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SURVEY OF TERNARY AND QUATERNARY METASTABLE
GAMMA-PHASE URANIUM ALLOYS

by

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SURVEY OF TERNARY AND QUATERNARY METASTABLE GAMMA-PHASE URANIUM ALLOYS

Victor W. Storhok, Arthur A. Bauer,
and Ronald F. Dickerson

A survey of the effects of ternary and quaternary alloying on the stability and properties of uranium-zirconium, -niobium, and -molybdenum-base gamma-phase alloys was conducted. The effects of ternary and quaternary additions of chromium, molybdenum, niobium, ruthenium, vanadium, and zirconium on transformation kinetics, transformation temperature, hot hardness, and corrosion resistance were investigated.

Niobium or molybdenum additions to uranium-zirconium-base alloys increased thermal stability and hot hardness of the gamma phase and lowered transformation temperatures. These additions also generally resulted in improved corrosion resistance. Chromium, ruthenium, and vanadium additions also increased the thermal stability of the gamma phase and lowered transformation temperatures.

Zirconium increased the gamma-phase stability in uranium-niobium-base alloys, lowered transformation temperatures, and in some amounts increased hot hardness and improved corrosion resistance. Variable corrosion behavior of the uranium-niobium-zirconium alloys is probably attributable to lack of homogeneity. Molybdenum additions had either a negligible or detrimental effect on the thermal stability of the uranium-niobium gamma phase, although molybdenum did lower the temperature at which alpha uranium begins to decompose on heating. The addition of 1 w/o molybdenum to the 10 w/o niobium alloy or 3 w/o molybdenum to the 20 w/o niobium alloy resulted in maximum hardness of the gamma phase at elevated temperatures, the hot hardness decreasing with larger additions. Generally little effect of molybdenum on the corrosion resistance of uranium-niobium-base alloys was noted, although a 3 w/o addition was found to increase the corrosion life of the 10 w/o niobium alloy. Chromium, ruthenium, and vanadium additions, while slightly depressing the temperature of transformation on heating, exhibited little effect on other properties of the gamma phase.

Niobium additions of up to 3 w/o to the 7.5 w/o molybdenum-base alloy and of 1 w/o to the 10 and 12 w/o molybdenum-base alloys increased the thermal stability of the gamma phase; larger niobium additions decreased stability. A possible slight increase in the temperature of gamma formation on heating accompanied the addition of niobium. Ruthenium increased gamma stability more effectively, while it depressed the temperature of transformation to gamma. However, ruthenium decreased the hot hardness of the uranium-molybdenum gamma phase both as a ternary addition and as a quaternary addition to uranium-molybdenum-niobium alloys. Niobium additions to the 7.5 w/o molybdenum alloy increased hot hardness, while additions above 1 w/o to the 10 and 12 w/o molybdenum alloys decreased hot hardness. Ruthenium and niobium additions both increased the corrosion resistance of uranium-molybdenum alloys.

Zirconium additions were found to be generally detrimental to thermal stability, hot hardness, and corrosion resistance of the uranium-molybdenum gamma phase, while vanadium and chromium additions exhibited a negligible effect.

INTRODUCTION

Metastable gamma-phase uranium alloys have been of considerable interest as possible fuel materials and considerable effort has been expended on their development. To date, the major effort has been devoted to binary alloys of uranium with either molybdenum or niobium, these alloys exhibiting promise as reactor fuels because of the sluggishness with which the metastable gamma phase transforms at low temperatures. The ability to retain the gamma phase in metastable equilibrium is essential for radiation stability and corrosion resistance which result from the essential anisotropy of the body-centered-cubic gamma structure and the absence of the highly corrodible alpha-uranium phase.

This program was undertaken to investigate the possibility of increasing the temperature range of applicability of these alloys by increasing the thermal stability of the gamma phase through ternary and quaternary alloying. An additional advantage expected to accompany alloying would be increased high-temperature strength as a result of solid-solution alloying.

In addition to uranium-molybdenum and -niobium-base alloys, uranium-zirconium alloys were selected for study. While transformation of the gamma phase occurs extremely rapidly in this alloy system, it is possible to retain the gamma phase on quenching. Because of the low thermal-neutron cross section of zirconium, fairly extensive alloying with zirconium is possible before these alloys are ruled out of consideration. Consequently, the possibility of developing a metastable gamma-phase uranium-zirconium alloy was felt to hold sufficient promise to bear investigation.

Alloy additions for study were selected on the basis of their known gamma-stabilization behavior and included chromium, molybdenum, niobium, ruthenium, vanadium, and zirconium.

EXPERIMENTAL PROCEDURE

Alloys were prepared by arc-melting techniques and were cast into wire-bar shapes. Specimens for differential thermal analysis were cut from the end of each wire bar, after which the remainder of the bar was hot rolled to plate. From this plate, specimens were prepared and heat treated for studies of transformation kinetics, hot-hardness measurements, and corrosion testing.

Alloy Preparation

Materials used in alloy preparation included center-cut biscuit uranium, crystal-bar zirconium, triple-sintered niobium, high-purity molybdenum, crystal-bar chromium, vanadium, and ruthenium. In order to minimize the possibility of introducing oxides or other impurities to the alloys, the charges were prepared immediately prior to melting. Charge preparation generally consisted of electrolytic cleaning of the uranium, chemical pickling of zirconium, and a general surface cleaning of the other materials using solvents and/or mechanical action.

Each alloy was melted at least eight times in a tungsten-tip arc furnace before being cast in a wire-bar-shaped water-cooled copper mold. The wire-bar castings were approximately 3 in. long and 1/2 in. in diameter, and weighed 100 to 150 g, depending on the alloy.

After cutting a differential-thermal-analysis specimen from the end of each bar, the bars were rolled to flat thicknesses of 100 to 125 mils. Temperatures of fabrication for the various base alloys were as follows:

Uranium-20 w/o zirconium	1500 F
Uranium-40 w/o zirconium	1450 F
Uranium-10 w/o niobium	1650 F
Uranium-20 w/o niobium	2000 F
Uranium-7.5 w/o molybdenum	1600 F
Uranium-10 w/o molybdenum	1800 F
Uranium-12 w/o molybdenum	1800 F

Several alloys cracked severely on rolling and, since it was not the intent of this investigation to become involved in fabrication problems, the alloys were dropped from the program. These alloys and the attempted temperatures of fabrication are given below:

Uranium-10 w/o niobium-2 w/o ruthenium	1850 F
Uranium-7.5 w/o molybdenum-3 w/o niobium-1 w/o ruthenium	1600 F
Uranium-10 w/o molybdenum-2 w/o ruthenium	1800 F
Uranium-10 w/o molybdenum-2 w/o niobium-1 w/o ruthenium	1800 F
Uranium-12 w/o molybdenum-2 w/o ruthenium	1800 F
Uranium-12 w/o molybdenum-3 w/o niobium-2 w/o ruthenium	1800 F

In addition, attempts to roll uranium-30 w/o niobium, both as the binary alloy and with ternary additions of zirconium and molybdenum, at 2200 F were unsuccessful.

Transformation-Kinetics Studies

A reasonably good indication of gamma stability, at least at a particular temperature, can be gained by measuring and comparing microhardness values of gamma-quenched alloy specimens which have been isothermally aged for various times. The beginning of transformation is indicated by an increase in hardness as precipitation occurs.

