the smaller state spaces of the uranium-niobium-zirconium ternary system. The uncertainty as to the extent of the $\beta + \gamma$ region in the uranium-zirconium system introduces some uncertainty as to its range in the uranium-niobium-zirconium ternary system. However, it appears definite that 4 w/o Nb or less will eliminate the $\beta + \gamma$ region, and therefore the uncertainty as to its range extends to only a small portion of the ternary system. The $\beta + \gamma$ region is the major point of difference between the uranium-zirconium diagrams reported by D. Summers-Smith⁽³⁾ and by Rough et al.⁽⁴⁾ As mentioned earlier, the present investigation assumes the construction of Summers-Smith to be correct.

The evidence for the $\beta + \gamma$ region as shown is indirect, as in none of the X-ray specimens has there been any indication of retained β . Furthermore, the low niobium content of the $\beta + \gamma$ alloys makes retention of γ very dependent upon the quenching rate, with the result that γ usually transforms to α during the quench. Metallographically it is quite simple to trace the lower bounding surface of the γ phase, but difficult to distinguish between the $\beta + \gamma$ and $\alpha + \gamma$ regions. Typical microstructures for four alloys which were $\beta + \gamma$ at the transformation temperature are shown in Figure 41. The martensitic structure in the 2 w/o Zr, 1 w/o Nb alloy identifies the phase which was γ_1 and the white phase was β , although at room temperature both are α . A precise determination of the uranium-niobium binary system revealed a distinct change of slope between the $(\beta + \gamma)/\gamma$ and $(\alpha + \gamma)/\gamma$ lines at 668°C, the temperature of the α to β transformation. Similarly in the

Figure 41. Microstructures of Four Alloys Quenched from the $\beta + \gamma$ Range

uranium-zirconium binary as reported by D. Summers-Smith,⁽³⁾ a slight change of slope exists at the $\alpha \rightarrow \beta$ temperature. The change of slope must exist in the ternary alloys as well. It happened that no experimental alloys were at the right composition to demonstrate the change of slope in the ternary alloys.

The evidence for the $\beta + \gamma$ field is principally the shape of the lowered bounding surface of the γ phase; hence these data are presented in some detail in the form of a vertical section. The vertical section at the 20 w/o Zr level is shown in Figure 42, and the photomicrographs corresponding to the experimental points (again designated by letters) are shown in Figure 43.

The $\alpha + \gamma$ Region

The $\alpha + \gamma$ region occupies a large volume of the uranium-niobium-zirconium ternary phase diagram. Its origins are the β to α transformations, 668°C in the uranium-niobium and 663°C in the uranium-zirconium binary systems. As the δ phase does not form above approximately 606°C, all transformations between 606°C and 663°C are of the type $\gamma \rightleftharpoons \alpha + \gamma$, or essentially a rejection of alpha from gamma. With increasing Zr content, gamma U becomes stable at lower temperatures until the δ phase is formed at 606°C. In contrast, with increasing niobium content γ uranium eventually becomes stable at room temperature. The present investigation shows that 10 w/o Nb eliminates the δ phase, and that further increases in niobium content in the presence of zirconium stabilize the γ phase to lower temperatures.

Metallography. As the rejection of α from γ is unmistakable by metallographic examination, a major effort was made to locate the $\gamma \rightleftharpoons \alpha + \gamma$ temperature for all of the alloys involved in this investigation which lie outside the $\beta + \gamma$ and $\delta + \gamma$ ranges. The evidence is presented in the form of isothermal sections which are substantiated with photomicrographs for two sections. All specimens for a given isothermal section were heat treated together in the same evacuated Vycor capsule to insure uniformity of temperature. This technique is necessary due to the flatness of the $(\alpha + \gamma)/\gamma$ surface, which means that a small error in temperature involves a relatively large error in the position of the phase boundaries. It is believed that the temperature reported for the various isothermal sections is correct to within $\pm 1^\circ\text{C}$.

