Facsimile Price \$ 3.65

Microfilm Price \$ 1.16

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

This paper was submitted for publication in the open literature at least 6 months prior to the issuance date of this Microcard. Since the U.S.A.E.C. has no evidence that it has been published, the paper is being distributed in Microcard form as a preprint.

IS 474

THE URANIUM-RHENIUM ALLOY SYSTEM*

R. J. Jackson, D. E. Williams and W. L. Larsen

Institute for Atomic Research and Department of Metallurgy

Iowa State University, Ames, Iowa

MASTER

ABSTRACT

The phase diagram of the uranium-rhenium alloy system is presented along with a discussion on transformation kinetics of the uranium solid solutions.

The phase diagram is of the double eutectic type with the intermediate phase having the composition URe_2 . This phase exhibits allotropy at 180°C and melts congruently at 2200°C . URe_2 reacts sluggishly with the uranium solid solutions below 750°C to form the peritectoid compound U_2Re . Eutectic reactions occur at 1105 and 2105°C at respective compositions of 10.5 and 65.5 wt. % Re. Eutectoid reactions occur at 643 and 681°C at compositions of 1.4 and 6 wt. % Re, respectively. The maximum solubility of rhenium in α uranium is about 0.4 wt. % at 643°C and in β uranium is 1.9 wt. % at 681°C . The solubility of rhenium in γ uranium is 6 wt. % at 681°C and increases to about 7 wt. % at 975°C . The solubility of uranium in rhenium is 0.6 wt. % at room temperature with little variation up to 2000°C .

Alloys of β and γ uranium containing more than about 1.2 and 7 wt. % Re, respectively, can be readily supercooled to room temperature.

* Contribution No. 1255. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

Rapid cooling of γ alloys containing less than about 7 wt. % Re resulted in a direct $\gamma \rightarrow \alpha'$ transformation — the α' state being a supersaturated α phase having a banded microstructure. Evidence is presented for the existence of two transition states, one involving the γ phase decomposition and the other the $\beta \rightarrow \alpha$ transformation. Also, the sequence of phase changes involved in cooling the uranium solid solutions is discussed.

INTRODUCTION

The investigation of the uranium-rhenium alloy system was undertaken as part of a general program to increase the knowledge concerning the alloying behavior of uranium. A search of the literature revealed only two significant research studies dealing with uranium-rhenium alloys. These articles described the structure determination of the URe_2 compound by HATT¹, and tentative phase relationship studies conducted at Fulmer Research Institute in England and reported by ROUGH AND BAUER² in their compilation of uranium and thorium phase diagrams.

ALLOY PREPARATION

The uranium used in the preparation of alloys was from a direct cast ingot produced at the Hanford Works of the General Electric Company. The rhenium was first grade metal purchased from the Chase Brass and Copper Company in the form of 0.040-in. strip. A partial chemical analysis of both metals is given in Table I.

All the alloys were prepared by melting under an inert atmosphere in a nonconsumable tungsten electrode arc furnace. The melting procedure has been discussed by WILLIAMS AND LEVINGSTON³. Some difficulty arose in dissolving rhenium in the uranium-rich liquid. This

TABLE I
CHEMICAL ANALYSIS OF THE CONSTITUENT METALS

Impurity Atom	Amount Present [*]	
	Uranium	Rhenium
Al	20 ppm ^{**}	not detected
C	36 ppm	150 ppm ^{**}
Ca		trace
Cr	2 ppm ^{**}	trace
Cu		trace
Fe	18 ppm ^{**}	not detected
H	4 ppm	not determined
Mg	3 ppm	trace
Mn	5 ppm	not detected
Ni	10 ppm	not detected
Pb	5 ppm	not detected
Si	22 ppm	not detected

* Spectrographic analysis unless indicated otherwise.

** Gravimetric analysis.

difficulty was minimized either by using smaller rhenium particles or by employing a URe_2 compound master alloy. Spectrographic analysis indicated no contamination from the copper hearth or the tungsten electrode. The weight changes on melting were such that in most cases the apparent uncertainty in composition was about 0.2 wt. % or less. For these reasons the intended composition was assumed to be the actual composition.

Most of the alloys were heat treated in a tantalum container under vacuum to improve homogeneity. Alloys containing less than 61 wt. % rhenium, the composition of the compound URe_2 , were heat treated for one week at 900°C. Those containing more than 61 wt. % rhenium were heat treated at 1300°C for 11 days.

ALLOY EXAMINATION

The alloys were examined by standard techniques. All the experiments which required heating of the specimens were conducted at

pressures of 10^{-5} mm of mercury or less and when necessary a tantalum container was used to hold the specimens.

Melting Point Determinations. The method of WILLIAMS⁴ was used to obtain solidus data. The solidus temperatures obtained from the necked-down bar specimens were determined by observing the temperature at which molten metal disrupted the black-body conditions by causing a dark spot to appear at the bottom of the pyrometer sight hole. Approximate liquidus values were determined by an extension of the above method. To obtain the liquidus temperature from experimental data a plot of black-body vs. surface temperature was made. After the black body was destroyed due to filling of the hole with liquid, the true temperature was estimated by an extrapolation of the curve. The last corrected temperature reading taken before the alloy bar melted completely in two was considered to be the approximate liquidus temperature.