Aging treatments employed in this investigation are listed below:

Uranium-zirconium-base alloys	10, 100, 1000, and 10,000 sec at 500 C
Uranium-niobium-base alloys	10, 100, 1000, and 10,000 min at 550 C
	1, 10, 100, and 1000 hr at 475 C
Uranium-molybdenum-base alloys	1, 10, 100, and 1000 hr at 500 C

In some instances, intermediate aging times were also employed. The short-time aging treatments were conducted in a lead bath, while the longer treatments were carried out in evacuated Vycor capsules. Prior to aging, all specimens were solution heat treated 4 hr at 900 C and water quenched.

Metallography was also used to verify results obtained through hardness measurements. A standard preparation procedure was followed. Specimens were given a final grinding on 600-grit paper and polished with levigated alumina, followed by Blue Diamond and Linde B. Etching techniques varied from alloy to alloy. The following etchants were used on uranium-zirconium alloys:

- (1) 85 cm³ H₂O, 10 cm³ HNO₃, 5 cm³ HC₂H₃O₂, 5 drops HF
- (2) 60 cm³ oxalic acid, 40 cm³ HNO₃, 5 drops HF
- (3) 30 cm³ lactic acid, 30 cm³ HNO₃, 5 drops HF.

All the above etchants were applied by swabbing. Uranium-niobium alloys were etched with one of the following etchants, depending on composition and heat treatment:

- (1) 18 parts acetic acid, 1 part chromic acid (10 g CrO₃ and 118 cm³ H₂O) applied electrolytically at 20 v dc for approximately 20 sec
- (2) 85 cm³ H₂O, 15 cm³ HNO₃, 5 drops HF, 4 g CrO₃, applied by swabbing.

The 18-to-1 chromic acid electrolytic etchant was also employed on maximum molybdenum alloys. Another electrolytic etchant used on uranium-molybdenum alloys contained 1 part HNO₃ to 1 part acetic acid. Vacuum-cathodic etching was also employed for a uranium-7.5 w/o molybdenum-2 w/o ruthenium alloy.

Hot Hardness

To gain some indication of alloying on hot strength, hot-hardness measurements of all alloys were made. Diamond pyramid hardness numbers were generally obtained at room temperature and at 300, 500, 600, 700, and 900 C. Specimens were heated in a vacuum resistance furnace and hardness indentations were obtained employing a standard Vickers indenter and a load of 730 g. Measurements were made after indentations had been made at all temperatures of interest and the specimens had cooled and were removed from the furnace. Prior to testing, all alloy specimens were water quenched after being heat treated at 900 C for 4 hr.

Corrosion Testing

With a few exceptions, all alloys were corrosion tested in high-temperature degassed water. Although corrosion properties of several of the alloys could undoubtedly be improved by various heat treatments, all alloys were tested in the gamma-quenched condition, as this was the condition of interest. Initial tests were conducted in 500 F water to enable a comparison of relative corrosion resistance to be made among the alloys. Higher temperature water would likely have resulted in such rapid disintegration of some of the alloy specimens that no comparison could have been made. Alloys which exhibited small weight changes in 500 F water were subsequently tested in 680 F water. However, in several cases alloys were put on test in 680 F water without prior testing at 500 F.

Corrosion specimens were approximately 1/2 in. square and 0.100 to 0.120 in. thick. After heat treating, these specimens were abraded to remove oxides and surface defects, weighed, measured, and placed on test. Examination of the alloys was made after exposures of 24, 72, and 168 hr, and every 168 hr thereafter. This examination consisted of a determination of weight change per square centimeter and a visual inspection to determine the type of attack and the surface condition. Weight change was calculated on the basis of the original surface area of the uncorroded specimen. Metallographic examinations of several of the alloys were performed to investigate possible internal attack or transformation.

Thermal Analysis

To gain some indication of the effect of alloying on the temperature of gamma decomposition and the temperature of complete gamma solution at a particular alloy composition, thermal-analysis data were obtained on all alloys. Two thermal-analysis techniques were employed: differential thermal analysis and time-temperature analysis.

Differential-thermal-analysis data were obtained by conventional techniques employing a graphite block as the neutral specimen. The differential heating curve was recorded on an X-Y recorder. A heating rate of 3 C per min was employed for this technique.

Time-temperature analysis involved intimately sandwiching a Chromel-Alumel thermocouple between two 1/8-in. -square by 1/16-in. -thick specimens of the alloy in question. This assembly was rapidly heated in a tungsten-wound resistance furnace and the heating curve recorded on a high-speed recorder. Phase changes were indicated by a change in slope of the heating curve. All thermal analyses were performed in a vacuum.

The sluggish gamma-phase transformation rate of some of the alloys on cooling necessitated aging heat treatments of 24 hr at 500 C followed by slow cooling (20 C per hr) to 300 C and furnace cooling to room temperature. Even so, no indications of transformation could be detected for several alloys.

RESULTS AND DISCUSSION

As a result of the data obtained in this study, the effects of ternary and quaternary alloying on gamma stability, hot hardness, corrosion resistance, and transformation temperature were determined.

Transformation-Kinetics Studies

Transformation-kinetics studies were conducted on all alloys to gain an indication of the effect of alloying additions on gamma stability. The results reported are based on alloys given a solution heat treatment at 900 C. Raising or lowering this temperature

could possibly change the aging time required for hardening to begin. However, it is doubtful that changing the temperature would result in a change in relative effects of alloying additions.

Uranium-Zirconium Alloys

Increasing ternary additions of either niobium or molybdenum to the uranium-20 w/o and -40 w/o zirconium-base alloys resulted in progressively slower transformation. Figure 1 illustrates the increasing stability of the gamma phase in uranium-40 w/o zirconium-base alloys with increasing amounts of niobium.

Molybdenum additions acted in much the same manner. The optimum gamma stability for uranium-zirconium-base alloys studied in this survey was observed among quaternary alloys containing molybdenum and niobium. A uranium-20 w/o zirconium-3 w/o niobium-3 w/o molybdenum alloy did not show any appreciable hardness increase until after 100 sec of aging, while a uranium-10 w/o zirconium-5 w/o niobium-3 w/o molybdenum alloy did not begin to harden until after aging about 1000 sec. Apparently a 2 w/o increase in niobium outweighs the effect on gamma stability resulting from the 10 w/o zirconium decrease.

Ternary additions of chromium, ruthenium, and vanadium also appear to improve gamma stability of the uranium-20 w/o zirconium-base alloy. However, none of these is as effective in comparable quantities as is either niobium or molybdenum.

Uranium-Niobium Alloys

Increasing zirconium additions to uranium-10 w/o niobium-base alloys resulted in progressively improved gamma stability at 550 C. However, when aged at 475 C, these alloys, while generally transforming more slowly than at 550 C, did not exhibit this continuous decrease in rate of transformation with increasing additions of zirconium. Apparently the degree of shift in the nose of the transformation "C-curve" accompanying zirconium additions influences the rate of transformation observed. Figures 2 and 3 illustrate the hardness-versus-aging time curves obtained for these alloys when aged at these temperatures. In a uranium-20 w/o niobium-10 w/o zirconium alloy, there was no evidence of increase in hardness after aging 10,000 min at 550 C. When aged at 475 C, however, this alloy did show effects of aging. Thermal-analysis data indicate the transformation temperature of the alloy is probably below 550 C, accounting for the lack of transformation on aging at this temperature. Actually, hardness measurements gave only slight indications of transformation for any uranium-20 w/o niobium-base alloy. Metallographic examination proved to be more valuable in these cases. Figure 4 compares the microstructure of an alloy with a 5 w/o zirconium addition with one with 10 w/o zirconium. Both alloys were aged equal times at 550 C.