As mentioned earlier, the course of the $(\alpha + \gamma)/\gamma$ line is related to the monotectoid valley which bounds the $\gamma_1 + \gamma_3$ miscibility gap. Referring to Figure 18, it is seen that the $(\alpha + \gamma)/\gamma_1$ line intersects the $(\alpha + \gamma_1 + \gamma_3)/(\alpha + \gamma_1)$ line on the monotectoid valley; hence determination of the intersection point of the above-mentioned lines gives a point on the valley. It happens that the microstructure of $\alpha + \gamma_3$ is characteristically

FIGURE 42. VERTICAL SECTION AT 20 w/o Zr

Figure 43. Microstructures of Six Specimens on the 20 w/o Zr Vertical Section
(Letters Refer to Positions on Figure 42)

A 676°C 0.8 w/o Nb, 20 w/o Zr

19,698

500X

C 670°C 20 w/o Zr, 1.5 w/o Nb

19,696

500X

B 670°C 20 w/o Zr, 0.8 w/o Nb

19,695

500X

F 654°C 20 w/o Zr, 1.5 w/o Nb

19,693

500X

D 654°C 20 w/o Zr

19,691

500X

E 654°C 20 w/o Zr, 0.8 w/o Nb

19,692

500X

lamellar, while that of $\alpha + \gamma_1$ is never lamellar. Thus the presence of a small amount of lamellar structure indicates that the $\alpha + \gamma_1 + \gamma_3$ field has been entered. This point is illustrated in the isothermal section at 626°C, Figure 19, in which the alloys of 6 w/o Nb + 2 w/o Zr, 8 w/o Nb + 2 w/o Zr, 10.5 w/o Nb + 2 w/o Zr lie within the $\alpha + \gamma_1 + \gamma_3$ region and exhibit a mixture of lamellar and non-lamellar $\alpha + \gamma$, as shown in Figure 20. In contrast, Figure 18 shows the isothermal section at 630° to 632°C. The microstructure of the three above-mentioned alloys at 630°C to 632°C (not included in the report) shows no trace of lamellar structure. Hence it is concluded that the presence of lamellar $\alpha + \gamma$ is a fairly sensitive and reliable index to the presence of γ_3 . Over 82 specimens were examined in order to delineate the phase boundaries near the $\gamma_1 + \gamma_3$ monotectoid valley. The data are shown for brevity in Table I. Greatest weight in drawing the phase diagram was given to the runs at 626°C for 19 days and at 630°C for 14 days, as it became apparent that equilibrium was not reached in some of the shorter runs. All runs confirmed the lamellar nature of $\alpha + \gamma_3$ and the non-lamellar nature of $\alpha + \gamma_1$.

It was not considered practical to use X-ray diffraction in the $\alpha + \gamma_1 + \gamma_3$ field since there is a coincidence of line position between the relatively few weak lines of the γ_3 pattern and the strong lines of the complex α uranium pattern. Therefore the identification of γ_3 in the presence of α and γ_1 was considered uncertain by this method.

Below the $\gamma_1 + \gamma_3$ critical point the microstructure of the $\alpha + \gamma_{1,3}$ region becomes lamellar, as is shown in Figure 22, which illustrates the microstructures at 621°C of 8 alloys. The increased amount of γ in the 10.5 w/o Nb + 4 w/o Zr alloy is evidence that this composition lies closest to the γ field.

Insufficient alloys were examined to permit tracing the $(\alpha + \gamma)/\gamma$ line definitely at temperatures below 621°C. However, an alloy of 20 w/o Zr + 10 w/o Nb rejects α at 595°C, as shown in the 20 w/o Zr vertical section, Figure 42. From the 20 w/o Zr vertical section the $\gamma/\alpha + \gamma$ line appears to fall quite steeply with increasing Nb.

Electrical resistivity. The electrical resistivity at room temperature was measured for three ternary alloys after various high-temperature isothermal treatments. The alloys contained 2 w/o Nb + 1 w/o Zr, 2 w/o Nb + 4 w/o Zr and 2 w/o Nb + 8 w/o Zr, respectively. The isothermal treatment consisted of heating the capsule containing the resistivity specimens to 800°C for 1 hour, transferring it quickly to another furnace at some temperature between 590° and 720°C, holding for 24 hours, then water quenching. The experimentally measured resistivities are shown in Figure 44 as a function of temperature. The shapes of the curves indicate that the high and low-temperature ends of the curve, little or no

