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# Argonne National Laboratory

A STUDY OF URANIUM-FISSIUM ALLOYS  
CONTAINING TECHNETIUM

by

R. W. Bohl and M. V. Nevitt

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by

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Metallurgy Division

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# A STUDY OF URANIUM-FISSIUM ALLOYS CONTAINING TECHNETIUM

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R. W. Bohl and M. V. Nevitt

## ABSTRACT

The equilibrium microstructures and the kinetics of gamma decomposition of uranium-fissium alloys containing technetium were studied and compared with the characteristics of similar alloys which did not contain technetium. The technetium concentration in the fissium was 12.5 w/o, and the uranium-fissium alloys that were examined contained from 3 w/o to 10 w/o fissium.

The presence of technetium does not result in the presence of any new phases; it produces only minor changes in the phase relationships and in the stability of the gamma-uranium solid solution. Studies of aging behavior and of the structure of slowly cooled alloys indicate that the gamma is slightly more sluggish in its transformation characteristics in the presence of technetium. On this basis, it appears that the property measurements made earlier on uranium-fissium alloys which did not contain technetium can be reliably applied to true fissium alloys.

## INTRODUCTION

In the pyrometallurgical reprocessing of metallic uranium fuel, a majority of the fission product elements are removed from the uranium by volatilization or by selective oxidation and drossing. The free energies of formation of the oxides of certain elements, however, are so close to those of uranium that these elements are not removed. This group of elements, dubbed "fissium" (Fs), consists of Zr, Nb, Mo, Tc, Ru, Rh and Pd. They will accumulate in the fuel during reprocessing in the proportion estimated by Koch<sup>(1)</sup> as:

Zr	1.26 w/o	Ru	33.21 w/o
Nb	0.13 w/o	Rh	0.47 w/o
Mo	43.18 w/o	Pd	3.79 w/o
Tc	12.5 w/o		

Zirconium, although it is not removed by oxidation, can be scavenged from the melt by carbon. Thus, there is a great deal of interest in the properties of uranium-fissium alloys with and without the presence of zirconium.

Zegler and Nevitt<sup>(2)</sup> have completed a comprehensive study of the structure and properties of uranium-fissium alloys. Because of the unavailability of technetium at the time of their work, a synthetic fissium composition was used in which Mo and Ru were substituted for the missing technetium.

Recently, technetium has become obtainable in small quantities, so that alloys having the full complement of fissium elements can be made. The purpose of this investigation was to examine the phase relationships and some of the transformation kinetics of uranium-fissium alloys containing Tc, in order to determine how closely the alloys of Zegler and Nevitt approached the properties of the true fissium alloys. Cast, slowly cooled, annealed, and gamma-treated and aged alloys have been investigated by metallographic, microhardness, and X-ray diffraction techniques, and the results compared with the previous work. The restricted scope of the present study is due to the limited time available to one of the investigators (summer appointment), as well as to the small amount of technetium available for making alloys.

## EXPERIMENTAL PROCEDURE

Alloys were prepared from high-purity uranium (99.98 w/o) and alloying elements which, except for technetium, had a purity of 99.85 w/o or better. The technetium contained 3 w/o of impurities which, it is believed, consisted mainly of oxides. The crude, as-received technetium was melted to produce a bright metallic button and a nonmetallic residue which was removed before making alloys.

The five alloy compositions selected for investigation were: 3 w/o Fs, 5 w/o Fs, 8 w/o Fs, 10 w/o Fs, and 5 w/o Fs-2.25 w/o Zr. All of the studies were carried out with specimens prepared from five 25-gm buttons, one of each alloy composition, which were arc melted on a water-cooled copper hearth in a helium-argon atmosphere. The charges and the intended compositions are given in Table I. No chemical analyses were obtained because analytical procedures for technetium-bearing alloys have not been developed. As can be seen in Table I, which also gives the weights of the cast samples, the changes in weight that occurred upon melting were of the order of several parts per thousand, and therefore the true compositions of the alloys probably do not differ significantly from the intended compositions. Remelting of the buttons six times achieved homogeneity, which was confirmed by density measurements and metallographic examination.

Table I  
AS-CHARGED ANALYSES OF URANIUM-FISSIUM ALLOYS

Melt Number	3095		3096		3097		3098		3099	
	gm	w/o	gm	w/o	gm	w/o	gm	w/o	gm	w/o
Zirconium	0.009	0.036	0.016	0.064	0.025	0.10	0.032	0.128	0.563	2.252
Niobium	0.001	0.004	0.002	0.008	0.003	0.012	0.003	0.012	0.002	0.008
Molybdenum	0.324	1.296	0.540	2.16	0.864	3.456	1.080	4.32	0.540	2.16
Technetium	0.094	0.376	0.156	0.624	0.250	1.00	0.313	1.252	0.156	0.624
Ruthenium	0.249	0.996	0.415	1.66	0.664	2.656	0.830	3.32	0.415	1.66
Rhodium	0.044	0.176	0.074	0.296	0.119	0.476	0.148	0.592	0.074	0.296
Palladium	0.028	0.112	0.047	0.188	0.076	0.304	0.095	0.38	0.047	0.188
Uranium	24.25	97.0	23.75	95.0	23.00	92.0	22.50	90.0	23.20	92.8
Total Fissium	0.749	3.00	1.250	5.00	2.001	8.00	2.501	10.00	1.250	5.00
Total	25.000		25.000		25.000		25.000		25.000	
Weight of Button	25.013		24.994		24.921		24.962		25.001	
Change on Melting	+0.013	+0.05	-0.006	-0.02	-0.079*	-0.32	-0.038	-0.14*	+0.001	+0.004

\*Few droplets ejected on remelting; negligible effect on analysis.

Density measurements were carried out by a carbon tetrachloride-displacement technique on the as-cast buttons and repeated on half buttons after sectioning. The excellent agreement of these values, as reported in Table II, is a good indication of the absence of gross segregation or porosity. Subsequent density determinations with half buttons quenched from a 66-hr homogenizing anneal at 825°C showed insignificant changes from the as-cast values.

Table II  
DENSITY OF CAST AND HOMOGENIZED URANIUM-FISSIUM ALLOYS

Alloy	As-cast Alloys				825°C Homogenized			Change on Homogenization
	Whole Button	Half 'a'	Half 'b'	Avg	Half 'a'	Half 'b'	Avg	
3% Fs	18.379	18.382	18.387	18.383	18.382	18.385	18.384	+0.001
5% Fs	18.034	18.030	18.028	18.031	18.028	18.021	18.024	-0.007
8% Fs	17.680	17.680	17.686	17.682	17.669	17.674	17.672	-0.010
10% Fs	17.458	17.456	17.456	17.456	17.454	17.454	17.454	-0.002
5% Fs - 2.25% Zr	17.524	17.517	17.518	17.520	17.538	17.551	17.545	+0.025

Approximately one-half of each cast sample was retained in the as-cast condition and the remaining half was homogenized in the gamma-uranium range for 66 hr at 825°C and water quenched. All subsequent heat treatments were performed with specimens taken from material in this condition. Equilibrium studies were carried out by long anneals at 700, 650, 600 and 500°C. Aging studies were made at 600, 500 and 375°C. Heat treatments lasting longer than 2 hr were conducted with specimens wrapped in molybdenum foil and sealed in evacuated Vycor capsules. Shorter heat treatments were conducted by wrapping small specimens in foil and attaching them to slender rods which were immersed in lead baths for the required times. The good thermal contact between the specimens and the heating medium and the small size of the specimens

(minimum dimension about 1 mm) insured nearly instantaneous heating and cooling. Careful examination of the heat-treated specimens revealed only a slight superficial oxidation.