Differential Thermal Analysis. Differential thermal analysis was also used to locate phase transformations. Specimens varied in size from 2 to 20 g. Heating rates, while held constant during a given run, were varied from 10 to 60°C/h, generally being 30°C/h. Nickel or tantalum was used as the neutral body and alumina as the insulation. Pt/Pt-Rh thermocouples were pressed into holes drilled in the center of the neutral body and the test specimen. Temperatures were read directly with manually operated high precision potentiometers or automatically recorded with a Mosely "Autograf" x-y recorder. A proportional band program controller was used to assure a linear heating and cooling rate.

Quenching. Two methods of quenching were used in the metallographic investigation of the alloys. The method for quenching from temperatures

below 1000°C consisted of joining a sample to a thermocouple bead and then suspending the unit in a vertical silica tube which was surrounded by a vertical tube furnace. The head through which the thermocouple wires passed was provided with a thin glass window sealed on with a silicone vacuum grease. Above this was a reservoir that could be filled with water. When the specimen was ready to be quenched, the reservoir was filled with ice water and the cover glass broken allowing the evacuated silica tube to be filled with water almost instantaneously. At the same time, the furnace was lowered rapidly away from the tube.

A sample to be quenched from above 1000°C was machined into a bar of small cross section which was then placed between two large water-cooled electrodes and heated by its own electrical resistance. The true temperature of the specimen was measured with an optical pyrometer utilizing the relationship between the surface temperature and true temperature observed in the solidus and liquidus determinations. When the power was turned off, the large water-cooled electrodes produced a rapid cooling of the specimen. Cooling rates of approximately 750°C/sec were attained in this manner.

Metallography. Standard mechanical polishing techniques were used for metallographic preparation of alloys. A chemical etchant composed of 6 parts by weight of $K_3Fe(CN)_6$, 2 parts KOH, and 92 parts H_2O satisfactorily etched the rhenium and URe_2 phases. The U_2Re phase was revealed by extended polishing and could be further delineated by ion bombardment etching. The α phase alloys could generally be satisfactorily etched with an electrolyte containing 36 parts by weight of HNO_3 (70%), 1 part citric acid, and 63 parts H_2O . Etching by ion bombardment was

used for the γ and β phase alloys and for the difficulty etched α phase alloys.

X-Ray Diffraction. Phase identification and phase boundary determinations were conducted by x-ray diffraction methods using copper radiation with a Norelco diffractometer, a 114.6 mm Debye-Scherrer camera, or a 120 mm symmetrical back-reflection focusing camera. The high temperature x-ray work was performed with equipment similar to that described by CHIOTTI⁵.

The x-ray specimens were in the form of either a flat bar or fine powders. The bar specimens used in the diffractometer were mechanically polished and were often etched. For heat treated massive specimens containing a uranium phase it was necessary to remove up to 0.1 mm of surface to reach areas that were free of UO_2 and UC. To prepare powder specimens, alloys containing 40 to 99 wt. % Re were readily crushed while alloys containing less than 40 wt. % Re were reduced to powder by filing. Only material passing a 200 mesh screen was used. The powder was treated magnetically to remove any iron contamination and was then given a stress-relief anneal. Surface contamination during annealing was a problem for powders containing a uranium phase. When this happened, the powders were used in the as-filed condition. To produce the specimens for the Debye-Scherrer camera a glass fiber coated with a hydrocarbon grease was rolled in the powder. For the back-reflection camera and diffractometer the powder was spread on a transparent sheet and affixed to it with transparent tape or a cement-acetone mixture.

CONSTITUTIONAL DIAGRAM

Figures 1 and 2 show the constitutional diagram resulting from this investigation. Figures 3-14 are photomicrographs representative of the observed microstructures.

Solidus and Liquidus. The results of the melting point determinations are listed in Table II. The solidus results established the eutectic temperatures as being $1105 \pm 5^\circ$ and $2105 \pm 40^\circ\text{C}$. The liquidus values are considered only approximate and for this reason the liquidus line is dotted. An independent determination of the U- URe_2 eutectic isotherm temperature by differential thermal analysis yielded a value of 1103°C which is in good agreement with data of Table II.

TABLE II
SOLIDUS AND LIQUIDUS TEMPERATURES

Composition (wt. % Re)	Solidus temperature ($^\circ\text{C}$)	Liquidus temperature ($^\circ\text{C}$)
2	1124	1124
5	1104	1114
10	1103	
20	1107	
20	1107	
25	1112	1200
30	1104	1410
40	1105	1740
50	1113	2025
55	1104	2120
60	2116	2200
61	2200	
65	2145	2170
70	2070	2175
75	2135	2230
80	2085	2250
90	2085	2300
95	2125	2830

The eutectic compositions were determined by optical metallography of as-cast alloys and are in qualitative agreement with the

Fig. 1. The uranium-rhenium phase diagram.

Fig. 2. The eutectoid regions.