Table I

MICROSTRUCTURAL FEATURES OF SPECIMENS ISOTHERMALLY TRANSFORMED BETWEEN 619°C and 638°C

Time	Temperature by		6 Nb 2 Zr	6 Nb 4 Zr	7.5 Nb	8 Nb 2 Zr	8 Nb 4 Zr	10.5 Nb	10 Nb 2 Zr	10 Nb 4 Zr	7 Nb 10 Zr	4 Nb 20 Zr	7 Nb 20 Zr	25 Nb 1-1/2 Zr	25 Nb 4-1/2 Zr	25 Nb 7-1/2 Zr
	CrAl	PtRh														
65 hrs	621°C	621°C	$\alpha + \gamma$	$\alpha + \gamma$	$\alpha + \gamma$	$\alpha + \gamma$	$\alpha + \gamma$	$\alpha + \gamma$	$\alpha + \gamma$	$\alpha + \gamma$						
162 hrs	619-624	622-626	Pearlite + primary α ?	2 phase pearlitic patches	Fine particles	Pearlite + γ	5-10% α in γ	Fine Pearlite	5% Pearlite in γ	1-2% α in γ or all γ						
144 hrs	625-626		40% α in γ	20% α in γ	Pearlite	5% α in γ	5% α in γ	Pearlite	1% α in γ	1% α in γ	1% α in γ		Trace of α in γ			
42 hrs	625?		Pearlite + $\alpha + \gamma$ (20% α)	15% α in γ	Pearlite	1% pearlite in γ	1% α in γ	95% Pearlite + 5% γ	γ	γ	2% α in γ					
65 hrs	627-628	624-626	30% α in γ	25% α in γ	Pearlite	1% α in γ	1% α in γ	99% Pearlite	1% α in γ	γ						
44 hrs	630-631	627-628	15% α in γ	10% α in γ	99% Pearlite	γ	γ	15% Pearlite 85% γ	γ	γ						
19 days	626-630		35% α in γ	35% α in γ	Pearlite	10% α + Pearlite in γ	3% α in γ	Pearlite	6% α in γ	5% α in γ	15% α in γ		γ	All Pearlite	1% Pearlite in γ	γ
68 hrs	630-635	634	25% α in γ	20% α in γ	Pearlite	1% α in γ	1% α in γ	Pearlite	γ	γ						
143 hrs	630-632		20% α in γ	10% α in γ	Pearlite	1% α in γ	Trace α in γ	Pearlite		50% α in γ	γ		γ			
167 hrs	625-637	622-631	$\alpha + \gamma$	α Network in γ boundary	Pearlite	5% α patches of Pearlite	10% α in γ	Pearlite	1% α in γ	Almost all γ						
14 days		630-632 (new std)	α in γ	α in γ	Pearlite	α in γ	α in γ	Pearlite	γ	γ	α in γ	α in γ	α in γ			
69 hrs	637-638		1% α	1% α in γ	2% α				γ							
26 hrs	638							γ	γ	γ						

change in quantity of phases present with temperature occurred. In the central temperature range, the relatively flat part of the curve indicates a considerable change in quantity of phase present with a change in temperature.

Figure 44. Electrical Resistivity at Room Temperature vs Isothermal Transformation Temperature.

18,410

The above interpretation was confirmed and expanded by the phase diagram as developed by metallographic examination. From the equilibrium isothermal sections of the phase diagram the percentage of gamma phase can be calculated by the law of levers, because a line through the pure uranium corner and through the point representing an experimental alloy lies on a conode. A plot of the calculated gamma percentage vs transformation temperature is shown in Figure 45 for the three ternary alloys discussed above. These three curves are quite similar in shape to the experimentally determined curve of room-temperature resistivity vs isothermal transformation temperature (Figure 44). Considering the 8 w/o Zr, 2 w/o Nb alloy, it appears that the high resistivity when quenched from above 674°C was due to a 100% martensitic structure, which had been 100%

FIGURE 45
ISOTHERMAL TRANSFORMATION TEMPERATURE VS
PER CENT EQUILIBRIUM GAMMA PHASE

gamma at the transformation temperature. As the percentage of beta or alpha increased (percentage of gamma decreased) at lower transformation temperatures the resistivity decreased. From 640°C down, both the resistivity curve and the percentage of gamma curve become more nearly vertical, indicating little change in relative quantities of the two phases at lower temperatures.

A similar analysis of the data for the 2 w/o Nb, 1 w/o Zr and 2 w/o Nb, 4 w/o Zr alloys shows that the resistivity curve correlates well with the phase diagram. Comparison of the three resistivity curves with each other indicates a marked increase in resistivity of both martensite and metastable gamma with increasing zirconium content.