Molybdenum additions to uranium-10 w/o niobium-base alloys had an almost negligible effect on gamma stability. Transformation was slowed slightly by 1 w/o molybdenum, while 3 and 5 w/o molybdenum increased transformation rates a small amount. Among uranium-20 w/o niobium-base alloys, molybdenum additions seem to have a detrimental effect on gamma stability.

FIGURE 1. HARDNESS DATA FOR ISOTHERMALLY TRANSFORMED URANIUM-40 w/o ZIRCONIUM-BASE ALLOYS

FIGURE 2. HARDNESS DATA FOR URANIUM-10 w/o NIOBIUM-BASE ALLOYS
ISOTHERMALLY TRANSFORMED AT 550 C

FIGURE 3. HARDNESS DATA FOR URANIUM-10 w/o NIOBIUM-BASE ALLOYS ISOTHERMALLY TRANSFORMED AT 475 C

500X

RM9681

- a. Alloy with 5 w/o zirconium addition; note transformation

500X

RM9685

- b. Alloy with 10 w/o zirconium addition; notice absence of transformation

FIGURE 4. COMPARISON OF THE EFFECTS ON STABILITY OF 5 AND 10 w/o ZIRCONIUM ADDITIONS TO A URANIUM-20 w/o NIOBIUM ALLOY

Both alloys were heat treated 4 hr at 900 C and water quenched, and aged 10,000 min at 550 C and water quenched.

Ternary additions of 2 w/o vanadium had little effect on gamma stability while 0.5 w/o chromium resulted in some improvement over the binary uranium-10 w/o niobium alloy.

Uranium-Molybdenum Alloys

Small additions (3 w/o to uranium-7.5 w/o molybdenum and 1 w/o to uranium-10 and -12 w/o molybdenum) of niobium to uranium-molybdenum-base alloys resulted in decreased transformation rates at 500 C. However, the addition of greater amounts of niobium resulted in faster transformation. In Figure 5 are typical hardness-versus-aging curves for uranium-10 w/o molybdenum alloys.

Additions of 2 w/o ruthenium to uranium-7.5 w/o and -12 w/o molybdenum-base alloys also had a gamma-stabilizing effect. On the basis of these results, quaternary alloys containing niobium and ruthenium were prepared. Alloys in which the niobium content was held to 2 w/o or less had reasonably good thermal properties. Increasing niobium above this resulted in more rapid transformation rates.

Alloys containing ruthenium were generally difficult to fabricate, probably as a result of the formation of the compound U_2Ru . Metallography of the uranium-7.5 w/o molybdenum-2 w/o ruthenium alloy revealed the presence of a minor second phase, interpreted to be U_2Ru . The structure is illustrated in Figure 6. Examination of the uranium-molybdenum-ruthenium phase diagram indicates the relative amount of U_2Ru increases at higher molybdenum contents.⁽¹⁾

Increasing zirconium contents up to 10 w/o resulted in progressively poorer gamma stability of uranium-7.5 w/o molybdenum-zirconium alloys at 500 C. Also, a uranium-12 w/o molybdenum-base alloy with a 5 w/o addition of zirconium transformed faster than one with 3 w/o zirconium. This behavior can be explained by the presence of the compound $ZrMo_2$, which has been observed in similar alloys.⁽²⁾ The formation of this compound ties up the molybdenum, thereby effectively decreasing gamma-phase alloy content. Increasing the zirconium content led to the formation of greater quantities of $ZrMo_2$ and lower gamma stability. A quaternary uranium-7.5 w/o molybdenum-5 w/o zirconium-3 w/o niobium alloy also transformed quickly.

Ternary additions of 0.5 w/o chromium to the uranium-7.5 w/o molybdenum-base alloy improved gamma stability slightly, while 2 w/o vanadium proved detrimental.

Small additions of cerium (0.18 w/o) or lanthanum (0.25 w/o), made to check the effect of these fission products, appeared to improve the gamma stability of uranium-12 w/o molybdenum-base alloys. However, these alloys cast poorly and had numerous microcracks.

(1) References at end.

FIGURE 5. HARDNESS DATA FOR ISOTHERMALLY TRANSFORMED URANIUM-10 w/o MOLYBDENUM-BASE ALLOYS

250X

RM9799

FIGURE 6. URANIUM-7.5 w/o MOLYBDENUM-2 w/o RUTHENIUM ALLOY

Solution heat treated 4 hr at 900 C, water quenched, and aged 1 hr at 500 C. The two-phase structure is probably gamma solid solution plus the compound U_2Ru .

Hot Hardness

The effects of alloying additions on hot hardness of the gamma phase are probably best indicated by hardness values reported at temperatures above 500 C. Below this temperature hardness is very dependent on the aging characteristics of the alloys. Since all alloys tested were initially gamma quenched, increasing hardness and resistance to softening on heating at the lower temperatures is associated with precipitation hardening and transformation of the metastable gamma phase. Alloys which soften most rapidly on heating to 500 C are either those in which the gamma phase is least stable and therefore overaging is observed, or those which exhibit the most stable gamma phase and in which aging occurs very slowly.

Uranium-Zirconium Alloys

None of the uranium-zirconium-base alloys exhibited exceptional hardness at either 700 or 900 C. However, uranium-20 w/o and -40 w/o zirconium alloys became progressively harder at high temperatures with increasing additions of niobium or molybdenum. As can be seen from Table 1, there is little difference in hardening effects observed between these two additions. Figure 7 presents typical hot-hardness curves for uranium-20 w/o zirconium with additions of niobium. At lower temperatures, these alloys show decreasing hardness with increasing niobium or molybdenum, probably because of the gamma-stabilizing effect of these additions.

Additions of chromium, ruthenium, or vanadium had little effect on hot hardness in uranium-20 w/o zirconium-base alloys. There appears to be some relationship between hardening effects and improvement of gamma stability, as none of the above three elements had much effect on gamma stability, while niobium and molybdenum improved hot hardness and gamma stability. It is possible that this is mere coincidence.

Uranium-Niobium Alloys

Optimum hot-hardness values for uranium-niobium-base alloys studied in this program were generally observed among alloys with a narrow range of ternary additions. Increasing or decreasing the ternary addition from this optimum composition resulted in decreased hardness. As can be seen from Table 2, 1 w/o zirconium or molybdenum additions produced the highest hardness at 900 C among uranium-10 w/o niobium-base alloys. Increasing either of these ternary additions above this value resulted in progressively lower hot hardness. Among uranium-20 w/o niobium-zirconium alloys, 5 w/o zirconium produced a diamond pyramid hardness of 119 at 900 C, this being the highest hardness observed for any alloy in this program. The optimum molybdenum addition to the uranium-20 w/o niobium-base alloy appears to be 3 w/o. Additions of 2 w/o vanadium to the uranium-10 w/o niobium-base alloy decreased hardness considerably, while 0.5 w/o chromium had little effect.