Phase identification by X-ray diffraction was carried out with alloys in three different conditions: as cast, slowly cooled, and annealed to establish equilibrium structures at 825, 700, 650, 600 and 500°C. The patterns were obtained from small needle specimens prepared by grinding from the samples which had received a heat treatment. The results of the X-ray identification are given in Table III.

Table III  
IDENTIFICATION OF PHASES BY X-RAY DIFFRACTION

Treatment	Alloy				
	3% Fs	5% Fs	8% Fs	10% Fs	5% Fs-2.25% Zr
As Cast	$\alpha'$	$\gamma$	$\gamma$	$\gamma$	$\alpha' + \text{ZrRu}$
Slow Cooled	$\alpha + \gamma + \text{U}_2\text{Ru}(\text{tr})$	$\alpha + \gamma + \text{U}_2\text{Ru}$	$\gamma + \text{U}_2\text{Ru} + \alpha(\text{tr})$	$\gamma + \text{U}_2\text{Ru}$	$\alpha + \gamma + \text{ZrRu}$
825°C, 66 hr, WQ	$\alpha'$	$\gamma$	$\gamma$	$\gamma$	$\alpha' + \text{ZrRu}$
700°C, 4 days, WQ	$\alpha'$	$\gamma$	$\gamma + \text{U}_2\text{Ru}$	$\gamma + \text{U}_2\text{Ru}$	$\alpha' + \text{ZrRu}$
650°C, 10 days, WQ	$\alpha + \beta + \text{U}_2\text{Ru}$	$\alpha + \gamma + \text{U}_2\text{Ru}$	$\gamma + \text{U}_2\text{Ru}$	$\gamma + \text{U}_2\text{Ru}$	$\alpha + \beta + \text{ZrRu}$
600°C, 20 days, WQ	$\alpha + \gamma + \text{U}_2\text{Ru}$	$\alpha + \gamma + \text{U}_2\text{Ru}$	(no spec)	$\gamma + \text{U}_2\text{Ru}$	$\alpha + \gamma + \text{ZrRu}$
500°C, 30 days, WQ	$\alpha + \delta + \text{U}_2\text{Ru}$	$\alpha + \delta + \text{U}_2\text{Ru}$	$\alpha + \delta + \text{U}_2\text{Ru}$	$\alpha + \delta + \text{U}_2\text{Ru}$	$\alpha + \delta + \text{ZrRu}$

For the metallographic studies the specimens were mounted in Bakelite, ground on SiC abrasive paper through 600 grit, polished on cloth laps charged with diamond through one micron, and finally electropolished and etched in an electrolyte of phosphoric acid, ethylene glycol, and ethyl alcohol in a ratio of 8:5:5. An open-circuit voltage of 25 v was found to give excellent results on all specimens; the polishing time varied from 3 to 30 sec, depending on the structure.

Hardness tests were made with the Bergsman Hardness Tester, which used a 200-gm load and a 136° diamond indenter. Results of the tests (see Tables IV page 14 and Table V page 22) are given as Vickers hardness numbers.

Because of the presence in the alloys of technetium, which is a beta emitter, certain special precautions had to be taken in specimen preparation to avoid contamination of equipment. Operations which were apt to create fine particles, such as sectioning and grinding, were done by hand inside plastic bags. Electrolytes and other solutions were retained for special waste disposal. Otherwise, the alloys were treated in the same manner as other uranium alloys.

### DISCUSSION OF DATA

Interpretation of the microstructures produced in the uranium-fissium alloys was greatly aided by reference to the results of Dwight's study<sup>(3)</sup> of the U-Mo-Ru system. The vertical section through the uranium corner of the ternary system at the Mo:Ru ratio found in fissium, shown in Figure 1, was particularly helpful. Although fissium contains elements besides Mo and Ru, the latter account for the bulk of the fissium content, and no phases other than those reported for the U-Mo-Ru system have been found in the U-Fs alloys.

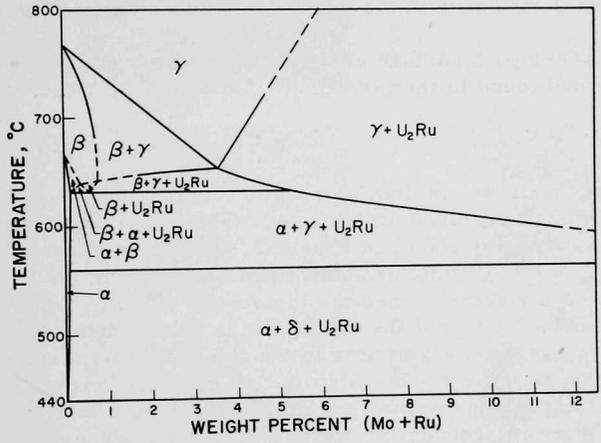


Figure 1  
Vertical Section through Uranium-rich Corner of U-Mo-Ru System at the Mo:Ru Ratio of 1.0:0.8.<sup>(3)</sup> Micro No. 30162.

A short summary of the phases found in these alloys is given below. The compositions and temperature limits of stability of the last three phases have not been established, and undoubtedly some solubility for other fissium elements exists.

Gamma: B.c.c. solid solution based on the gamma phase of elemental uranium. Forms directly from the melt and persists to as low as about 550°C, at which it decomposes eutectoidally. Easily retained by quenching in alloys containing greater than 5 w/o Fs.

Beta: Tetragonal solid solution based on the beta phase of elemental uranium. Forms in alloys containing less than about 5 w/o Fs. Decomposes eutectoidally at about 635°C. Can be retained with difficulty by quenching alloys low in fissium.

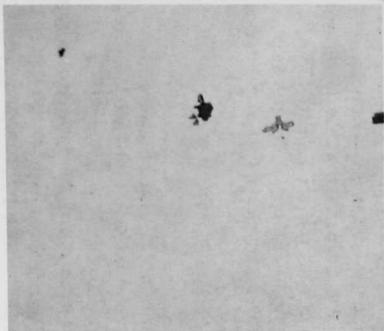
Alpha:	Dilute orthorhombic solid solution based on the alpha phase of elemental uranium. Maximum solubility for fissium is less than 0.25 w/o.
Martensitic alpha ( $\alpha'$ ):	A distorted orthorhombic structure formed by quenching gamma which has less than about 5 w/o fissium.
U <sub>2</sub> Ru:	Monoclinic compound described by Berndt. <sup>(4)</sup>
Delta:	Tetragonal MoSi <sub>2</sub> -type compound isostructural with the delta phase in the uranium-molybdenum system. <sup>(5)</sup>
ZrRu:	CsCl-type structure based on the equiatomic compound found in the zirconium-ruthenium system.

### As-cast Alloys

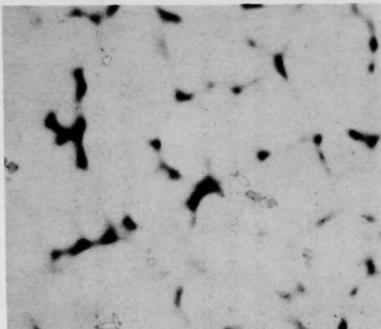
Because the alloys were arc melted on a water-cooled copper hearth, the as-cast structures are those which result from a very rapid cooling rate. Microstructures are shown in Figure 2. All of the alloys begin solidification as the b.c.c. gamma uranium solid solution. In the 3 w/o Fs alloy, the gamma has transformed to martensitic alpha ( $\alpha'$ ) on cooling, and the etchant does not reveal the coring which is undoubtedly present. The fast cooling has retained gamma in the 5 w/o Fs alloy, and coring of the solid solution is evident. The 8% and 10% Fs alloys show increased amounts of coring of the retained gamma, and in both alloys some U<sub>2</sub>Ru has formed in the interdendritic regions where the concentration of Fs is higher.