The Delta or UZr_3 Phase

The delta phase has been reported in the uranium-zirconium binary system by many investigators. It is generally believed to have a range of stability roughly between UZr_2 and UZr_3 . From the observation that the lattice parameter of delta, when considered as cubic, is close to three times that of a gamma UZr_3 alloy, some investigators believe that delta is the product of an ordering transformation.

The present investigation is concerned only with the relation of the binary delta phase to the ternary phase diagram. Five ternary alloys were investigated, four of which contained δ after proper heat treatment. The isothermal section at 500°C, shown in Figure 46, was drawn from the summarized data obtained from 13 X-ray diffraction patterns (Table II). As δ is formed at 606°C in the U-Zr system, the isothermal section at 500°C is well within the temperature range of δ stability.

X-ray diffraction patterns were also taken on several of the same alloys after transforming at 470°C to 480°C. The data from the latter specimens indicate that the γ field contracts towards the niobium corner with decreasing temperature, with an accompanying expansion of the $\delta + \gamma$ field. The limit of the γ field at room temperature was not determined, but is thought to be less than 20 w/o Nb.

It was noted that a faint but definite α Zr pattern appeared repeatedly on diffraction patterns of alloys containing 20 w/o Zr to approximately 50 w/o Zr and quenched from temperatures ranging from 1000° to 480°C. The presence of α Zr as a stable phase could not be reconciled with the microstructure, or with the other phases which were definitely present. Its presence may be due to reaction with a gas such as nitrogen or oxygen thus forming a quaternary in which α Zr solid solution is one of the stable phases.

FIGURE 46 ISOTHERMAL SECTION AT 500°C

Table II

X-RAY DIFFRACTION DATA FOR ISOTHERMALLY
TRANSFORMED SPECIMENS LYING CLOSE TO THE δ UZr₃ PHASE REGION

Composition, w/o			Heat Treatment		X-Ray No.	Results
U	Zr	Nb	Temperature	Time		
50	40	10	1015°C	24 hr, w. q.	4835	γ 3.46 + α Zr
50	40	10	500°C	2 weeks, w. q.	5082	γ , 3.519 vsl. α Zr
50	40	10	470°C	2 weeks, w. q.	5082	γ , 3.523 vsl. α Zr
50	40	10	449°C	1 week, w. q.	4794	γ , 3.524 + sl. α Zr
51	47	2	476°C	78 hrs. w. q.	5068	δ + Zr ? or γ ?
49	47	4	500°C	2 weeks, w. q.	5145	δ , γ + α Zr + α U ?
49	47	4	480°C	3 weeks, w. q.	5147	δ , vsl. γ
46	47	7	500°C	2 weeks, w. q.	5146	δ , γ + vsl α Zr
46	48	7	480°C	3 weeks, w. q.	5148	δ , γ , vsl. α Zr
23	70	7	710°C	94 hrs., w. q.	5150	γ + α Zr
23	70	7	627°C	19 days, w. q.	5151	γ + α Zr
23	70	7	500°C	10 days, w. q.	5161	γ + α Zr
23	70	7	470°C	10 days, w. q.	5162	γ + δ + α Zr

RELATION OF IRRADIATION DATA TO PHASE DIAGRAM

Before the uranium-niobium-zirconium phase diagram was developed, a need arose for information concerning the effect of heat treatment on corrosion resistance and on irradiation stability. This problem was restricted to a ternary alloy containing 5 w/o Zr and $1\frac{1}{2}$ w/o Nb. It was found, by trial and error experimentation, that specimens quenched from the gamma range to give a martensitic, or supersaturated alpha, structure exhibited good corrosion resistance but grew excessively under irradiation. The corrosion resistance of the alloy to high temperature aqueous media is discussed in a separate topical report.⁽¹⁴⁾ The above-mentioned experimental work revealed that specimens transformed between 620° and 650°C exhibited minimum irradiation growth. It is the purpose of this section to correlate the empirical findings with the ternary phase diagram.

It happens that the irradiation specimens on which the above conclusions were drawn were not in equilibrium at the temperature at which they were irradiated. Some had not reached equilibrium at the temperature of heat treatment due to insufficient time. It is necessary to consider the structure of the irradiation specimens in relation to both the equilibrium diagram and to the TTT curve for the particular alloy (5 w/o Zr, $1\frac{1}{2}$ w/o Nb). In addition, the question of metastable gamma retention vs a martensitic-type gamma transformation affects the microstructure and presumably also the irradiation stability.