TABLE 1. HOT-HARDNESS DATA FOR URANIUM-ZIRCONIUM ALLOYS

Alloy Addition, w/o	DPH at Indicated Temperature					
	Room	300 C	500 C	600 C	700 C	900 C
<u>Uranium-10 w/o Zirconium Base</u>						
5 niobium-3 molybdenum	304	322	282	88.6	40.9	11.7
<u>Uranium-20 w/o Zirconium Base</u>						
Base alloy	482	354	225	--	27.4	7.5
1 niobium	386	376	247	--	32.3	7.8
3 niobium	334	322	183	--	32.6	8.8
5 niobium	284	292	249	--	41.1	12.8
1 molybdenum	385	342	263	--	27.9	7.2
3 molybdenum	344	352	270	--	32.9	7.9
5 molybdenum	321	321	242	--	42.4	10.3
2 vanadium	383	282	218	69.1	30.6	7.6
2 ruthenium	425	--	251	62.0	28.1	5.1
0.5 chromium	440	361	277	69.6	30.4	6.5
3 niobium-3 molybdenum	291	314	345	82.5	42.6	13.4
<u>Uranium-30 w/o Zirconium Base</u>						
Base alloy	370	320	264	48.0	30.4	8.1
3 niobium	224	199	186	69.0	34.5	11.1
3 molybdenum	270	239	219	83.4	40.4	10.9
<u>Uranium-40 w/o Zirconium Base</u>						
Base alloy	235	184	134	--	20.8	9.2
1 niobium	201	234	204	--	23.8	--
3 niobium	200	211	213	--	29.1	10.5
5 niobium	197	191	190	--	33.0	13.8
1 molybdenum	212	254	231	--	24.1	7.0
3 molybdenum	241	154	219	--	33.8	10.7
5 molybdenum	268	239	225	--	48.3	12.0

FIGURE 7. TYPICAL HOT HARDNESS CURVES FOR URANIUM-20 w/o ZIRCONIUM-BASE ALLOYS

TABLE 2. HOT-HARDNESS DATA FOR URANIUM-NIOBIUM-BASE ALLOYS

Alloy Additive, w/o	DPH at Indicated Temperature					
	Room	300 C	500 C	600 C	700 C	900 C
<u>Uranium-10 w/o Niobium Base</u>						
Base alloy	230	193	148	-	50.4	18.5
1 zirconium	288	155	117	-	75.1	27.6
3 zirconium	291	190	135	-	64.0	23.7
5 zirconium	288	224	170	104.0	55.1	16.5
10 zirconium	279	198	142	-	65.9	22.2
1 molybdenum	313	218	147	-	78.5	29.7
3 molybdenum	269	167	142	-	40.6	16.0
5 molybdenum	309	178	141	-	34.1	15.9
2 vanadium	297	329	213	38.3	33.0	7.6
0.5 chromium	309	316	189	77.3	51.1	16.0
5 zirconium-3 molybdenum	319	233	189	140.0	84.8	26.1
<u>Uranium-15 w/o Niobium Base</u>						
Base alloy	316	306	281	109.0	41.2	11.5
5 zirconium	300	244	190	137.0	101.0	37.1
3 molybdenum	339	245	205	115.0	63.4	25.1
<u>Uranium-20 w/o Niobium Base</u>						
Base alloy	341	253	199	191.0	143.0	-
3 zirconium	326	231	205	144.0	95.2	37.0
5 zirconium	318	255	205	188.0	165.0	119.0
10 zirconium	288	224	189	140.0	113.0	41.9
3 molybdenum	349	251	202	185.0	136.0	62.0
5 molybdenum	318	231	193	102.0	42.9	30.7

Uranium-Molybdenum Alloys

Additions of niobium to uranium-7.5 w/o molybdenum-base alloys resulted in increased hot hardness, the higher niobium alloys exhibiting the higher hardness values (see Table 3). However, among uranium-10 and -12 w/o molybdenum alloys, maximum hot-hardness values were observed in the binary alloys and in alloys with 1 w/o niobium. Increasing niobium resulted in lowered hot hardness. A possible explanation is that two gamma phases are formed when more niobium is added, one being essentially a uranium-molybdenum gamma phase and the other a niobium-molybdenum-rich gamma phase. This would reduce the amount of alloying addition in solid solution and hence reduce solid-solution hardening. Figure 8 illustrates the two-phase structure observed in a uranium-12 w/o molybdenum-5 w/o niobium alloy, and Figure 9 presents a graphic illustration of the effects of niobium additions on hardness at various temperatures.

A 2 w/o ruthenium addition decreased the hot hardness of the uranium-7.5 w/o molybdenum-base alloy by a substantial amount. Also quaternary alloys containing ruthenium and niobium exhibited lower hot hardness. This softening tendency by ruthenium was unexpected, as uranium-molybdenum alloys containing ruthenium generally were brittle and showed poor fabricability.

Among uranium-7.5 w/o molybdenum-base alloys, a 10 w/o addition of zirconium increased hot hardness slightly. Evidently enough $ZrMo_2$ is formed at this composition to produce dispersion hardening. At lower zirconium concentrations, the hot-hardness values were generally lessened. Uranium-12 w/o molybdenum alloys also exhibited decreased hot hardness with increasing zirconium contents. Apparently the molybdenum tied up in $ZrMo_2$ reduces solid-solution hardening, while not enough $ZrMo_2$ is formed to result in dispersion hardening.

Small additions of vanadium and chromium also reduced hot hardness.

Corrosion Testing

From corrosion data for tests run in 500 and 680 F water there appears to be some relationship between gamma stability and corrosion resistance, particularly in 680 F water. Alloys with poor gamma stability transformed during testing and failed by rapid oxidation. However, in some cases alloys with improved gamma stability also failed rapidly; hydride formation or cracking resulting from quenching and transformation-induced stresses were responsible for these failures.

Uranium-Zirconium Alloys

Corrosion properties of uranium-20 w/o zirconium with additions of niobium in 500 F were generally rather poor. While corrosion rates for these alloys were relatively low, they failed by cracking within short times. Additional heat treatment would very likely improve the corrosion life of these alloys. Among the uranium-40 w/o zirconium-niobium alloys, corrosion rates decreased with increasing niobium both in 500 and 680 F water. The binary and 1 w/o niobium alloys exhibited very low initial weight changes in 500 F water. However, this later proved to be misleading, as the alloys showed severe internal oxidation at the grain boundaries, which probably offset surface weight losses.

TABLE 3. HOT-HARDNESS DATA FOR URANIUM-MOLYBDENUM-BASE ALLOYS

Alloy Addition, w/o	DPH at Indicated Temperature					
	Room	300 C	500 C	600 C	700 C	900 C
<u>Uranium-7.5 w/o Molybdenum Base</u>						
Base alloy	264	124	89.9	-	41.6	12.8
1 zirconium	268	139	114.0	-	48.6	12.6
3 zirconium	290	151	104.0	-	28.1	12.6
5 zirconium	302	260	255.0	92.5	27.9	-
10 zirconium	327	273	254.0	114.0	45.4	13.2
1 niobium	262	178	150.0	91.3	45.4	12.3
3 niobium	285	206	170.0	140.0	79.4	24.1
5 niobium	292	204	167.0	120.0	80.9	-
2 vanadium	203	238	229.0	45.3	19.1	5.0
2 ruthenium	292	186	147.0	73.5	33.4	8.2
0.5 chromium	266	166	122.0	75.2	37.8	8.5
5 zirconium-3 niobium	334	211	165.0	104.0	50.1	16.2
2 ruthenium-3 niobium	297	202	158.0	69.5	29.9	8.1
2 ruthenium-2 niobium	297	203	164.0	79.3	33.4	8.5
<u>Uranium-10 w/o Molybdenum Base</u>						
Base alloy	290	-	160.0	111.0	70.9	17.6
1 niobium	294	199	165.0	121.0	67.9	18.3
3 niobium	292	190	153.0	83.9	45.9	13.0
5 niobium	287	192	150.0	45.0	53.4	14.9
2 ruthenium-3 niobium	290	194	153.0	84.8	41.3	10.6
1 ruthenium-2 niobium	308	219	177.0	120.0	63.0	14.9
<u>Uranium-12 w/o Molybdenum Base</u>						
Base alloy	323	-	154.0	133.0	76.3	27.6
1 niobium	323	244	177.0	139.0	85.0	24.0
3 niobium	303	227	171.0	114.0	65.2	17.0
5 niobium	299	208	167.0	111.0	62.9	17.0
1 ruthenium-2 niobium	318	233	187.0	123.0	56.8	14.1
3 zirconium	293	225	183.0	106.0	51.3	15.5
5 zirconium	296	-	198.0	75.7	24.6	9.7

500X

RM10501

FIGURE 8. URANIUM-12 w/o MOLYBDENUM-5 w/o NIOBIUM ALLOY

Solution heat treated 4 hr at 900 C, water quenched, and aged 1 hr at 500 C. The two-phase structure is interpreted as consisting of uranium-molybdenum- and niobium-molybdenum-rich gamma phases.