Fig. 3. The 1 wt.% Re alloy water quenched after 12 h at 690°C showing acicular α in a β matrix. Ion bombardment etch. X120

Fig. 4. The 4 wt.% Re alloy water quenched after 43 h at 700°C showing retained β (raised areas) and decomposed γ . Ion bombardment etch. X940

Fig. 5. The 6 wt.% Re alloy water quenched after 43 h at 700°C showing the banded microstructure of the α' state amidst prior γ grain boundaries. Ion bombardment etch. X500

Fig. 6. The 6 wt.% Re alloy heated at 900°C for one week and cooled at 9°C/h showing eutectoid mixture of α uranium and U_2Re . Ion bombardment etch. X680

Fig. 7. The 8 wt.% Re alloy water quenched after 72 h at 975°C showing globules of URe_2 in γ matrix. Ion bombardment etch. X500

Fig. 8. The 10.5 wt.% Re as-cast alloy showing eutectic structure of fine URe_2 particles in γ matrix. Ion bombardment etch. X250

Fig. 9. The 20 wt.% Re alloy heated 3 weeks at 700°C and furnace cooled showing primary URe_2 (dark) with eutectoid and peritectoid U_2Re (white) in α uranium matrix (grey). Etchant: $\text{K}_3\text{Fe}(\text{CN})_6$, KOH, H_2O . X250

Fig. 10. The 25 wt.% Re alloy heated one week at 900°C and slow cooled showing primary URe_2 in unetched eutectic matrix. Etchant: $\text{K}_3\text{Fe}(\text{CN})_6$, KOH, H_2O . X500

Fig. 11. The 61 wt.% Re as-cast alloy showing the URe_2 microstructure. Etchant: $\text{K}_3\text{Fe}(\text{CN})_6$, KOH, H_2O . X500

Fig. 12. The 65 wt.% Re as-cast alloy showing eutectic structure of URe_2 particles in rhenium matrix. Etchant: $\text{K}_3\text{Fe}(\text{CN})_6$, KOH, H_2O . X1220

Fig. 13. The 75 wt.% Re alloy heated 11 days at 1300°C and slow cooled showing primary rhenium in eutectic matrix. Etchant: $\text{K}_3\text{Fe}(\text{CN})_6$, KOH, H_2O . X1200

Fig. 14. The 99 wt.% Re alloy heated 7 h at 2000°C and slow cooled showing rhenium matrix with URe_2 at grain boundaries. Etchant: $\text{K}_3\text{Fe}(\text{CN})_6$, KOH, H_2O . X500

liquidus data. Because of the atypical appearance of the U- URe_2 eutectic, the method used to locate the eutectic composition was to microscopically determine the amount of proeutectic URe_2 present and then to extrapolate to zero concentration of proeutectic URe_2 . A U- URe_2 eutectic composition of 10.5 wt. % Re (see Fig. 8) was deduced in this manner. The URe_2 -Re eutectic alloy exhibited a more typical eutectic microstructure. Metallographic observation of the as-cast 63.5, 65 and 66.5 wt. % alloys showed the composition of this eutectic to be 65.5 wt. % Re. The eutectic structure is shown in Fig. 12.

URe_2 Intermediate Phase. Solidus temperature measurements and metallography indicated that an intermediate phase existed at 61 wt. % Re, corresponding to the stoichiometric formula URe_2 . This phase was observed to melt congruently at 2200°C and to have a gravimetrically determined density of 18.53 g/cm³ at 24°C. The interplanar spacings obtained from Debye-Scherrer and back-reflection photographs as well as metallographic findings indicate the low temperature solubility range of the URe_2 phase to be much less than one weight percent. Figure 11 is a photomicrograph of this intermediate phase.

HATT¹, on the basis of x-ray studies, reported that above 180°C, URe_2 has a C14 Laves structure whereas below this temperature a lower symmetry orthorhombic structure is observed. The room temperature structure proposed by HATT has been verified in this investigation and is hereafter referred to as $\text{URe}_2(\text{L})$. Some evidence for a possible stacking disorder in $\text{URe}_2(\text{L})$ was observed. Weissenberg photographs showed splitting of the reflections along the [100] and [010] axes as well as in transverse directions. The splitting of reflections in the transverse directions was due to small misorientations within the single crystal.

The splitting of reflections along the $[100]$ and $[010]$ axes implied the possible existence of two distinct structures having slightly different a_0 and b_0 lattice parameters.

The allotropic transformation observed by HATT was substantiated by differential thermal analysis. The results of 11 analyses using various heating and cooling rates showed that at rates of 40°C/h or less the allotropic transformation temperature is $180 \pm 2^\circ\text{C}$ and that only a small heat effect is associated with the transformation.

U_2Re Intermediate Phase. A 20 wt. % Re alloy heat treated for three weeks at 700°C showed the development of an envelope around the primary URe_2 dendrites. The microstructure of this nonequilibrated three-phase alloy is shown in Fig. 9. The grey matrix is α uranium, the white phase is U_2Re and the dark material which is enclosed by the white envelope is primary URe_2 .

Due to the sluggish nature of this reaction the composition of the U_2Re phase was determined by a quantitative metallographic analysis. Point counts were made on the two-phase 5 and 10 wt. % alloys and on the three-phase 12.5 and 20 wt. % alloys. Each alloy was subjected to approximately 1200 counts. These point counts yielded an average composition of 27.8 wt. % Re for the unknown phase. This value compares favorably with the stoichiometric composition of 28.1 wt. % Re for a 2:1 atom ratio. Thus the composition of the unknown phase was concluded to be U_2Re .