The transformation kinetics of the uranium-niobium-zirconium alloys are covered in detail in a separate report,⁽¹⁰⁾ from which Figures 47 and 48 are taken. The irradiation data are discussed by J. H. Kittel and S. H. Paine.⁽¹⁵⁾

It had been determined earlier that, under conditions of continuous cooling from the gamma range to room temperature, the resultant hardness is dependent upon the temperature at which the gamma phase began to transform. This dependence is shown in Figure 47. In the case of the irradiation specimens which were continuously cooled, the transformation temperature, which was not measured directly, can be deduced by taking the temperature from Figure 47 which corresponds to the measured hardness (before irradiation). These irradiation specimens which were isothermally transformed, of course, have a measured transformation temperature, though it is necessary to refer to the TTT curve, Figure 48, to be sure that sufficient time was allowed for transformation to occur.

In Figure 49, the transformation temperature (for both continuously cooled and isothermally transformed specimens) is plotted against G_i , the irradiation growth rate, in microinches/inch/ppm burnup. It is apparent that 20 of the 24 available data points fall within the shaded band. Of the four which do not, two can be explained. Of the remaining two, one lies close to the band, leaving only one real exception.

FIGURE 47

HARDNESS VS. TRANSFORMATION TEMPERATURE FOR SWAGED 5 w/o Zr-1 $\frac{1}{2}$ w/o Nb
SPECIMENS CONTINUOUSLY COOLED FROM THE GAMMA RANGE

Figure 49. Irradiation Growth of 5 w/o Zr - $1\frac{1}{2}$ w/o Nb Alloy

The plot of irradiation growth rate vs transformation temperature (Figure 49) shows that specimens quenched from the gamma range (i.e., those which transformed at 450°C, as determined by a thermal arrest) have a large irradiation growth rate and that specimens quenched from 620°C to 650°C have a low irradiation growth rate, although some scatter exists. No data exist for temperatures between 650°C and 677°C, which is unfortunate in that the β and γ field is present from 677°C to 663°C. However, the microstructure is shown in Figure 50 for four temperatures in this range. The irradiation stability of specimens transformed in the $\beta + \gamma$ field is thus totally unknown. Though irradiation data is lacking from $\beta + \gamma$ alloys, it is known that alloys quenched from 650° to 677°C consist at room temperature of alpha particles (originally beta) in a martensite matrix. In view of the known large irradiation growth of martensite, it is a logical assumption that the irradiation growth of a specimen decreases as the proportion of martensite decreases. The shaded band in Figure 49 is drawn to include most of the experimentally determined points for 5 w/o Zr, $1\frac{1}{2}$ w/o Nb alloy specimens.

The shaded band in Figure 49 demonstrates that a low irradiation growth rate can be obtained by transforming from 620° to 650°C under the conditions of this experiment (i.e., swaged 5 w/o Zr - $1\frac{1}{2}$ w/o Nb rods, with 0.044 to 0.048% indicated burnup). It is of interest to attempt to discover the factors underlying this favorable growth rate. The most obvious explanation is that the microstructure consists of alpha particles in a gamma matrix, and the growth of the alpha particles is absorbed to some extent by the more plastic gamma phase. This explanation requires the presence of alpha and gamma and the following argument is presented in support of this explanation.

In Figure 33 there is shown a vertical section which passes through the 5 w/o Zr - $1\frac{1}{2}$ w/o Nb alloy and also lies on a conode, due to its origin at the α uranium corner. The law of levers can be applied to this vertical section and by such an application the percentage of gamma phase at eight temperatures was calculated, assuming equilibrium conditions. The solid line in Figure 49 shows the per cent of gamma as a function of transformation temperature on the same scale as the irradiation growth rate. The point to be made from Figure 49 is that the temperature of minimum irradiation growth corresponds roughly with the temperature of maximum change of slope in the per cent gamma curve. That is to say, a transformation temperature from 650° to 620°C results in a large improvement in irradiation stability and a large quantity of alpha present, whereas temperatures below 620°C result in a worsening of irradiation stability and in only a small further increase in quantity of alpha. It is to be noted that quantity of alpha equals 100 minus the quantity of gamma, the latter quantity being the parameter which is plotted in Figure 49.