FIGURE 9. EFFECT OF NIOBIUM ADDITIONS ON HARDNESS OF URANIUM-12 w/o MOLYBDENUM ALLOYS AT VARIOUS TEMPERATURES

The corrosion behavior of uranium-20 w/o zirconium-molybdenum alloys in 500 F water improved with increasing molybdenum contents, while corrosion life of any of these alloys in 680 F water was too short to make any valid comparison. The uranium-40 w/o zirconium-molybdenum alloys also show improved corrosion properties in 500 and 680 F water with increasing amounts of molybdenum. While Table 4 shows the 3 w/o molybdenum alloy to have a very low corrosion rate in 500 F water, bowing of the specimen indicates that internal oxidation is probably canceling surface weight losses.

Quaternary alloys with both molybdenum and niobium additions exhibited relatively low corrosion rates in 500 F water. A 2 w/o vanadium addition to the uranium-20 w/o zirconium alloy, while improving the corrosion resistance over the binary alloy, was not very promising. However, a 2 w/o addition of ruthenium resulted in longer corrosion life in both 500 and 680 F water.

The corrosion behavior of these uranium-zirconium alloys is apparently related to the thermal stability of the gamma phase. By decreasing the rate at which alpha uranium forms by gamma-phase decomposition, increased corrosion life may be expected.

Uranium-Niobium Alloys

Corrosion data for the uranium-niobium alloys are given in Table 5. All uranium-niobium-base alloys tested in 500 F water had very low corrosion rates. Increasing zirconium additions resulted in progressively lower corrosion rates among uranium-10 w/o niobium alloys, while additions of chromium, molybdenum, and vanadium had very little effect.

In 680 F water, however, increasing zirconium additions above 1 w/o in uranium-10 w/o niobium-base alloys resulted in decreased corrosion life, although the 1 w/o addition resulted in a marked reduction in the corrosion rate. A 3 w/o molybdenum addition produced the longest corrosion life among the uranium-10 w/o niobium alloys.

A uranium-20 w/o niobium alloy and a uranium-20 w/o niobium-5 w/o zirconium alloy had the best corrosion resistances in 680 F water of any uranium-niobium-base alloys. Similar alloys with 3 and 10 w/o zirconium additions had short corrosion lives. Since all of these alloys would be expected to exhibit superior corrosion resistance on the basis of gamma stability, this anomalous behavior can best be explained as being caused by local inhomogeneities with resultant alloying depletion in some areas. Metallographic examination of a corroded and cracked uranium-20 w/o niobium-10 w/o zirconium specimen showed it to be attacked only in certain areas, while the remainder of the alloy was not attacked or transformed. Inhomogeneity is believed responsible for the apparent decrease in corrosion resistance with increasing zirconium additions in the uranium-10 w/o niobium-base alloys also.

Uranium-Molybdenum Alloys

In 500 F water, a 1 w/o addition of zirconium to a uranium-7.5 w/o molybdenum alloy resulted in a marked improvement in corrosion resistance over the binary alloy. However, increasing the zirconium addition above 1 w/o caused decreased corrosion resistance (see Table 6). Apparently, 1 w/o zirconium slows the hydride formation

TABLE 4. CORROSION DATA FOR URANIUM-ZIRCONIUM-BASE ALLOYS

Alloy Addition, w/o	Results of Tests in 500 F Water			Results of Tests in 680 F Water		
	Corrosion Life	Weight Change, mg/(cm ²)(hr)	Remarks	Corrosion Life	Weight Change, mg/(cm ²)(hr)	Remarks
<u>Uranium-10 w/o Zirconium Base</u>						
5 niobium-3 molybdenum	Broke at 3028 hr	-0.103	Some pitting attack	Disintegrated at 72 hr	--	--
<u>Uranium-20 w/o Zirconium Base</u>						
Base alloy	Taken off test at 72 hr	--	Very high weight loss	--	--	Not tested
1 niobium	Broke and cracked at 1344 hr	-0.051	--	Disintegrated at 72 hr	--	Completely oxidized
3 niobium	Cracked at 72 hr	--	Showed weight gain at 24 hr	--	--	Not tested
5 niobium	Cracked at 168 hr	-0.003	--	--	--	Not tested
1 molybdenum	Broke and cracked at 672 hr	-0.182	--	Disintegrated at 24 hr	--	Completely oxidized
3 molybdenum	Cracked at 168 hr	-0.026	--	--	--	Not tested
5 molybdenum	Broke at 3028 hr	-0.057	Some pitting attack	Disintegrated at 72 hr	--	Completely oxidized
3 niobium-3 molybdenum	Cracked at 1512 hr	-0.020	Some edge attack	Heavy attack at 72 hr, taken off test	--	--
2 vanadium	Cracked at 168 hr	-0.071	--	--	--	Not tested
2 ruthenium	Corrosion life >3028 hr	-0.058	Some pitting attack	Broke apart at 336 hr	-0.63	--
0.5 chromium	--	--	Not tested	Disintegrated at 24 hr	--	Completely oxidized

TABLE 4. (Continued)

Alloy Addition, w/o	Results of Tests in 500 F Water			Results of Tests in 680 F Water		
	Corrosion Life	Weight Change, mg/(cm ²)(hr)	Remarks	Corrosion Life	Weight Change, mg/(cm ²)(hr)	Remarks
<u>Uranium-30 w/o Zirconium Base</u>						
Base alloy	Disintegrated at 24 hr	--	--	--	--	Not tested
3 niobium	Disintegrated at 72 hr	--	Showed weight gain at 24 hr	--	--	Not tested
3 molybdenum	Cracked at 168 hr	+0.03	Showed weight gain at 72 hr	--	--	Not tested
<u>Uranium-40 w/o Zirconium Base</u>						
Base alloy	Bowing at 504 hr, taken off test	+0.022	Internal oxidation	--	--	Not tested
1 niobium	Bowing at 504 hr, taken off test	+0.018	Internal oxidation	Disintegrated at 24 hr	--	Completely oxidized
3 niobium	Corrosion life >3028 hr	-0.054	Some pitting attack	Disintegrated at 72 hr	-0.99	--
5 niobium	Corrosion life >3028 hr	-0.042	Attack at one corner	Disintegrated at 840 hr	-0.79	--
1 molybdenum	Bowing at 504 hr, removal from test	+0.024	Internal oxidation	Bowed 72 hr, taken off test	--	--
3 molybdenum	Broke at 3028 hr	-0.056	Probable internal oxidation	Disintegrated at 72 hr	--	--
5 molybdenum	Corrosion life >3028 hr	-0.005	Even corrosion	Disintegrated at 840 hr	-0.20	--