For the quantitative analysis it was necessary to know the densities of the phases present. Knowing the density of the α solid solution, a gravimetric density determination combined with a quantitative phase

analysis on the two-phase 10 wt. % Re alloy yielded a density of 18.97 g/cm³ at 24°C for the U₂Re phase.

The nature of the microstructure indicated the U₂Re phase formed via a peritectoid reaction. To determine the temperature of the peritectoid reaction isotherm, alloys of compositions 12.5, 20, 30, 40 and 50 wt. % Re were heat treated at 720°C for periods up to three weeks. These alloys were then subjected to differential thermal analysis. The results of these analyses, which are listed in Table III, show the temperature of the peritectoid reaction isotherm to be 750°C. Tracings of representative DTA heating curves are shown in Fig. 15.

The values listed in Table III that are in parentheses are ones obtained from alloys of nonequilibrium phase distribution and do not belong in the equilibrium diagram. As mentioned earlier, the homogenizing treatment consisted of heat treating at 900°C followed by slow cooling. This treatment did not produce any appreciable U₂Re other than that formed during the γ and β phase decompositions (see Fig. 10). Subsequent differential thermal analysis of these alloys yielded values for only the $\alpha \rightarrow \beta$ and $\beta \rightarrow \gamma$ transformations. Due to the sluggish nature of the $\text{URe}_2 + \gamma \rightarrow \text{U}_2\text{Re}$ reaction, the alloys heat treated at 720°C produced equilibrium structures only in the 40 and 50 wt. % alloys while the others still contained some unreacted uranium and URe₂. Thus, the $\alpha \rightarrow \beta$ and $\beta \rightarrow \gamma$ transformations were detected in the heat-treated 30 wt. % alloy.

The structure of the U₂Re phase was not determined nor were any efforts made to determine its compositional limits.

TABLE III
RESULTS FROM DIFFERENTIAL HEATING CURVES

Composition (wt. % Re)	Temperature of α - β transformation (°C)	Temperature of β - γ transformation (°C)	Temperature of U ₂ Re decomposition (°C)
0.0	663	771	
0.5	644-652	761	
	646-654		
	645-654	761	
1.0	644	740-765	
1.5	643		
	644	717-746	
	632	721-747	
2.0	642	684-745	
	648	682-730	
3.0	644	680-728	
	644	682-730	
5.0	644	683-698	
	642	682-705	
10.0	642	679	
	642	679	
12.5	646	683	752
20	643	679	
	645	680	752
	644	685	745
30	(643)	(678)	
	(644)	(680)	753
40	(644)	(679)	
			750
50	(644)	(678)	
	(642)	(679)	
			748

Eutectoid Transformations. It is evident from the data of Table III that the addition of rhenium to uranium produces a lowering of the transition temperatures such that two eutectoid reaction isotherms exist and that both terminate at the U₂Re intermediate phase. The temperatures of the α - β and β - γ eutectoid reaction isotherms are $643 \pm 3^\circ$ and $681 \pm 3^\circ\text{C}$, respectively. Figure 15 is representative of the types of differential heating curves obtained. An independent check on the eutectoid reaction

Fig. 15. Some typical differential heating curves.

isotherm temperatures of a 10 wt. % Re alloy using an electrical resistance-temperature method yielded values (shown in Fig. 2) compatible with those listed in Table III.

The eutectoid compositions were determined by metallography and differential thermal analysis. The fact that the β - γ eutectoid horizontal was detected in the thermal analysis of a 2 wt. % alloy indicated that the α - β eutectoid composition is probably less than this value. The results of metallographic examination of 0, 0.5, 1.0, 1.5 and 2 wt. % Re alloys heat treated in the β region and either slow cooled or quenched established the α - β eutectoid composition as about 1.4 wt. % Re.

An extrapolation of the $(\beta + \gamma)$ - γ phase boundary, determined by differential thermal analysis, indicated the β - γ eutectoid composition to be 6 wt. % Re. The metallographic results reported in Fig. 2 confirm this composition. Figure 4 shows the microstructure of a 4 wt. % Re alloy quenched from 700°C consisting of approximately equal amounts of retained β and decomposed γ phases. The microstructure of the 6 wt. % Re alloy quenched from 700°C is depicted in Fig. 5 and consists of a decomposed single phase which in this case is indicative of a eutectoid trough.

Terminal Solid Solutions. The limit of solubility of rhenium in α uranium is evident from thermal data. Since the α - β eutectoid reaction isotherm commences at less than 0.5 wt. % Re, the maximum solubility of rhenium in α uranium, which would most likely occur at the eutectoid temperature of 643°C, is less than 0.5 wt. % Re. Metallographic examination of a series of alloys containing 0.5, 1.0, 1.5 and 2.0 wt. % Re which had been heat treated in the β region and slow cooled, indicated a low temperature solubility

value of about 0.4 wt. % Re. X-ray diffraction results support the α solubility limits as determined by differential thermal analysis and metallography. The powder data from the γ treated and slow cooled 1 and 3 wt. % Re alloys showed nearly identical d values and these differed in magnitude from the d values observed for a pure uranium sample treated in an identical manner indicating the solubility to be less than one weight percent.