The abrupt decrease in hardness accompanying the increase in Fs concentration from 3 to 5 w/o (see Table IV) reflects the change in the structure of the matrix, since the gamma phase is much softer than  $\alpha'$ . The 5 w/o, 8 w/o, and 10 w/o Fs alloys progressively increase in hardness due to solid-solution hardening of the retained gamma and the presence of U<sub>2</sub>Ru. The 5 w/o Fs-2.25 w/o Zr alloy behaves similarly to the 3 w/o Fs alloy, since the Zr forms a very stable ZrRu compound and hence effectively robs the matrix of the gamma-stabilizing ruthenium. The matrix in this alloy is again  $\alpha'$ , with the ZrRu appearing as an interdendritic network constituent as well as a fine precipitate rejected from solid solution.

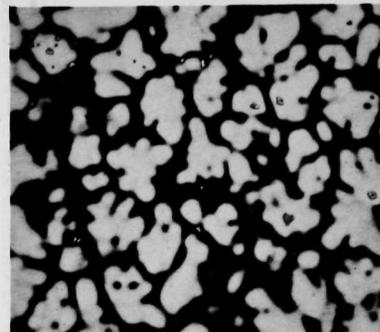
All alloys contained inclusions in the form of a few scattered gray UO<sub>2</sub> particles and an unidentified white phase usually found clustered near or enveloping the UO<sub>2</sub> particles. This phase was also present in the alloys of Ziegler and Nevitt. It is likely that the oxide inclusion was introduced



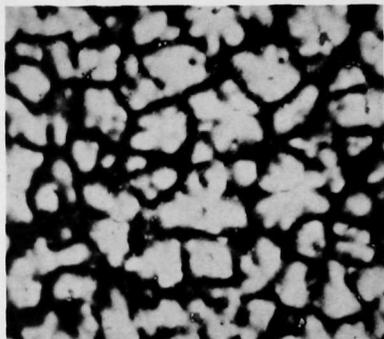
(a) 3% Fs Martensitic Alpha.  
Micro No. 32474.



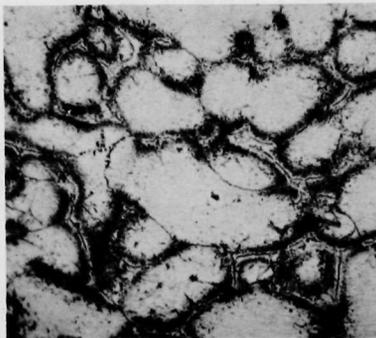
(b) 5% Fs Cored Gamma.  
Micro No. 32475.



(c) 8% Fs Cored Gamma plus  $U_2Ru$  (dark inter-dendritic constituent). Micro No. 32476.



(d) 10% Fs Cored Gamma plus  $U_2Ru$  (dark inter-dendritic constituent).  
Micro No. 32478.



(e) 5% Fs-2.25% Zr Martensitic Alpha plus  $ZrRu$  (thin network and precipitate).  
Micro No. 32479

Figure 2  
Microstructures of As-cast  
Uranium-Fissium Alloys

Magnification: 500X  
Etchant: Phosphoric Acid

with the technetium. Since the amounts of the inclusions were small, and they were not affected in amount or shape by subsequent heat treatment, their presence was ignored.

### Slowly Cooled Alloys

Previously homogenized alloys were reheated to 825°C for 24 hr, after which power to the furnace was cut off. The alloys cooled at an average rate of 2°C/min to 400°C and were then quenched.

The hardnesses of the slowly cooled alloys were generally higher than those of the quenched alloys and increased in a consistent manner with fissium content, indicating a dispersion-hardening action. Typical microstructures are shown in Figure 3. The 3 w/o Fs alloy shows a Widmanstätten alpha structure with a fine mixture of gamma and U<sub>2</sub>Ru between the alpha plates. It appears likely that the beta formation is completely suppressed, with alpha forming directly from the gamma, followed by the rejection of U<sub>2</sub>Ru at a lower temperature. Some gamma is retained as it becomes enriched in fissium content during the formation of alpha.

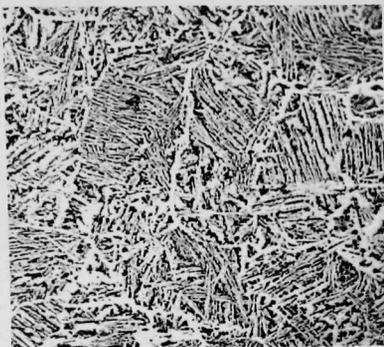
In the 5 w/o Fs alloy some U<sub>2</sub>Ru appears at the grain boundaries; as the temperature decreases alpha and U<sub>2</sub>Ru are simultaneously precipitated in a fine dispersion. Again, a considerable amount of gamma is retained.

The 8 w/o and 10 w/o Fs alloys also show a coarse primary structure of U<sub>2</sub>Ru and a finer structure in the bulk of the grain. Some alpha is associated with the matrix in the 8 w/o Fs alloy, but none can be resolved in the 10 w/o Fs alloy.

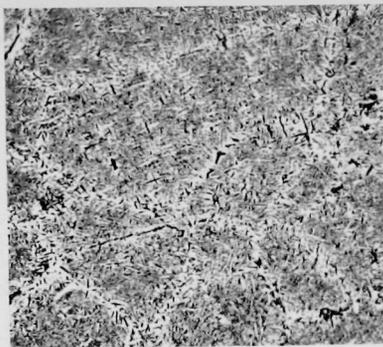
The 5 w/o Fs-2.25 w/o Zr alloy shows the same distribution of ZrRu particles as is found in the homogenized alloy and has a matrix consisting of Widmanstätten alpha in a gamma matrix. Its formation is similar to that of the 3 w/o alloy, except that the gamma matrix does not contain U<sub>2</sub>Ru, since much of the ruthenium is contained as ZrRu. The [gamma → alpha plus delta plus U<sub>2</sub>Ru] eutectoid reaction is easily suppressed in all alloys, and some gamma is found in each of the structures.

### Equilibrium Structures

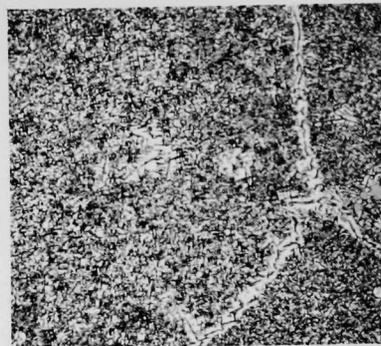
Alloys homogenized at 825°C, water quenched, and subsequently given long anneals at 700 (for 4 days), 650 (for 10 days), 600 (for 20 days) and 500°C (for 30 days) are designated as "equilibrium" alloys. It is believed that these treatments produced the equilibrium compositions and amounts of phases to be expected at these temperatures, although it is recognized that continued annealing might produce further coalescence and coarsening of the phases present. The structures were examined



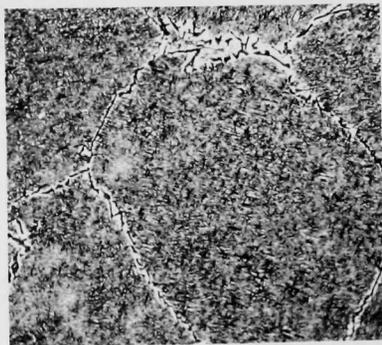
(a) 3% Fs Widmanstatten Alpha, in Matrix of Gamma plus U<sub>2</sub>Ru. Micro No. 32797.