Figure 50. Microstructures of Isothermally Transformed 5 w/o Zr - 1-1/2 w/o Nb Alloy

18 hrs. 658°C

19,367

500X

24 hrs. 664°C

19,368

500X

67 hrs. 668°C

19,369

500X

22 hrs. 672°C

19,370

500X

As the transformation temperature is lowered, the rejection of larger amounts of alpha continues. Because alpha can contain less than 1/2 w/o of either zirconium or niobium, the remaining gamma must become enriched in zirconium and niobium. Therefore, at some transformation temperature, gamma enrichment will reach the point where the martensitic transformation can no longer occur, and the gamma will be retained at room temperature in a metastable state. The temperature at which this occurs can be approximated as follows. Experimentally, it was found that the dashed band in Figure 51 divided the uranium-niobium-zirconium system into two parts, i.e., compositions above the line could be retained as metastable gamma by a drastic quench of a small specimen; compositions below the band would always transform during the quench. The experiments referred to were by water quenching small specimens from 800° to 900°C, at which temperature the structure was all gamma.

Referring now again to Figure 33, the composition of the gamma can be read as a function of temperature. The gamma composition is plotted on the composition triangle of Figure 51 as the solid line. The intersection of the band and solid lines give the gamma composition and temperature at which niobium and zirconium enrichment permit the gamma to be retained in a metastable state. That is, transformation temperatures below 660°C permit a structure at room temperature of alpha and metastable gamma. This calculation is a rough approximation due to the unknown effect of the restraint imposed by the alpha particles on the gamma to martensite transformation. However, it may be significant that the temperature below which gamma can be retained is approximately the same as the temperature of minimum irradiation growth. The tentative conclusion to be drawn from the above argument is that either the dispersion of alpha in a gamma matrix existing at 620°C, or the replacement of martensite by metastable gamma after quenching or perhaps both, is the factor responsible for the low irradiation growth.

Below 620°C, apparently some other effect than that discussed above, is dominant, and is presumed to be the effect of alpha particle size. It may also be true that the effect reported by M. L. Bleiberg et al.⁽¹¹⁾ and S. T. Konobeevsky et al.⁽¹²⁾ also is influential. This effect, stated briefly, was the reversion of a U - 9 w/o Mo alloy from the stable alpha plus epsilon phases to the metastable gamma phase after irradiation at temperatures of 50°C. The small alpha particles formed below 620°C should be more readily reverted by irradiation than a large alpha particle, which may explain the decreasing irradiation stability with decreasing alpha particle size.

FIGURE 51
METASTABLE GAMMA RETENTION
IN QUENCHED SPECIMENS

Note: Alloys above the band may be retained as a metastable gamma phase. Those below may not. The straight line gives the temperatures corresponding to equilibrium composition of the gamma phase in the U-5w/o Zr-1-1/2 w/o Nb alloy.

At any rate, the development of the ternary equilibrium diagram opens the way to a quantitative study of the factors affecting irradiation growth. It is suggested that if the temperature of transition between martensite and metastable gamma occurs consistently at the transformation temperature which gives optimum stability, this fact should be proven by further work. Such a relation would be of theoretical and practical importance.

URANIUM ALLOY THEORY

From the experimentally determined ternary phase diagram several trends are evident which may lead to a fuller understanding of the theory of alloys as applied to uranium.

The Uranium-Zirconium-Niobium Ternary Solid Solution

With additions of either niobium or zirconium to uranium, the high-temperature, body-centered cubic gamma phase becomes stabilized at lower temperatures, down to some limiting temperature at which a monotectoid reaction or compound formation occurs. With the addition of both niobium and zirconium to form a ternary alloy the same stabilizing effect on the gamma phase is noted. The question then arises as to whether the isothermal line joining the limiting gamma compositions of the binary systems will be straight, convex or concave toward the solvent. The work of Hume-Rothery on copper and silver-base ternary alloys illustrated a fundamental principle: that a straight line is the result of a constant electron: atom ratio, but that deviation from a straight line results from lattice distortions introduced by the solute atoms. If the electron: atom ratios of the alloy were the dominant factor, one would expect a straight line. However, in the uranium-niobium-zirconium ternary system the line at 700°C is concave toward the solvent, which is gamma uranium. The $(\beta + \gamma)/\gamma$ line at 700°C is shown in Figure 52.