The maximum solubility of rhenium in β uranium was found by extrapolating a straight line drawn through the β - γ transformation temperatures determined for the 0, 0.5, 1 and 1.5 alloys to intersect the eutectoid horizontal. This gave a solubility value of 1.9 wt. % Re at 681°C.

The γ solid solution was investigated by metallography and the results are plotted in Fig. 2. Figure 5 shows the remnants of the single-phase microstructure present in a 6 wt. % Re alloy at 700°C. Figure 7 shows the typical two-phase microstructure present in the 8 wt. % Re alloy at 975°C. The results of these and similar metallographic examinations indicated a solubility of 6 wt. % Re at 680°C which increased with temperature to a value of 7 wt. % at 975°C.

Uranium doesn't dissolve to any appreciable extent in the hexagonal rhenium lattice. Lattice parameters were calculated from Debye-Scherrer photographs of heat-treated powders of compositions 97, 99 and 100 wt. % Re. The heat treatment consisted of holding at 1100°C for six days followed by cooling to room temperature at a rate of 13°C/h. The Nelson-Riley extrapolation function was employed and yielded lattice parameters of $a_0 = 2.761 \text{ \AA}$ and $c_0 = 4.458 \text{ \AA}$ for pure rhenium and identical values of $a_0 = 2.762 \text{ \AA}$ and $c_0 = 4.460 \text{ \AA}$ for each of the two alloys. The

experimental error was less than $\pm 0.001 \text{ \AA}$. Using these experimentally determined lattice parameters and by assuming Vegard's law to hold, the solubility of uranium in rhenium was calculated to be approximately 0.6 wt. %.

The limited solubility of uranium in rhenium indicated by x-ray diffraction results was confirmed by metallography. Figure 14 shows the two-phase microstructure present in the 99 wt. % alloy. A 97 wt. % Re alloy quenched from 2000°C had about the same amount of second phase present as did a slow-cooled alloy of the same composition. This indicates there is little variation in solubility with temperature up to 2000°C .

Phase Identification. As mentioned earlier, most of the as-cast and heat-treated alloys were examined through Debye-Scherrer photographs and through optical examination of polished and etched surfaces. In addition, extensive use was made of an x-ray diffractometer in investigating the kinetics of the uranium transformations and the formation of U_2Re .

The URe_2 phase was difficult to identify crystallographically in diffractometer patterns of massive specimens. However, metallographic identification was readily made and, in addition, this phase could be readily identified by filing or crushing the alloy and using the 200 mesh powder in a diffractometer.

No irregularities were noted in the diffraction patterns or microstructures of alloys on the rhenium rich side of the URe_2 phase. On the uranium side of the URe_2 phase nonequilibrium alloys were observed. The following two sections discuss the nature of these alloys.

REACTION KINETICS: RETENTION OF STABLE PHASES

Incomplete U_2Re Formation. The slow rate of formation of U_2Re led to alloys containing nonequilibrium quantities of U , URe_2 and U_2Re . For alloys of near stoichiometric U_2Re composition containing initially small URe_2 dendrites, equilibrium could be obtained by heat-treating for 12 weeks at $715^\circ C$. As the composition of the alloys approached URe_2 stoichiometry, the time required for equilibration was lessened as would be expected.

Gamma Phase Retention. Water quenching from the γ region or arc melting of 25 g buttons on a cold hearth resulted in retention of the γ phase for alloys containing more than about 7 wt. % Re . Likewise, vacuum quenching*, at least in the case of a 20 and 30 wt. % alloy, was sufficient to capture the γ phase. Figures 16a and 16b contrast the diffractometer pattern of a retained γ alloy with that of pure γ uranium. Un-annealed filings taken from retained γ alloys resulted in diffractometer patterns that were very diffuse and non-readable.

The retained γ phase showed considerable stability. For example, no decomposition of the retained γ phase in a 10 wt. % Re alloy was detected after aging at room temperature for 18 months. Similarly, an 8 wt. % Re alloy composed of retained γ when heated at $95^\circ C/h$ underwent an exothermic reaction between $484-550^\circ C$ and an endothermic reaction at $648^\circ C$. The first inflection was due to the decomposition of γ to α while the second was the result of the equilibrium $\alpha \rightarrow \beta$ transformation. The decomposition of the retained γ phase was also observed in a high

* Vacuum quenching refers to removal of the furnace from around an evacuated Vycor tube containing the specimen. An average cooling rate of about $2^\circ C/sec$ between 800 and $400^\circ C$ at the center of a 12 g specimen was obtained in this manner.

Fig. 16. X-ray diffractometer patterns showing the relationship of γ' and α' to the equilibrium structures: (a) idealized γ uranium pattern at 24°C as calculated from tabulated data; (b) the 8 wt.% Re as-cast alloy showing γ pattern; (c) the 8 wt.% Re alloy heated 16 h at 865°C and water quenched showing γ' pattern; (d) the 6 wt.% Re alloy heated 2 h at 950°C and water quenched showing $\beta\alpha + \alpha'$ pattern; (e) the 6 wt.% Re alloy heated 16 h at 865°C and water quenched showing α' pattern; and, (f) the 1 wt.% Re alloy heated 7 days at 900°C and cooled at 9°C/hr showing the α pattern.

temperature diffractometer. A diffractometer pattern of a retained γ sample heated to 510°C and held one hour showed equilibrium α and U_2Re (plus UO_2 reflections caused by surface contamination).