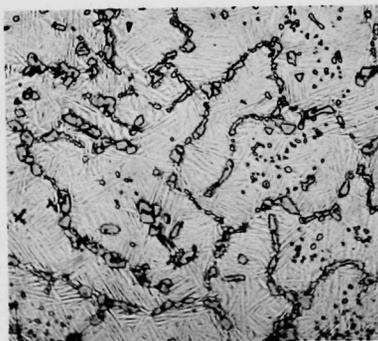
(b) 5% Fs Alpha (matrix), Gamma and U<sub>2</sub>Ru (dark acicular constituent). Micro No. 32798.



(c) 8% Fs Gamma (matrix), Alpha and U<sub>2</sub>Ru (dark acicular constituent). Micro No. 32799.



(d) 10% Fs Gamma (matrix) and U<sub>2</sub>Ru (acicular constituent and grain boundary network). Micro No. 32800.



(e) 5% Fs-2.25% Zr Widmanstatten Alpha in Gamma Matrix, plus ZrRu (gray particles) Micro No. 32801.

Figure 3

Microstructures of Slowly Cooled Uranium-Fission Alloys. Homogenized 66 hr at 825°C, reheated to 825°C for 24 hr, cooled to 400°C at 2°C/min, then water quenched.

Magnification: 500X

Etchant: Phosphoric Acid

metallographically, by X-ray diffraction, and by microhardness testing, and the findings in all three aspects of the study will be integrated in following discussion. Tables III and IV and Figures 4 through 8 provide the detailed results.

Table IV

VICKERS HARDNESS NUMBERS OF AS-CAST  
AND HEAT-TREATED URANIUM-FISSIUM ALLOYS\*

Heat Treatment	Alloy				
	3% Fs	5% Fs	8% Fs	10% Fs	5% Fs - 2.25% Zr
As Cast	342	181	255	280	332
Cooled at 2°C/min from 825 to 400°C	295	385	385	368	354
66 hr at 825°C, water quenched	288	175	255	274	264
66 hr at 825°C, plus 4 days at 700°C, water quenched**	288	136	237	279	319
66 hr at 825°C, plus 10 days at 650°C, water quenched	281	176	217	261	306
66 hr at 825°C, plus 20 days at 600°C, water quenched	254	298	261	314	329
66 hr at 825°C, plus 30 days at 500°C, water quenched	330	378	403	511	397

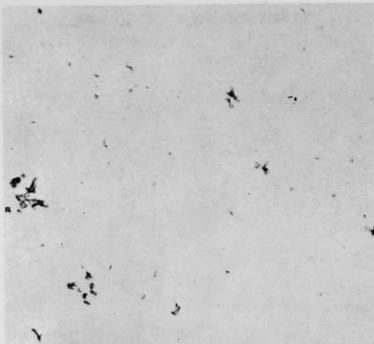
\*Values are averages of at least 5 measurements.

\*\*Cooling during quench from 700°C was probably more rapid than during quench from 825°C because the specimens quenched from the latter temperature had a larger mass.

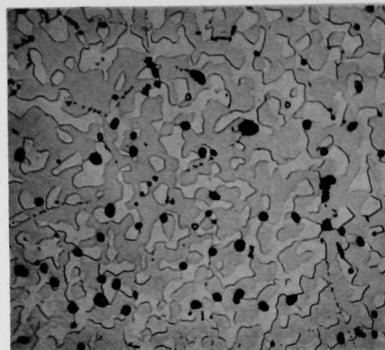
All of the alloys are b.c.c. gamma at 825°C (see Table III). At low fission contents, the gamma cannot be retained by quenching; it decomposes entirely or in part to martensitic alpha. Since gamma is considerably softer than  $\alpha'$ , the effect of the martensitic transformation on the properties of the alloys is quite drastic. Thus, Table IV shows that the Vickers hardness number (VHN) of the 3 w/o Fs alloy quenched from 825°C is 288,



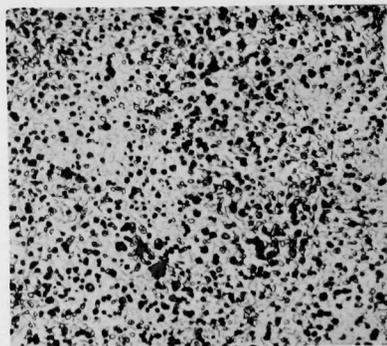
(a) As Homogenized at 825°C.  
Martensitic Alpha.  
Micro No. 32494.



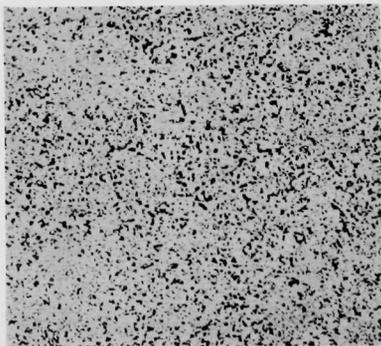
(b) 4 Days at 700°C.  
Martensitic Alpha.  
Micro No. 32802.



(c) 10 Days at 650°C. Gamma  
(matrix), Beta (white) and U<sub>2</sub>Ru  
(dark). Micro No. 32807.



(d) 20 Days at 600°C. Alpha plus  
Gamma Matrix and U<sub>2</sub>Ru  
(dark). Micro No. 32879.



(e) 30 Days at 500°C. Alpha Matrix,  
Delta and U<sub>2</sub>Ru (finely dispersed  
constituent). Micro No. 32874.

Figure 4  
Microstructures of Annealed and Quenched  
Uranium-3% Fissium Alloys. Specimens  
were initially homogenized 66 hr at 825°C  
and water quenched.

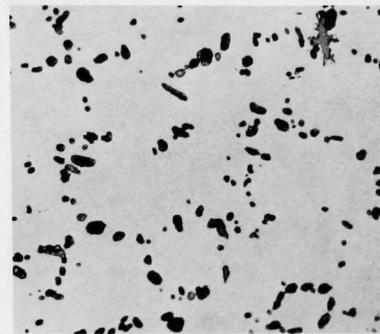
Magnification: 500X  
Etchant: Phosphoric Acid



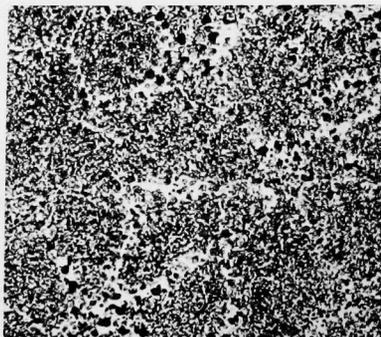
(a) As Homogenized at 825°C. Retained Gamma. Micro No. 32495.



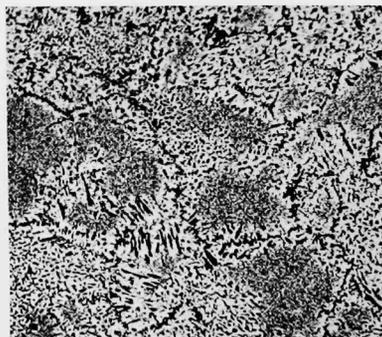
(b) 4 Days at 700°C. Retained Gamma. Micro No. 32803.



(c) 10 Days at 650°C. Gamma plus U<sub>2</sub>Ru (dark). Micro No. 32808.



(d) 20 Days at 600°C. Alpha, Gamma and U<sub>2</sub>Ru. Micro No. 32880.

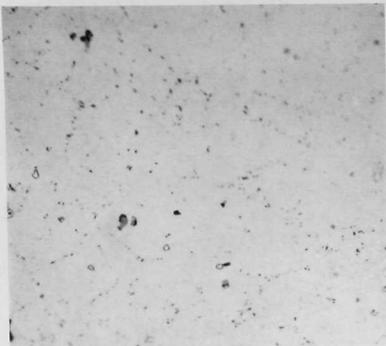


(e) 30 Days at 500°C. Alpha, Delta and U<sub>2</sub>Ru. Micro No. 32875.