The explanation for the concave curvature is that advanced by Hume-Rothery,⁽¹³⁾ in which it is considered that the lattice distortion is the dominant factor in fixing the curvature of the line. It happens that niobium decreases the lattice parameter, and zirconium increases the lattice parameter of gamma uranium, that is, the one solute relieves the distortion introduced by the other. The isoparametric plot is shown in Figure 39. Because of this partial compensation the gamma structure is enabled to exist at higher uranium contents (i.e., lower total niobium plus zirconium contents) than when either niobium or zirconium is present alone.

If this theory is correct, it follows that other ternary systems which exhibit similar characteristics should also have a $(\beta + \gamma)/\gamma$ line concave towards the gamma region. Such systems are uranium-zirconium-molybdenum, uranium-titanium-niobium, uranium-titanium-molybdenum.

Figure 52. $\gamma/\beta + \gamma$ Line at 700°C

19843

Breakdown of One Gamma into Two Gamma Phases

The uranium-zirconium, uranium-niobium and niobium-zirconium systems are all examples of systems in which a broad solid solution exists at high temperatures, but at lower temperatures breaks down into two solid solutions, both of which are also body-centered cubic but of different lattice spacing. A more familiar example of the miscibility gap is the aluminum-zinc system, although in the latter system a single face-centered cubic phase breaks down into two face-centered cubic phases.

The uranium-niobium-zirconium system is of particular interest in that relatively small amounts of the third element were found to merge the two body-centered cubic gammas together into a single gamma. In the case of the uranium-zirconium miscibility gap, less than 2 a/o Nb is sufficient to cause the two gamma phases to merge, whereas in the uranium-niobium system less than 15 a/o Zr is sufficient to merge the two gamma phases.

It should be noted that the uranium-zirconium miscibility gap is relatively small, extending over approximately 30 a/o Zr and 40°C in span, and requiring a substitution of only one niobium atom in 25 unit cells (each unit cell contains two atoms) to eliminate the miscibility gap. The potent effect of niobium suggests an electronic effect. However, as each body-centered cubic unit cell is adjacent to 26 others, it is possible that a lattice contraction caused by introducing a niobium atom into one unit cell could relieve strains sufficiently in the 26 adjacent unit cells to permit formation of a single gamma.

The miscibility gap in the uranium-niobium system is larger than that of the uranium-zirconium system, the former ranging over approximately 60 a/o Nb and 170°C. The 15 a/o Zr which is required to close the uranium-niobium miscibility gap requires a substitution of a zirconium atom in every six uranium-niobium atoms or in every third unit cell. The significant observation is that the introduction of one solute which relieves the lattice distortion caused by the other solute causes the closing of the miscibility gap. This is true both for a solute (niobium) which shrinks the expanded uranium-zirconium lattice and a solute (zirconium) which expands the contracted uranium-niobium lattice.

If the above explanation is correct, it follows that molybdenum should also close the miscibility gap in the uranium-zirconium system, because molybdenum counteracts the lattice expansion due to zirconium. Molybdenum should be ineffective in closing the miscibility gap in the uranium-niobium system because it would further aggravate the lattice contraction due to niobium. Of course, it may prove that electronic factors play a more important role in the closing of the miscibility gap than can at present be estimated.

ACKNOWLEDGMENTS

The assistance rendered by various members of the Argonne Metallurgy Division is gratefully acknowledged. The project was initiated under the direction of H. H. Chiswik. R. S. Lindberg, R. M. Scott, R. A. Conner, Jr., and H. W. Knott gave valuable help in preparation of metallographic specimens and in taking diffraction patterns.