Some additional information regarding the decomposition of the rhenium saturated γ phase at slow cooling rates was obtained. Differential thermal cooling curves from alloys of composition 12.5, 20, 30, 40 and 50 wt. % Re showed an inflection at about 570-490°C on cooling from 900°C at approximately 90°C/h. This transformation temperature could apparently be raised by starting at a lower temperature and cooling at a lower rate. For example, the 30 and 40 wt. % alloys cooled at 50°C/h from 780 and 720°C, respectively, showed one inflection each at 585-500 and 652-570°C, respectively. Diffractometer patterns showed the uranium phase present at room temperature to be α uranium. It is concluded that for these alloys the transformations on cooling are not well defined and that the thermal curves show considerable undercooling and overlapping of two transformations. The two transformations are believed to be due to $\gamma \rightarrow \alpha'$ and $\alpha' \rightarrow \alpha$ transformations rather than to the equilibrium $\gamma \rightarrow \beta$ and $\beta \rightarrow \alpha$ transformations. This possibility is discussed later.

Beta Phase Retention. As in the case of the γ solid solution, the β solid solution containing sufficient rhenium could be readily supercooled to room temperature. Diffractometer patterns of alloys of composition 1.5, 3.0, 6.0 and 12.5 wt. % Re which were cooled rapidly from the β region consisted of β phase reflections and in the latter two cases of β plus U_2Re reflections. Vacuum quenching was sufficient, at least in the case of the 6 wt. % Re alloy, to capture the β phase. Figures 17a and 17b show

diffractometer patterns for an idealized β structure at 24 °C and the retained β structure present in a 1.5 wt. % alloy cooled at 400 °C/h from 850 °C.

Diffractometer patterns from alloys of composition 0.5 and 1.0 wt. % Re which were water quenched from the β region (710 and 690 °C, respectively) showed partial decomposition to α in both alloys, the decomposition being greatest in the 0.5 wt. % alloy. Figure 3 shows the microstructure of a β quenched one weight percent Re alloy. Differential thermal analysis of the 0.5 and 1.5 wt. % Re alloys cooled at 45 °C/h from the γ region showed only slight undercooling of the γ - β transformation while the β $\rightarrow$ α transformation temperature was depressed considerably. The β $\rightarrow$ α transformation occurred at 432 °C for the 0.5 alloy and did not occur in the 1.5 alloy indicating a retention of the β phase in the latter case. Thus it is concluded that the β solid solution is completely and easily retained to room temperature in alloys containing about 1.2 wt. % or more rhenium.

The retained β solid solution was rather stable in that no decomposition was detected after pressing at 16,000 psi (1.5 wt. % alloy), immersion in liquid nitrogen for 30 min (3.0 wt. % alloy) or aging at room temperature for five weeks (12.5 wt. % alloy). Heating the 12.5 wt. % Re alloy for two weeks at 630 °C followed by cooling at 3.5 °C/h resulted in an α + U_2Re structure and a decrease in hardness from VHN-480 to VHN-380.

A change in transformation characteristics occurs between 3 and 4 wt. % Re on cooling from the γ region. Alloys of composition 1.5, 3.0 and 4.0 wt. % Re alloys were heat treated at 850 °C and cooled at approximately 400 °C/h. Diffractometer patterns of these alloys showed the

Fig. 17. X-ray diffractometer patterns showing stages in the $\beta \rightarrow \alpha$ transformation in a 1.5 wt. % Re alloy: (a) idealized β uranium pattern at 24°C as calculated from tabulated data; (b) the 1.5 wt. % Re alloy heated 15 h at 850°C and cooled at 400°C/h showing retained β pattern; (c) above sample heated 5 min at 150°C and aged 49 days at 24°C showing $\beta + \beta'$ pattern; (d) above sample heated 23 h at 635°C and furnace cooled showing $\alpha + \beta'$ pattern; (e) pattern of 200 mesh powder filed from above sample showing α structure; and, (f) the 1 wt. % alloy heated 7 days at 900°C and cooled at 9°C/h showing the α pattern.

1.5 and 3.0 wt. % alloys to be β phase, while the 4 wt. % alloy was principally α with some U_2Re present. Differential thermal cooling curves of the 1.5 and 3 wt. % alloys showed only the $\gamma \rightarrow \beta$ transformation. This occurred at 730-700°C at 48°C/h for the 1.5 wt. % alloy and at 677-630°C for the 3 wt. % alloy at 100°C/h. A cooling curve of a 5 wt. % alloy verified the presence of α in the 4 wt. % alloy in that two overlapping inflections were detected, one at 614°C and the other at 560°C. A possible explanation for these happenings is that in the 1.5 and 3.0 wt. % Re alloys the sequence of phase changes at these cooling rates is normal (i. e., $\gamma \rightarrow \beta \rightarrow \alpha$), whereas in the 4 wt. % alloy the sequence is $\gamma \rightarrow \alpha' \rightarrow \alpha$.