Figure 5

Microstructures of Annealed and Quenched Uranium-5% Fissium Alloys. Specimens were initially homogenized 66 hr at 825°C and water quenched.

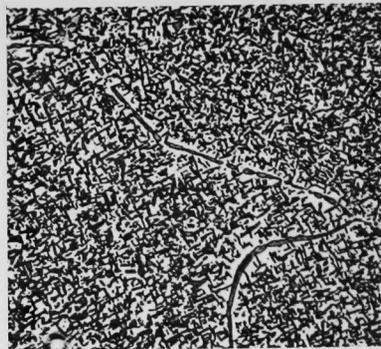
Magnification: 500X  
Etchant: Phosphoric Acid



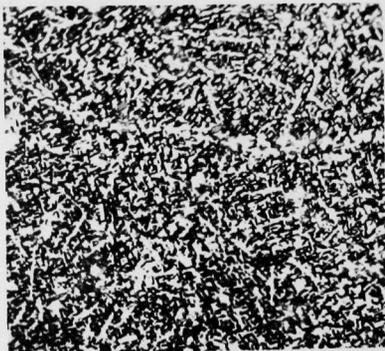
(a) As Homogenized at 825°C. Retained Gamma. Micro No. 32496.



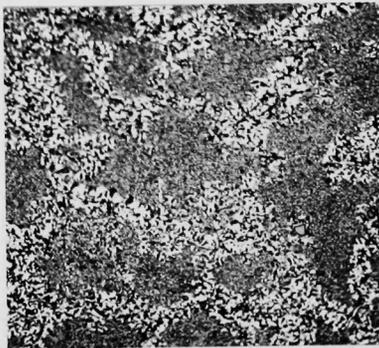
(b) 4 Days at 700°C. Gamma plus U<sub>2</sub>Ru (dark). Micro No. 32804.



(c) 10 Days at 650°C. Gamma plus U<sub>2</sub>Ru (dark). Micro No. 32809.



(d) 20 Days at 600°C. Gamma, Alpha and U<sub>2</sub>Ru. Micro No. 32881.



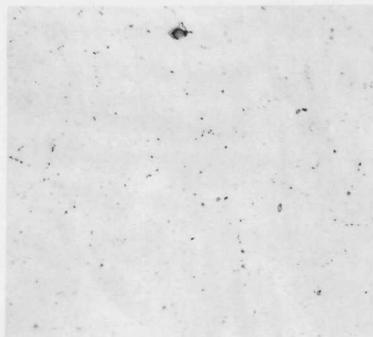
(e) 30 Days at 500°C. Alpha, Delta and U<sub>2</sub>Ru. Micro No. 32876.

Figure 6

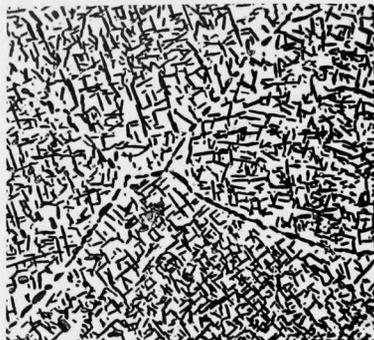
Microstructures of Annealed and Quenched Uranium-8% Fissium Alloys. Specimens were initially homogenized 66 hr at 825°C and water quenched.

Magnification: 500X

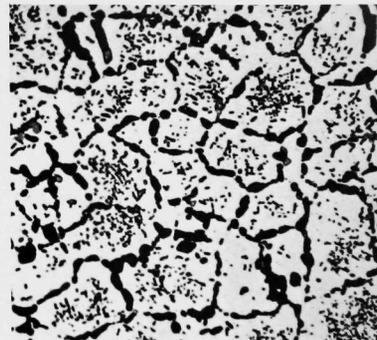
Etchant: Phosphoric Acid



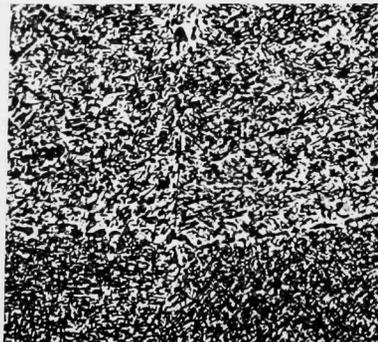
(a) As Homogenized at 825°C. Retained Gamma. Micro No. 32497.



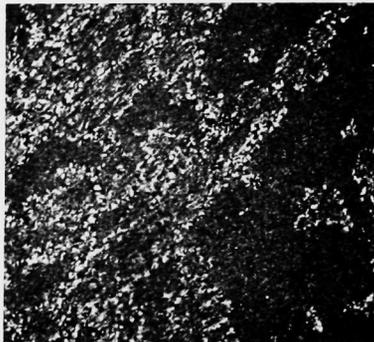
(b) 4 Days at 700°C. Gamma plus U<sub>2</sub>Ru (dark). Micro No. 32805.



(c) 10 Days at 650°C. Gamma plus U<sub>2</sub>Ru (dark). Micro No. 32810.



(d) 20 Days at 600°C. Gamma, U<sub>2</sub>Ru and Alpha. Micro No. 32882.



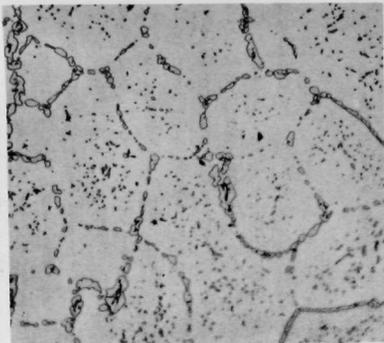
(e) 30 Days at 500°C. Alpha, Delta and U<sub>2</sub>Ru. Micro No. 32877.

Figure 7

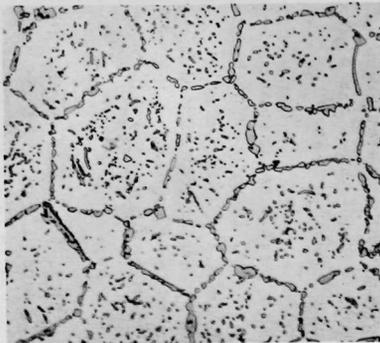
Microstructures of Annealed and Quenched Uranium-10% Fissium Alloys. Specimens were initially homogenized 66 hr at 825°C and water quenched.

Magnification: 500X

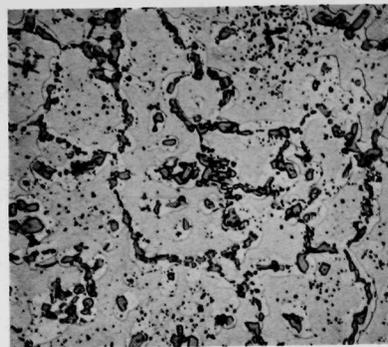
Etchant: Phosphoric Acid



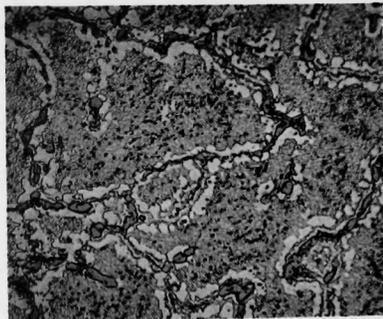
(a) As Homogenized at 825°C. Martensitic Alpha Matrix plus ZrRu Network. Micro No. 32498.