APPENDIX I. CHEMICAL COMPOSITIONS OF EXPERIMENTAL ALLOYS

Heat No.	Nb w/o	Zr w/o	C ppm	N ppm	O ppm	Cu ppm	Fe ppm	Si ppm	Number of Analyses Averaged
CNY 4	1.50	5.08	116	36	562	8	55	250	
CNY 5	1.97	6.06	122	40	635	9	58	275	4
CNY 6	1.02	4.03	96	43	480	8	47	200	4
CNY 7	1.98	7.96	71	46	761	12	60	200	4
CNY 8	2.03	4.20	125	28	431	6	58	450	4
CNY 9	2.06	2.04	107	52	313	5	45	300	2
CNY 10	.47	----	39	84	56	5	45	200	2
CNY 11	.99	----	100	98	78	5	50	100	2
CNY 12	1.90	----	103	76	145	3	40	100	2
CNY 13	4.08	----	86	100	63	3	35	100	2
CNY 14	4.93	----	185	85	96	3	15	200	2
CNY 24	2.11	1.03	95	24	216	10	95	300	2
CNY 25	1.1	1.02	46	32	134	10	95	70	2
CNY 26	1.07	2.01	60	35	175	10	85	70	2
CNY 27	1.13	2.95	50	10	298	10	100	195	2
CNY 29	1.01	5.81	52	35	619	10	200	120	2
CNY 30	1.06	7.93	148	48	650	10	250	120	2
BMI 1	10.44	----	118	172	N.D.	G1000	27	100	4
BMI 2	7.07	10.01	90	139	N.D.	12	20	65	2
BMI 3	4.03	19.25	85	91	---	70	90	75	2
BMI 4	6.97	20.16	72	133	---	20	50	50	2
BMI 5	10.15	19.86	100	172	---	40	45	35	2
BMI 6	7.12	29.89	78	132	---	40	85	40	2
BMI 7	10.46	39.39	99	139	---	15	65	60	2
BMI 8	7.53	----	35	95	---	50	20	20	1
BMI 9	4.11	1.95	478	83	---	50	30	15	1
BMI 10	6.23	1.96	60	92	---	50	20	20	1
BMI 11	8.54	1.99	65	154	---	50	20	20	1
BMI 12	10.72	1.91	110	158	---	150	20	20	1
BMI 13	4.18	3.95	48	87	---	150	20	20	1
BMI 14	6.33	3.90	81	128	---	500	20	20	1
BMI 15	8.41	3.71	56	666	---	200	20	20	1
BMI 16	10.77	4.07	98	246	---	200	20	20	1
BMI 17	4.14	5.87	121	172	---	500	30	30	1

N.D. - 'No Determination'

BIBLIOGRAPHY

1. H. A. Saller and F. A. Rough, "Compilation of U. S. and U. K. Uranium and Thorium Constitutional Diagrams," BMI-1000 (June 1, 1955).
2. B. Sawyer, "The Uranium-Columbium Alloy System," ANL-4027 (October 1946).
3. D. Summers-Smith, "The Constitution of Uranium-Zirconium Alloys," J. Institute of Metals 83, 277 (1954-55).
4. F. A. Rough, A. E. Austin, A. A. Bauer and J. R. Doig, "The Stability and Range of the Zirconium-Uranium Epsilon Phase," BMI-1092 (May 28, 1956).
5. B. A. Rogers and D. F. Atkins, "Zirconium-Columbium Diagram," J. of Metals, September 1955, p. 1034.
6. A. G. Knapton, "The Systems Uranium-Titanium," J. Institute of Metals, 83, 497 (1954-55).
7. J. S. Bowles, C. S. Barrett and L. Guttman, "Crystallography of Cubic-Tetragonal Transformation in the Indium-Thallium System," J. of Metals, December 1950, p. 1478.
8. E. Scala, "Heat Treatment of a Uranium - 2% Molybdenum Alloy," unpublished.
9. P. Chiotti and O. N. Carlson, "Hanford Slug Program Quarterly Report, January - March, 1955," ISC-609 (June 16, 1955).
10. A. E. Dwight, "Kinetic Transformations in the Uranium-Rich U-Nb and U-Nb-Zr Systems," ANL-5582, to be published.
11. M. L. Bleiberg, L. J. Jones, and B. Lustman, "Phase Changes in Pile-Irradiated Uranium-Base Alloys," WAPD-T-300.
12. S. T. Konobeevsky, N. F. Pravdyuk and V. I. Kutaitsev, International Conference on the Peaceful Uses of Atomic Energy, A/CONF 8/P/681 (1955).
13. W. Hume-Rothery and G. V. Raynor, "The Structure of Metals and Alloys," p. 156, 1954.
14. J. E. Draley, S. Greenberg and W. E. Ruther, "High Temperature Aqueous Corrosion Resistance of Uranium Alloys Containing Minor Additions of Zirconium, Niobium and Tin," ANL-5530 (April, 1957)
15. J. H. Kittel and S. H. Paine, "Effects of Irradiation on the Corrosion-Resistant EBWR Reference Fuel Alloy, U - 5 w/o Zr - $1\frac{1}{2}$ w/o Nb," ANL-5639, to be published.