REACTION KINETICS: RETENTION OF METASTABLE PHASES

Distorted Alpha Structure (α'). Alloys containing less than about 7 wt. % Re when cooled rapidly from the γ region usually possessed a banded microstructure and a distorted α crystal structure which is referred to here as α' . The degree of difference between the equilibrium structure and the distorted α' structure increased with increasing rhenium content and was also influenced by the cooling rate. Figures 16e and 16f illustrate the differences in diffractometer patterns for the α and α' structures. Figure 5 shows the characteristic banded microstructure.

A qualitative explanation of the distorted α structure in the U-Mo system has been given by TANGRI AND WILLIAMS⁶ and this argument could possibly be extended to the U-Re system.

The α' structure was found to decompose to α on heating in the high temperature α region. For example, a 3 wt. % Re alloy previously water quenched from 865°C and α' in structure was heated 7 h at 575°C and furnace cooled. A diffractometer pattern of this alloy showed equilibrium α and weak U_2Re reflections.

Gamma Decomposition Phase (γ'). Quenching alloys containing about 7 wt. % Re or more from temperatures low in the γ region resulted in capturing the γ' transition state. For example, a 10 wt. % Re alloy water quenched from 800 and 715°C yielded structures of γ and γ' , respectively. Figures 16b and 16c show diffractometer patterns of the γ and γ' states in an 8 wt. % Re alloy. Metallography showed the γ' state to consist of regions of fine Widmanstätten structure intermixed with undisturbed regions. Thus it is concluded that the γ' state is most likely a mixture of γ uranium and a transformation product that has not yet attained its equilibrium arrangement. The possibility of the existence of an equilibrium γ' structure in the low temperature region of the γ field seems slight since a high temperature diffractometer pattern of a 10 wt. % Re alloy taken after one hour at 685°C showed only equilibrium γ (plus UO_2 and UC as surface contaminants).

$\beta \rightarrow \alpha$ Transition State ($\beta\alpha$). The retained β phase was observed to decompose to the α phase through an intermediate state referred to here as the $\beta\alpha$ transition state. The reflections attributed to this state are illustrated in Fig. 17 which shows various stages in the $\beta \rightarrow \alpha$ transformation in a 1.5 wt. % Re alloy. The initial β structure is shown in Fig. 17b and the resulting α structure in Fig. 17e. Figures 17c and 17d are intermediate stages and show the $\beta\alpha$ transition state in pseudoequilibrium with the β and α phases, respectively. In referring to these extraneous reflections as the $\beta\alpha$ transition state, no inference is meant as to the material giving rise to the reflections as necessarily being noncoherent with the parent β phase or the α phase reaction product.

The reflections attributed to the $\beta\alpha$ transition state occurred in diffractometer patterns of uranium-rich alloys cooled slowly from the β region. For example, diffractometer patterns of 5, 8 and 10 wt. % Re alloys cooled at $16^\circ\text{C}/\text{h}$ from the β region consisted of α , U_2Re and $\beta\alpha$ reflections. A DTA analysis of the 8 wt. % Re alloy cooled at $16^\circ\text{C}/\text{h}$ showed the β decomposition to occur at 621°C . Retained β alloys when heated would decompose to yield diffractometer patterns containing $\beta\alpha$ reflections. For instance, a 6 wt. % Re alloy initially composed of retained β when heated to 600°C ($250^\circ\text{C}/\text{h}$) and immediately furnace cooled yielded a diffractometer pattern consisting of $\beta\alpha$, α and U_2Re reflections.

Cold rolling of alloys containing the $\beta\alpha$ state didn't noticeably change the intensity of the $\beta\alpha$ reflections. However, heat treating in the high-temperature α region usually reduced the intensity of the $\beta\alpha$ reflections while filing of the specimen and use of the 200 mesh powder resulted in complete elimination of the extraneous reflections.

The $\beta\alpha$ transition state was not detected in either of the partially decomposed 0.5 and 1.0 wt. % Re alloys quenched from the β region, thus indicating sufficient rhenium was not present to stabilize the $\beta\alpha$ state.

Alloys of composition 5, 8, 10, 20 and 30 wt. % Re which were heat treated in the γ region and furnace cooled did not show the reflections attributed to the $\beta\alpha$ state. Likewise, alloys of similar compositions that were heat treated in the γ region and cooled at $9^\circ\text{C}/\text{h}$ did not show $\beta\alpha$ reflections. However, alloys of similar compositions furnace cooled or slow cooled from the β region did show $\beta\alpha$ reflections. This suggests that at moderately slow cooling rates for compositions greater than about 3.5 wt. % Re, the mode of decomposition is $\gamma \rightarrow \alpha' \rightarrow \alpha$.

It is interesting to note that the same 6 wt. % Re alloy whose α' diffraction pattern is shown in Fig. 16e, when quenched from 960°C gave the diffractometer pattern shown in Fig. 16d and a hardness of VHN-226. The diffractometer pattern is essentially that of the $\beta\alpha$ transition state.

Direct $\gamma \rightarrow \alpha'$ Transformation. A 3 wt. % Re alloy water quenched from the γ region had an α' structure while one cooled at approximately 400°C/h had a β structure. This suggests a direct $\gamma \rightarrow \alpha'$ transformation at fast cooling rates.