TABLE 5. CORROSION DATA FOR URANIUM-NIOBIUM-BASE ALLOYS

Alloy Addition, w/o	Results of Tests in 500 F Water			Results of Tests in 680 F Water		
	Corrosion Life	Weight Change, mg/(cm ²)(hr)	Remarks	Corrosion Life	Weight Change, mg/(cm ²)(hr)	Remarks
<u>Uranium-10 w/o Niobium Base</u>						
Base alloy	Corrosion life >3028 hr	-0.0012	Even corrosion	Disintegrated at 672 hr	-1.17	Corrosion rate accelerated rapidly with time
1 zirconium	Corrosion life >3028 hr	-0.0011	Greater attack on edges	Broke apart at 1176 hr	-0.17	Even attack until shortly before failure
3 zirconium	Corrosion life >3028 hr	-0.0006	Some pitting attack	Cracked at 72 hr	--	--
5 zirconium	--	--	Not tested	Disintegrated at 72 hr	--	--
10 zirconium	Corrosion life >3028 hr	-0.0004	Some attack at edges	Cracked at 72 hr	--	Some edge attack
1 molybdenum	Corrosion life >3028 hr	-0.0009	Even corrosion	Cracked at 162 hr	-0.03	Some edge attack
3 molybdenum	Corrosion life >3028 hr	-0.005	Some attack at edges	Disintegrated at 1344 hr	-0.35	Corrosion rate accelerated with time
5 molybdenum	Corrosion life >3028 hr	-0.0012	Even corrosion	Disintegrated at 1008 hr	-0.33	Ditto
5 zirconium-3 molybdenum	--	--	Not tested	Cracked at 72 hr	--	Some pitting attack
2 vanadium	Corrosion life >3028 hr	-0.0019	Some attack at edges	Disintegrated at 72 hr	--	Pitting attack at edges
0.5 chromium	Corrosion life >3028 hr	-0.004	Ditto	Cracked at 336 hr	-0.06	Some pitting attack
<u>Uranium-15 w/o Niobium Base</u>						
Base alloy	--	--	Not tested	Broke apart at 24 hr	--	Alloy probably was not homogeneous
5 zirconium	--	--	Not tested	Disintegrated at 336 hr	-0.09	Some pitting attack
3 molybdenum	--	--	Not tested	Disintegrated at 840 hr	-0.25	Some pitting attack

TABLE 5. (Continued)

Alloy Addition, w/o	Results of Tests in 500 F Water			Results of Tests in 680 F Water		
	Corrosion Life	Weight Change, mg/(cm ²)(hr)	Remarks	Corrosion Life	Weight Change, mg/(cm ²)(hr)	Remarks
<u>Uranium-20 w/o Niobium Base</u>						
Base alloy	--	--	Not tested	Corrosion life >1848 hr	-0.03	Even attack
3 zirconium	--	--	Not tested	Disintegrated at 840 hr	-0.16	Some pitting attack
5 zirconium	--	--	Not tested	Corrosion life >1848 hr	-0.02	Even attack
10 zirconium	--	--	Not tested	Cracked at 336 hr	-0.02	Pitting attack and cracking
5 molybdenum	--	--	Not tested	Disintegrated at 672 hr	-1.50	Pitting attack

TABLE 6 CORROSION DATA FOR URANIUM-MOLYBDENUM-BASE ALLOYS

Alloy Addition, w/o	Results of Tests in 500 F Water			Results of Tests in 680 F Water		
	Corrosion Life	Weight Change, mg/(cm ²)(hr)	Remarks	Corrosion Life	Weight Change, mg/(cm ²)(hr)	Remarks
Uranium-7.5 w/o Molybdenum Base						
Base alloy	Broke apart at 336 hr	-0.80	Hydride formation	--	--	Not tested
1 zirconium	Cracked at 3028 hr	-0.09	Some pitting attack	--	--	Not tested
3 zirconium	Broke apart at 3028 hr	-0.29	Some pitting attack and chipping	--	--	Not tested
5 zirconium	Cracked at 336 hr	-0.66	Internal oxidation	--	--	Not tested
10 zirconium	Cracked at 840 hr	-0.24	Internal oxidation	--	--	Not tested
1 niobium	Corrosion life >3028 hr	-0.02	Even attack	Disintegrated at 168 hr	-4.11	Very high weight loss
3 niobium	Corrosion life >3028 hr	-0.015	Even attack	Disintegrated at 672 hr	-0.50	Heavier attack on edges
5 niobium	Corrosion life >3028 hr	-0.005	Even attack	Disintegrated at 672 hr	-0.65	Heavy attack on one face and edge
5 zirconium-3 niobium	Corrosion life >3028 hr	-0.007	Pitting attack on edge	Disintegrated at 168 hr	-0.22	Heavier attack on corners
2 vanadium	Very heavy attack at 1512 hr, removed from test	-0.35	Edges and corners attacked	--	--	Not tested
2 ruthenium	Corrosion life >3028 hr	-0.015	Some pitting attack	Corrosion life >1848 hr	-0.28	Corrosion rate increased at 1344 hr, attack even
0.5 chromium	--	--	Not tested	Disintegrated 168 hr	-0.22	Even attack before failure

TABLE 6. (Continued)

Alloy Addition, w/o	Results of Tests in 500 F Water			Results of Tests in 680 F Water		
	Corrosion Life	Weight Change, mg/(cm ²)(hr)	Remarks	Corrosion Life	Weight Change, mg/(cm ²)(hr)	Remarks
<u>Uranium-7.5 w/o Molybdenum Base</u> (Continued)						
3 niobium-2 ruthenium	--	--	Not tested	Corrosion life >672 hr	-0.14	Some pitting attack
2 niobium-2 ruthenium	--	--	Not tested	Corrosion life >672 hr	-0.08	
<u>Uranium-10 w/o Molybdenum Base</u>						
1 niobium	--	--	Not tested	Corrosion life >672 hr	-0.27	
3 niobium	--	--	Not tested	Disintegrated 168 hr	-2.10	Edge and corner attack
5 niobium	--	--	Not tested	Disintegrated 672 hr	-0.35	Even attack before failure
3 niobium-2 ruthenium	--	--	Not tested	Corrosion life >672 hr	-0.02	Even attack
2 niobium-1 ruthenium	--	--	Not tested	Corrosion life >672 hr	-0.15	Even attack
<u>Uranium-12 w/o Molybdenum Base</u>						
1 niobium	--	--	Not tested	Disintegrated at 336 hr	-1.32	Large increase in corrosion rate after 72 hr
3 niobium	--	--	Not tested	Disintegrated at 336 hr	-1.85	Ditto
5 niobium	--	--	Not tested	Disintegrated at 336 hr	-2.63	Ditto
2 niobium-1 ruthenium	--	--	Not tested	Corrosion life >672 hr	-0.27	Even attack

which led to the failure of the binary alloy, while adding more zirconium results in the formation of ZrMo_2 , which ties up molybdenum and consequently decreases gamma stability. The higher zirconium alloys appeared to fail by oxidation.

Increasing niobium contents from 1 to 5 w/o resulted in progressively lower corrosion rates for the uranium-7.5 w/o molybdenum-niobium alloys in 500 F water. At 680 F, the alloy with a 3 w/o niobium addition exhibited the lowest corrosion rates. In transformation-kinetics studies, this alloy exhibited the greatest thermal stability of the alloys with niobium additions.