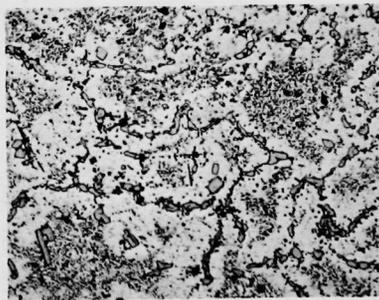
(b) 4 Days at 700°C. Martensitic Alpha Matrix plus ZrRu Network. Micro No. 32806.



(c) 10 Days at 650°C. Gamma Matrix plus Alpha (clear) and ZrRu (dark). Micro No. 32911.



(d) 20 Days at 600°C. Gamma Matrix, plus Alpha (clear) and ZrRu (dark). Micro No. 32883.



(e) 30 Days at 500°C. Alpha, Delta and ZrRu. Micro No. 32878.

Figure 8  
Microstructures of Annealed and Quenched Uranium-5% Fissium-2.25% Zirconium Alloys. Specimens were initially homogenized 66 hr at 825°C and water quenched.

Magnification: 500X  
Etchant: Phosphoric Acid

compared with 175 for the 5 w/o alloy quenched from the same temperature. With increasing fissium content the gamma is more readily retained by the quench. At the level of 5 w/o Fs the properties are very sensitive to cooling rate. The 5 w/o Fs alloy specimen quenched from 825°C weighed about 12 gm and had a VHN of 175, compared with 136 for another specimen of the same alloy, weighing about 0.2 gm, which was quenched from 700°C - also in the gamma range. The smaller mass of the latter specimen permitted faster cooling and more nearly complete suppression of the decomposition of the gamma. Further evidence of the instability of the 5 w/o Fs gamma phase is provided by the observation by Zegler and Nevitt of a distorted tetragonal gamma structure in their 5 w/o Fs alloys. This could be interpreted as a pre-precipitation clustering and distortion of the b.c.c. gamma lattice occurring during the quench. A tetragonal gamma observed in uranium-niobium alloys was similarly explained by Browne and Williamson.<sup>(6)</sup> That similar distortion of the gamma did not occur in the 5 w/o Fs alloy containing technetium quenched from 700°C may be attributed to the stabilizing effect of Tc and/or the faster quenching rate attained. The lower hardness of the as-quenched gamma is a good indication that any precipitation during the quench was suppressed.

As the fissium content increases, the transformation of gamma becomes increasingly sluggish and less sensitive to cooling rate. The hardness of the 8 w/o Fs alloy quenched from 825°C (see Table IV) is only slightly higher than that of the same alloy more drastically quenched from 700°C; quenching rate appears to have no effect on the hardness of the 10 w/o Fs alloy. The gamma is also observed to become harder due to solid-solution hardening.

A more expanded gamma-phase field in the U-Fs alloys compared with the U-Mo-Ru alloys is indicated in Table III and in Figures 5 through 7 by the presence of single-phase gamma structures in the 5 w/o Fs alloy at 700°C and in the 8 w/o and 10 w/o Fs alloys at 825°C, rather than the two-phase structures predicted by the isothermal section of the U-Mo-Ru system shown in Figure 1.

The behavior of the 5 w/o Fs alloy quenched from 650°C is difficult to interpret. The microstructure (see Figure 5) contains a few coarse particles of  $U_2Ru$  in a matrix which is presumed to be gamma on the basis of the U-Mo-Ru ternary diagram. The X-ray diffraction pattern, however, shows strong alpha lines and a distorted tetragonal gamma in addition to the  $U_2Ru$  lines (see Table III). It is difficult to explain the presence of alpha as a stable phase at such a high temperature; it may have originated by the partial decomposition of gamma during the quench and be present in a form not resolvable in the microstructure. It has already been seen that gamma in the 5 w/o Fs alloy is generally unstable, and the gamma in this specimen has been further depleted in alloy content by the formation of some  $U_2Ru$ . The possibility of partial decomposition of gamma can be

supported by consideration of the hardness data. The 650°C specimen has a VHN of 176, compared with the value of 136 for the 700°C specimen, which was entirely gamma phase. It is not likely that the increase of 40 points is due to the presence of  $U_2Ru$ , as consideration of other specimens shows a very mild hardening effect attributable to the formation of coarse  $U_2Ru$ . It is, thus, reasonable to credit the increase in hardness to partial decomposition of the gamma to alpha.

To explore the possibility of gamma decomposition in the 5 w/o Fs alloy during quenching or during subsequent room temperature aging, a needle-shaped specimen was held one week at 639° in an evacuated capsule and drastically quenched. An X-ray diffraction pattern was made immediately following quenching. The X-ray pattern again showed gamma, alpha and  $U_2Ru$ , but the lines of the alpha phase were much fainter than those in the pattern previously described, and the gamma phase did not show tetragonal distortion. Subsequent metallographic examination of this specimen disclosed the gamma and  $U_2Ru$  phases but not the alpha phase. There was somewhat more  $U_2Ru$  than in the specimen quenched from 650°C. It is believed that the experiment provided further evidence that in this alloy quenched from 650°C or 639°C alpha results from the partial transformation of gamma and is not an equilibrium phase at the annealing temperature.

It must be concluded that the structures present in the 5 w/o Fs alloy in the vicinity of 650°C are not retainable by quenching, and the microstructure is a better indication of the high-temperature structure than the diffraction patterns of the quenched alloys.

At 600°C, alloys up to 10 w/o Fs were in the alpha plus gamma plus  $U_2Ru$  field, whereas the 10 w/o Fs alloy apparently lies just outside in the gamma plus  $U_2Ru$  field. In the first three alloys the major phase shifts from alpha to gamma as the fissium content increases. In all of the alloys  $U_2Ru$  is a minor phase.

The hardnesses of all the alloys except 3 w/o Fs were higher when quenched from 600 than from 650°C. At the lower temperature, some alpha and increased amounts of  $U_2Ru$  formed, and the alloys contained less of the soft gamma phase. The 3 w/o Fs alloy was harder at 650°C, due primarily to the large amount of beta, which does not occur in the alloys with greater amounts of fissium.

At 500°C, all of the alloys contain alpha, delta and  $U_2Ru$  ( $ZrRu$  replaces  $U_2Ru$  in the case of the 2.25 w/o Zr alloy). These alloys are considerably harder than those quenched from 600°C. This is due to the absence of the gamma phase, the presence of delta, and the fact that the lower temperature of formation of the structure has produced the precipitated phases in a relatively fine dispersion. The hardness of the 500°C structures increases with fissium content, in direct relation to the amount of delta and  $U_2Ru$  present to harden the alpha matrix.

## Quenched and Aged Alloys

Hardness measurements and metallographic examinations were made on specimens quenched from 825°C and aged for various times at 375, 500 and 600°C. The hardness data are summarized in Table V and plotted in Figures 9, 10 and 11. The microstructures which were observed are described in the following discussion. No photomicrographs were taken during this portion of the study. The response of quenched uranium-fissium alloys to aging is a complex phenomenon because of differences in the initial quenched structures and because of the variety of final decomposition products, depending on the aging temperature. The possible formation of unknown transition products is another complicating factor. The aging curves show multiple peaks, and a detailed interpretation of the comparative behavior of the alloys is beyond the scope of this investigation.