The 3, 4 and 5 wt. % Re alloys and in some cases the 6 wt. % alloy which were cooled rapidly from the γ region possessed an α' structure. The microstructure of these alloys showed straight grain boundaries (see Fig. 5) which were those of the original γ phase. Had the α' phase formed via a double transformation (e. g., $\gamma \rightarrow \beta \rightarrow \alpha'$), the microstructure would be expected to be irregular. The diffractometer patterns of these alloys did not show any β or $\beta\alpha$ reflections indicating the β phase had not formed and thus is further evidence for a direct $\gamma \rightarrow \alpha'$ transformation.

SUMMARY OF REACTION KINETICS

The slow rate of formation of the U_2Re peritectoid phase led to alloys containing nonequilibrium quantities of U, URe_2 and U_2Re . Equilibrium conditions were achieved by heat treating the alloys for extended periods of time.

Rapid cooling of alloys containing about 7 wt. % Re or more from the γ region usually resulted in retention of the γ phase. This retained phase showed considerable stability.

Quenching alloys containing about 7 wt. % Re or more from temperatures low in the γ region resulted in capturing the γ' transition state.

This state appears to be a coherent mixture of γ uranium and a transformation product that has not yet reached its equilibrium arrangement. The possibility of an equilibrium γ' structure is disproven.

Rapid cooling of alloys containing less than about 7 wt. % Re from the γ region usually resulted in a distorted α structure labeled α' . This nonequilibrium structure was found to decompose to equilibrium $\alpha + \text{U}_2\text{Re}$ on heating below the β eutectoid isotherm.

The α' structure forms via a direct $\gamma \rightarrow \alpha'$ transformation on rapid cooling. Even at moderately slow cooling rates the reactions, for alloys containing more than about 3.5 wt. % Re, appear to be $\gamma \rightarrow \alpha' \rightarrow \alpha$.

Rapid cooling of alloys containing more than about 1.2 wt. % Re from the β region resulted in retention of the β phase. At lesser rhenium contents, partial retention of the β phase was observed. The β phase could also be retained by cooling alloys containing about 1.2-3.5 wt. % Re from the γ region at a moderate rate (e. g. , 400 or 90°C/h).

At rhenium contents greater than about 1.2 wt. %, the β phase was observed to decompose to the α phase through a transition state labeled $\beta\alpha$. Both quenched β and β formed from γ on cooling appeared to decompose via the reaction $\beta \rightarrow \beta\alpha \rightarrow \alpha$. The degree of reaction was increased markedly by filing the specimen and to a lesser extent by heating below the β eutectoid isotherm.

MECHANICAL CHARACTERISTICS

In general the alloys were brittle and not amenable to cold working. However, alloys containing large amounts of either retained γ or the α plus U_2Re mixture could be cold rolled successfully. For example,

two 10 wt. % Re alloys, one composed mainly of retained γ , the other of the α plus U_2Re mixture were given successful reductions in thickness of about 90% and 25%, respectively.

Alloys containing more than 40 wt. % Re showed a high resistance to abrasion and wear when subjected to filing or drilling. This abrasion resistance was found to increase with increasing rhenium content. However, no quantitative measurements were obtained.

Hardness measurements were obtained for a number of alloys and some are shown as a function of composition in Fig. 18. These measurements were made on polished and often etched surfaces with an Armstrong-Vickers hardness tester. The as-cast alloys are softer than the heat-treated ones in the region from about 8 to 61 wt. % Re because the relatively soft and ductile γ phase is present in a metastable form. The brittle nature of the URe_2 phase produced erroneously low hardness values for alloys in which it was present in large amounts. On the rhenium rich side of the URe_2 phase the hardness-composition relationship is linear. No appreciable change in hardness on heat treating was expected or observed for these rhenium-rich alloys since the microstructures were not altered significantly by the heat treatment.

ACKNOWLEDGMENTS

The authors wish to express appreciation to Dr. J. F. Smith for advice and helpful criticism during the course of the investigation.

Fig. 18. Some hardness values.

EL

REFERENCES

- ¹ B. A. HATT, Crystal structure of URe_2 , Acta Cryst., 14 (1961) 119.
- ² F. A. ROUGH and A. A. BAUER, Constitutional Diagrams of Uranium and Thorium Alloys, Addison-Wesley Publishing Company, Inc., Reading, Mass., 1958, p. 60.
- ³ D. E. WILLIAMS and H. L. LEVINGSTON, Arc melting in the tungsten electrode furnace, U.S. Atomic Energy Comm. Research and Develop. Rept. IS-262, Office of Technical Services, U. S. Department of Commerce, Washington 25. D.C., 1961.
- ⁴ J. T. WILLIAMS, Vanadium-zirconium alloy system, Trans. Am. Inst. of Mining, Metallurgical and Petroleum Eng., 203, (1955) 345.
- ⁵ P. CHIOTTI, Adaptation of a Geiger counter x-ray diffractometer for high temperature investigations, Rev. Sci. Instr., 25, (1954) 683.
- ⁶ K. TANGRI and G. I. WILLIAMS, Metastable phases in the uranium-molybdenum system and their origin, J. Nucl. Mat., 4, (1961) 226.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission.

A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights, or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission to the extent that such employee or contractor prepares, handles or distributes, or provides access to, any information pursuant to his employment or contract with the Commission.

ND