A uranium-7.5 w/o molybdenum-2 w/o ruthenium alloy exhibited the best corrosion behavior in 680 F water of any uranium-molybdenum-base alloy. This corrosion resistance can probably be attributed to gamma stability, which was the greatest of any of the uranium-7.5 w/o molybdenum-base ternary alloys tested.

Quaternary uranium-7.5 w/o molybdenum-niobium-ruthenium alloys had reasonably good corrosion resistance in 680 F water, although none was as promising as the uranium-7.5 w/o molybdenum-2 w/o ruthenium alloy.

Uranium-10 w/o molybdenum-niobium alloys had relatively high corrosion rates in 680 F water. However, a uranium-10 w/o molybdenum-3 w/o niobium-2 w/o ruthenium alloy corroded at a very low rate after 672 hr of test.

Uranium-12 w/o molybdenum-niobium alloys failed within a short time in 680 F water, having high corrosion rates. Increasing niobium levels resulted in progressively faster corrosion. A quaternary uranium-12 w/o molybdenum-2 w/o niobium-1 w/o ruthenium alloy survived 672 hr of test, although corrosion rates were high. Unfortunately, neither the uranium-10 nor 12 w/o molybdenum-2 w/o ruthenium alloy could be fabricated into corrosion specimens. From a thermal-stability standpoint, these alloys should have improved corrosion properties.

Thermal Analysis

Thermal-analysis experiments were conducted over the range of temperature in which transformation of the alloys occurs. As noted, two techniques were employed in obtaining these data, time-temperature and differential thermal analysis. The latter method is believed to provide the better indication of the absolute temperature at which transformation begins in the alloys, since the heating rate employed permits more nearly equilibrium transformation. The time-temperature thermal data provide primarily an indication of the relative effects of alloying.

Uranium-Zirconium Alloys

Niobium additions to uranium-zirconium alloys, as shown in Table 7, reduced the temperature at which the intermediate uranium-zirconium delta phase transformed to gamma on heating. In the uranium-20 w/o zirconium-base alloys, the thermal effect associated with this transformation was noted only in the alloy containing a 1 w/o niobium addition. Apparently this transformation is depressed sufficiently with higher niobium additions that the alpha-plus-gamma structure is retained at room temperature. The depression of this transformation is further evidenced by the data recorded for the

TABLE 7. THERMAL-ANALYSIS DATA FOR URANIUM-ZIRCONIUM-BASE ALLOYS

Alloy Addition, w/o	Transformation Temperature of Room-Temperature Structure on Heating, C	Temperature of Complete Transformation of Gamma on Heating, C
<u>Uranium-10 w/o Zirconium Base</u>		
5 niobium-3 molybdenum	598(a)	632(a)
<u>Uranium-20 w/o Zirconium Base</u>		
Base alloy	606(b)	701(b)
1 niobium	578-602(b)	672(b)
3 niobium	--	668(b)
5 niobium	--	643(a)
1 molybdenum	587-606(b)	674(b)
5 molybdenum	543(a)	639(a)
3 niobium-3 molybdenum	565(a)	632(a)
2 vanadium	588-604(a)	671(a)
2 ruthenium	566-584(b)	674(b)
0.5 chromium	596-603(b)	665(b)
<u>Uranium-30 w/o Zirconium Base</u>		
Base alloy	608(b)	684(b)
3 niobium	586-603(b)	658(b)
3 molybdenum	586(b)	664(b)
<u>Uranium-40 w/o Zirconium Base</u>		
1 niobium	566(b)	609(b)
3 niobium	564(b)	598(b)
5 niobium	440-551(a)	576(a)
1 molybdenum	582(b)	618(b)
3 molybdenum	579(b)	610(b)
5 molybdenum	565(b)	586(b)

(a) Differential thermal analysis.

(b) Time-temperature analysis.

40 w/o zirconium-base alloys. The trends are in general agreement with the published uranium-zirconium-niobium phase diagram⁽⁴⁾ which for equal niobium additions also indicated the more pronounced lowering of the gamma-to-delta transformation temperature in lower zirconium alloys.

Niobium also produced a marked decrease in the temperature of the alpha plus gamma-to-gamma transus temperature.

The effect of molybdenum additions was very similar to that of niobium. While slightly less pronounced, both the temperature at which alpha uranium begins to precipitate from the gamma phase and the temperature at which delta begins to form from the gamma phase were lowered by molybdenum additions.

Chromium, ruthenium, and vanadium additions were also found to increase the temperature range of gamma stability.

There appears to be a direct relationship in these alloys between thermal stability of the gamma phase and the temperature range of gamma-phase stability. Thus all of the additions investigated were found to both depress the temperature at which gamma-phase decomposition is initiated and to decrease the rate of thermal decomposition of the gamma phase.

Uranium-Niobium Alloys

Based upon the data recorded in Table 8, the principal effect of zirconium on uranium-niobium-base alloys appears to be to increase the temperature range over which alpha uranium decomposes to gamma on heating, particularly for additions up to 3 w/o. Thus little change was noted in the temperature at which alpha disappears completely, either for the uranium-10 or -20 w/o niobium-base alloys. However, as shown for the uranium-10 w/o niobium-10 w/o zirconium alloy, the temperature at which the transformation of alpha uranium is complete on heating was depressed by increasing amounts of zirconium. No evidence for transformation was obtained with the uranium-20 w/o niobium-5 or -10 w/o zirconium alloys. These specimens were aged at 500 C prior to analysis. Apparently either the transformation temperature of these alloys is lower than the aging temperature, or the transformation occurs so sluggishly that insufficient transformation occurred to produce a noticeable heat effect on reheating.

As with zirconium, molybdenum additions depressed the temperature at which alpha begins to decompose on heating. Also, the temperature at which the decomposition of alpha is complete appears to be little affected by molybdenum additions up to 5 w/o.

Chromium, ruthenium, and vanadium additions acted in a manner similar to zirconium and molybdenum. However, the temperature at which the transformation of alpha is complete on heating is apparently depressed by the addition of 2 w/o ruthenium.

Uranium-Molybdenum Alloys

Differential-thermal-analysis data obtained on uranium-molybdenum-base alloys are recorded in Table 9. Attempts to obtain additional data by time-temperature analysis, which involves heating at fairly rapid rates, were unsuccessful, the results

TABLE 8. THERMAL-ANALYSIS DATA FOR URANIUM-NIOBIUM-BASE ALLOYS

Alloy Addition, w/o	Beginning and End of Transformation to Gamma on Heating, C
<u>Uranium-10 w/o Niobium Base</u>	
Base alloy	654(a)
1 zirconium	650-654(a)
3 zirconium	611-656(a)
10 zirconium	594-623(a)
1 molybdenum	646-651(a)
3 molybdenum	-650(a)
5 molybdenum	615-646(b)
5 zirconium-3 molybdenum	598-632(b)
2 vanadium	632-649(b)
2 ruthenium	610-621(b)
0.5 chromium	632-649(b)
<u>Uranium-15 w/o Niobium Base</u>	
5 zirconium	610-632(b)
3 molybdenum	610-657(b)
<u>Uranium-20 w/o Niobium Base</u>	
Base alloy	652(a)
3 zirconium	622-652(b)
5 zirconium	Not detected
10 zirconium	Not detected
3 molybdenum	639-648(a)
5 molybdenum	598-654(b)

(a) Time-temperature analysis.

(b) Differential thermal analysis.