Table V  
VICKERS HARDNESS NUMBERS OF QUENCHED AND AGED URANIUM-FISSIUM ALLOYS\*

All specimens initially homogenized 66 hr at 825°C,  
aged for the times shown below, and water quenched

Aging Temp (°C)	Alloy	As Quenched	Aging Time (min)								
			2	6	20	60	120	500	4200	28800	43000
375	3% Fs	288	433	462	527	549	548	526	523	-	-
	5% Fs	175	215	222	261	376	532	516	548	-	-
	8% Fs	255	226	223	234	238	243	225	445	-	-
	10% Fs	274	261	275	283	281	290	297	383	-	-
	5% Fs - 2.25% Zr	286	286	374	483	491	497	532	565	-	-
500	3% Fs	288	480	513	442	422	422	420	385	-	330
	5% Fs	175	267	473	462	462	480	516	462	-	378
	8% Fs	255	229	230	241	354	429	510	491	-	403
	10% Fs	274	279	278	288	268	295	502	562	-	511
	5% Fs - 2.25% Zr	268	529	526	568	523	532	513	440	-	397
600	3% Fs	288	360	383	370	365	363	330	-	254	-
	5% Fs	175	134	150	187	284	272	315	-	298	-
	8% Fs	255	234	240	250	262	255	249	-	261	-
	10% Fs	274	269	278	361	342	322	330	-	314	-
	5% Fs - 2.25% Zr	286	374	401	385	385	395	385	-	329	-

\* Average of 306 measurements on each specimen.

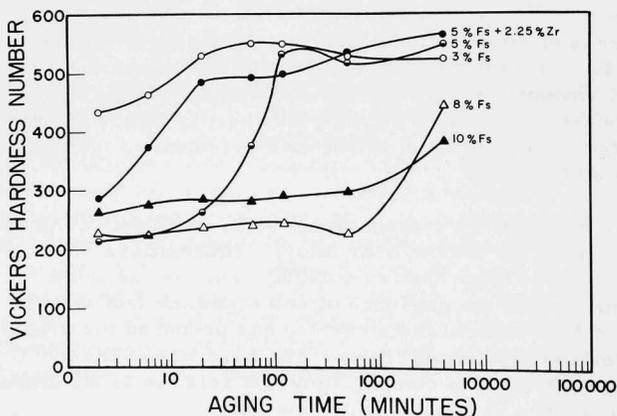


Figure 9

Effect of Aging at 375°C on  
Hardness of Uranium-Fissium  
Alloys. Macro No. 34272.

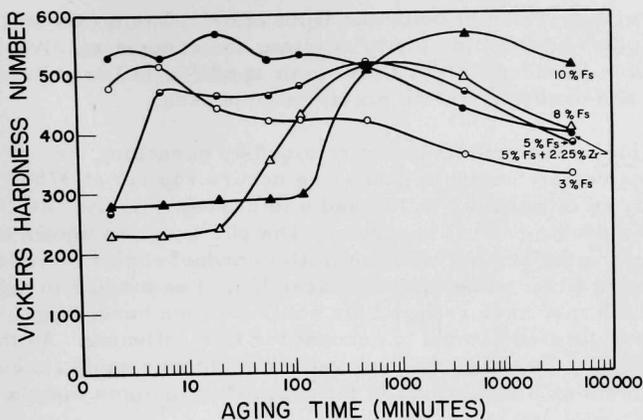


Figure 10  
Effect of Aging at 500°C on  
Hardness of Uranium-Fissium  
Alloys. Macro No. 34273.

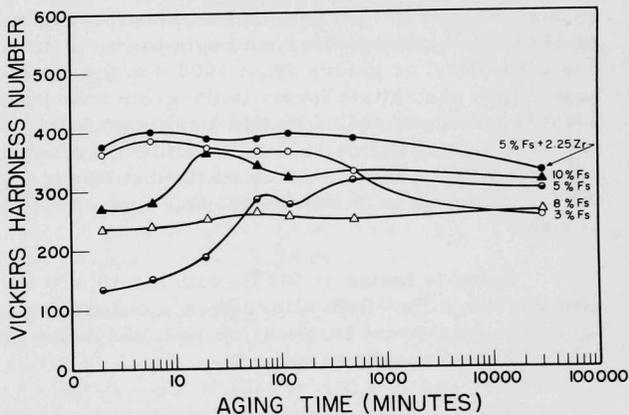


Figure 11  
Effect of Aging at 600°C on  
Hardness of Uranium-Fissium  
Alloys. Macro No. 34276.

3 w/o Fissium. This alloy shows an immediate response to aging, with at least two peaks appearing at each of the aging temperatures. The first probably represents the breakdown of the alpha-prime structure, and the second is due to precipitation of  $U_2Ru$  and delta ( $\gamma$  at 600°C). Maximum hardness is obtained at 375°C, with peaks of lower hardness attained in shorter times as the temperature increases. The microstructure shows some breakdown of the alpha prime corresponding to maximum hardness, but no resolvable precipitate was detected at aging times up to three days at 375°C.

At 500°C, a discontinuous breakdown of the alpha prime at the grain boundaries can be seen in 2 min, followed by the appearance of a boundary precipitate (probably delta and  $U_2Ru$ ) which gradually spreads into the grain,

producing a uniform dispersion of delta and  $U_2Ru$  after 500 min. Overaging has already taken place by the time the precipitate has become resolvable. A much lower peak is obtained in less than 6 min at  $600^\circ C$ , followed by rapid coalescence and overaging of the precipitated phases.

5 w/o Fissium. The gamma phase retained by quenching the 5 w/o Fs alloy is extremely unstable, and aging occurs rapidly at  $375^\circ C$  and  $500^\circ C$ , reaching an initial peak in 150 and 6 min, respectively. At both temperatures a double peak is observed. The  $600^\circ C$  series shows a peculiar softening as aging begins, with the initial hardness not recovered before 15 min of aging time. A relatively coarse  $U_2Ru$  has formed in the grain boundary, which may have relieved the solid-solution hardening strains of the supersaturated gamma to account for this softening. As the hardness begins to increase, alpha is observed. With longer aging times,  $U_2Ru$  continues to form as a dispersion in the alpha-plus-gamma matrix.

8 w/o and 10 w/o Fissium. As the fissium content of the alloys increases, the retained gamma becomes increasingly resistant to aging. At  $375^\circ C$  the hardness does not begin to rise before about 750 min for the 8 w/o Fs alloy, or before about 1000 min for the 10 w/o Fs. A rather heavy  $U_2Ru$  precipitate forms in the grain boundaries after about 500 min, but it is not accompanied by any significant hardness increase. As the hardness finally begins to rise, a uniform irresolvable dispersion appears throughout the structure. It is likely that this transformation is largely the formation of delta and the gradual conversion of the matrix from gamma to alpha.

Aging is faster at  $500^\circ C$ , with the 10 w/o Fs alloy more sluggish than the 8 w/o Fs. Both alloys show a coarse discontinuous precipitate prior to a significant hardness change, and a fine continuous precipitate as the hardness rises sharply.

At  $600^\circ C$  neither alloy exhibits a large increase in hardness, and the microstructures show initially a discontinuous followed by a continuous precipitation. At this temperature, however, the continuous precipitate rapidly coarsens, thus preventing large increases in hardness. The 10 w/o Fs alloy attains a higher hardness by virtue of the increased amount of precipitating delta and  $U_2Ru$  phases.

At all aging temperatures the 8 w/o Fs and 10 w/o Fs alloys show a decrease in hardness in the early states of aging similar to that noted in the 5 w/o Fs alloy aged at  $600^\circ C$ .

5 w/o Fs-2.25 w/o Zr. In the 5 w/o Fs alloy containing also 2.25 w/o Zr, the  $ZrRu$  phase appears unchanged throughout the aging, while the matrix behaves very much like that of the 3 w/o Fs alloy. The as-quenched alpha-prime matrix does not show any visible changes during the early stages of aging in the alpha-plus-delta-plus- $ZrRu$  field, although the hardness is increasing rapidly. During overaging, the decomposition

of the alpha prime is observed to initiate in the grain boundaries and to spread discontinuously through the volume of the grain. Upon aging at 600°C, alpha and gamma appear in the matrix during overaging.

## CONCLUSIONS

Since the primary objective of this study was to evaluate the effect of technetium on the behavior of uranium-fissium alloys, the conclusions are largely a comparison of the observations made on these alloys with the corresponding alloys of Zegler and Nevitt which did not contain technetium.

In general, uranium-fissium alloys with technetium are quite similar in structure and behavior to those in which Mo and Ru were substituted for technetium. There is some evidence that the stability range of the gamma phase is expanded when technetium is present. The 5 w/o Fs alloy quenched from 700°C and the 10 w/o Fs alloy quenched from 825°C are single-phase gamma, whereas Zegler and Nevitt found some U<sub>2</sub>Ru in their alloys after the same treatments.

Evidence of a slightly greater resistance to decomposition of technetium-bearing gamma is revealed in the slowly cooled structures. The structures of alloys containing technetium cooled at 2°C/min resemble the structures in the alloys of Zegler and Nevitt which were cooled at 4 to 7°C/min and are much finer than those of the alloys containing no technetium cooled at rates in the range of 0.4 to 3°C/min.

The aging response of the two series of alloys is quite similar. In Figures 12-16, the aging data of Zegler and Nevitt are superimposed on the data of this study. In the previous work, only the 5 w/o Fs, 10 w/o Fs, and 5 w/o Fs-2.25 w/o Zr alloys were studied in sufficient detail to obtain a good comparison at short aging times. The 10 w/o Fs alloy offers the best comparison with the present results, since the state of the matrix of the 5 w/o Fs alloys is too sensitive to the rate of cooling from the homogenizing temperature. The 10 w/o Fs alloy containing technetium is significantly more resistant to aging at 500°C, but the responses to 375°C and 600°C aging are nearly identical.

Although it was not the purpose of this work to fix the positions of the equilibrium phase boundaries, it appears that the range of the four-phase eutectoid, [beta → alpha plus gamma plus U<sub>2</sub>Ru], may extend beyond the 5w/o Fs composition suggested in the conclusions of Zegler and Nevitt.

In summary, differences between the behavior of the uranium-fissium alloys containing technetium and the technetium-free alloys described in ANL-6116(2) are of such minor character that the conclusions reached in the earlier study can be applied with confidence to the true uranium-fissium alloys.

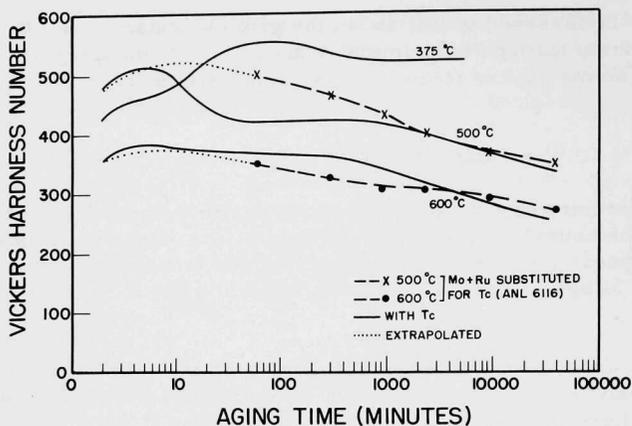


Figure 12  
Effect of Technetium  
on Aging of Uranium-  
3 w/o Fission Alloy.  
Macro No. 34277.

Figure 13  
Effect of Technetium  
on Aging of Uranium-  
5 w/o Fission Alloy.  
Macro No. 34278.

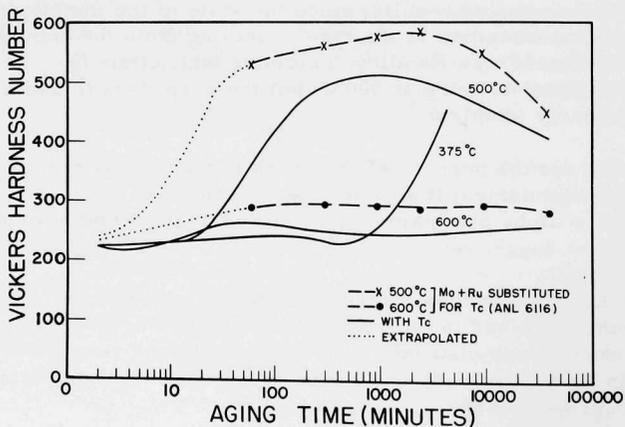
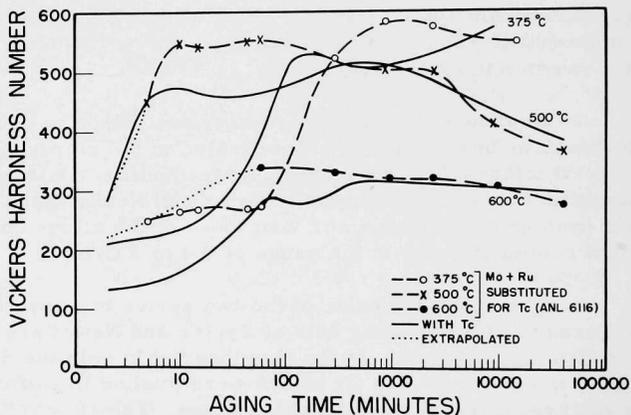


Figure 14  
Effect of Technetium  
on Aging of Uranium-  
8 w/o Fission Alloy.  
Macro No. 34279.

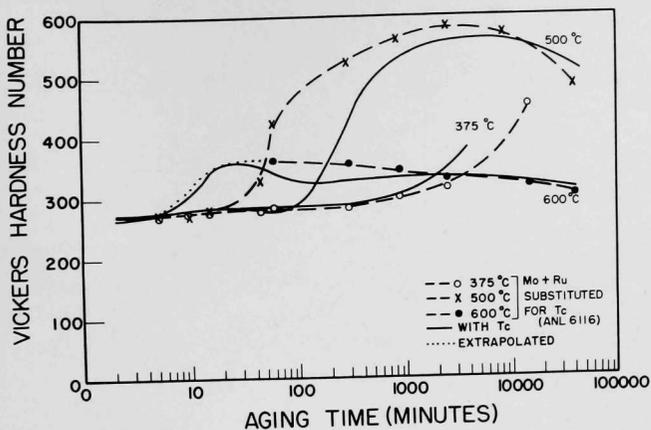


Figure 15  
Effect of Technetium  
on Aging of Uranium-  
10 w/o Fissium Alloy.  
Macro No. 34274.

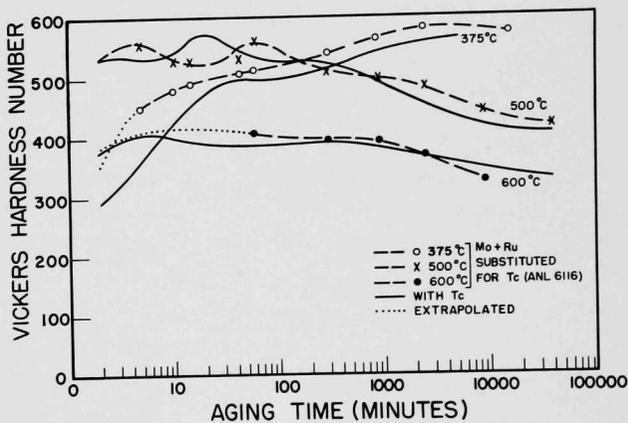


Figure 16  
Effect of Technetium  
on Aging of Uranium-  
5 w/o Fissium-  
2.25 w/o Zirconium  
Alloy. Macro No. 34275.

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