TABLE 9. DIFFERENTIAL-THERMAL-ANALYSIS DATA FOR
URANIUM-MOLYBDENUM-BASE ALLOYS

Alloy Addition, w/o	Beginning and End of Transformation to Gamma on Heating, C
<u>Uranium-7.5 w/o Molybdenum Base</u>	
<u>Uranium-12 w/o Molybdenum Base</u>	
3 zirconium	615-638
10 zirconium	593-649
1 niobium	599-638
5 niobium	579-624
5 zirconium-3 niobium	598-626
2 ruthenium	565-574
<u>Uranium-12 w/o Molybdenum Base</u>	
3 zirconium	560-606
5 zirconium	580-629

obtained being inconsistent and exhibiting great variability. Apparently the transformation of these alloys is sluggish on heating and, consequently, the temperatures at which heat effects are observed are sensitive to the rate of heating.

The addition of 3 w/o zirconium to the uranium-7.5 w/o molybdenum-base alloy raised the temperature at which gamma begins to form on heating as did the addition of 10 w/o zirconium. Based on available data concerning phase relationships in the uranium-molybdenum-zirconium system⁽²⁾, it appears doubtful that the transformation temperatures recorded are related to the decomposition of the uranium-molybdenum delta phase, which occurs at about 575 C in the binary alloy. The ternary 3 w/o zirconium alloy is close to the alloy composition at which alpha uranium and ZrMo_2 are the phases stable at room temperature, while in the uranium-7.5 w/o molybdenum-10 w/o zirconium alloy the phases stable at room temperature are alpha uranium, ZrMo_2 , and the uranium-zirconium delta phase.

The transformation temperatures recorded for the uranium-12 w/o molybdenum-3 and -5 w/o zirconium alloys indicate a slight lowering of the temperature at which the uranium-molybdenum delta phase begins to decompose on heating. In these alloys sufficient delta is present along with alpha and ZrMo_2 to produce a detectable heat effect. The temperature recorded for the end of transformation is that associated with the disappearance of the alpha phase on heating.

The effect of niobium on the transformation temperature of the uranium-7.5 w/o molybdenum-base alloy appears slight, the temperature being raised slightly. Ruthenium apparently depresses the temperature at which delta decomposes to gamma on heating.

SUMMARY AND CONCLUSIONS

During the course of this program it was observed that, as expected, gamma-phase stability was greatest in the uranium-molybdenum system and least in the uranium-zirconium system. The gamma phase in the uranium-niobium system exhibited intermediate stability. It was further observed that in each system substantial improvement in stability and strength properties could be imparted by ternary or quaternary alloying.

Additions of niobium or molybdenum to uranium-20 and -40 w/o zirconium-base alloys were found to result in fairly pronounced increases in thermal stability of the gamma phase. Chromium, ruthenium, and vanadium additions also effected slight improvements in stability. Niobium and molybdenum additions were also observed to increase the hot hardness of the uranium-zirconium gamma phase; chromium, ruthenium, and vanadium exhibited little effect. All additions were observed to increase the temperature range of gamma stability over that of the base alloys, depressing the temperature at which alpha begins to precipitate from the gamma phase and depressing the temperature at which gamma decomposes to the intermediate uranium-zirconium delta phase. With the exception of chromium, whose effect was not determined, all additions also effected some reduction in the corrosion rate of the base alloys. However, corrosion lives were generally rather short, the short lives probably being associated with failure by transformation-induced stresses.

Results were more variable in uranium-niobium-base alloys. Zirconium additions were found to increase the thermal stability of the gamma phase and to depress the temperature at which alpha uranium begins to decompose to gamma on heating. Fairly large additions, 10 w/o zirconium to the uranium-10 w/o niobium-base alloy, and 5 w/o zirconium to the uranium-20 w/o niobium-base alloy, were required to depress the temperature at which the alpha phase disappears completely on heating. Zirconium also appeared to improve the corrosion resistance of uranium-niobium-base alloys, although results were variable as a result of alloy inhomogeneity. Optimum increases in hot hardness of the gamma phase were achieved with a 1 w/o addition of zirconium to the uranium-10 w/o niobium-base alloy and with 5 w/o addition to the 20 w/o niobium alloy. From the viewpoint of corrosion behavior and hot strength, the uranium-20 w/o niobium-5 w/o zirconium alloy possessed the best combination of any of the uranium-niobium-base alloys tested.

Molybdenum additions to the uranium-10 w/o niobium-base alloy had a negligible effect on the thermal stability of the gamma phase, a 1 w/o addition effecting a slight decrease in transformation rate. In the 20 w/o niobium alloy, molybdenum additions were detrimental to gamma stability. Molybdenum was also observed to depress the temperature at which the alpha-uranium phase begins to decompose to gamma on heating but to have very little effect on the temperature at which the decomposition of alpha is complete on heating. As with zirconium additions, molybdenum additions must apparently be controlled for optimum hot hardness: 1 w/o molybdenum to the 10 w/o niobium alloy or 3 w/o molybdenum added to the 20 w/o niobium alloy were found to result in maximum hardness of the gamma phase at elevated temperatures. In general, molybdenum additions exhibited little effect on the corrosion resistance of uranium-niobium-base alloys, although a 3 w/o molybdenum addition was found to increase the corrosion life of the 10 w/o niobium alloy.

Chromium, ruthenium, or vanadium additions were not observed to exhibit any pronounced effects on either thermal stability, corrosion resistance, or hot hardness of uranium-niobium-base alloys. All three additions, however, did slightly depress the temperature at which alpha-uranium decomposition begins on heating.

Additions of up to 3 w/o niobium to the uranium-7.5 w/o molybdenum-base alloy and the addition of 1 w/o niobium to 10 and 12 w/o molybdenum alloys were observed to result in increased thermal gamma-phase stability, while greater amounts of niobium were detrimental to stability. A possible slight increase in the temperature at which gamma forms on heating was noted with niobium additions. Ruthenium was also found to be very effective in increasing the stability of the gamma phase; ruthenium was also observed to depress the delta-to-gamma transformation temperature. In quaternary combination, 2 w/o ruthenium and 2 w/o niobium when added to the binary alloys also resulted in improved thermal stability, while increasing the niobium content to 3 w/o was responsible for decreased stability.

Niobium additions to the uranium-7.5 w/o molybdenum-base alloy also increased the hot hardness of the gamma phase, although in the 10 and 12 w/o molybdenum alloy additions above 1 w/o niobium were found to be responsible for decreased hot hardness. The decreased hot hardness and decreased thermal stability of the gamma phase at higher niobium additions is believed to result from the formation of two gamma phases and resultant alloy depletion of the uranium-molybdenum gamma phase. Ruthenium additions were found to decrease the hardness of both the uranium-molybdenum-base and uranium-molybdenum-niobium-base alloys.

Niobium additions to uranium-molybdenum-base alloys were observed to be responsible for decreased corrosion rates. However, 2 w/o ruthenium additions were found to be more effective in increasing corrosion resistance than equivalent amounts of niobium. A uranium-7.5 w/o molybdenum quaternary alloy containing niobium and ruthenium also exhibited improved corrosion resistance, although ruthenium alone was more effective in increasing corrosion resistance.

Zirconium additions were found to be generally detrimental to uranium-molybdenum-base alloys. Apparently the formation of $ZrMo_2$ resulting from this addition is responsible for depletion of the molybdenum content of the gamma phase. Consequently, decreased thermal stability, decreased hot hardness, and decreased corrosion resistance result.

Vanadium and chromium additions generally exhibited a negligible effect on uranium-molybdenum-base alloy behavior.

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