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Reactions of Uranium and the Platinide Elements. II. The Uranium-Rhodium System*

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The phase diagram of the uranium-rhodium system was constructed from data obtained by thermal analysis, metallographic examination, and x-ray diffraction. The system is characterized by four intermetallic compounds: U_4Rh_3, formed peritectically near 1155 °C and having a solid state transformation at about 720 °C; U_3Rh_4, formed peritectically near 1450 °C; U_3Rh_5, formed peritectically near 1550 °C; and URh_3, melting congruently at about 1700 °C. One eutectic occurs near 865 °C and 24.5 atomic percent (a/o) rhodium, and a second near 1393 °C and 87 a/o rhodium. The maximum solid solubility of rhodium in uranium is approximately 8 a/o, and of uranium in rhodium is approximately 3 a/o.

Key Words: Phase diagram, intermetallic compounds, solubility, rhodium, uranium.

1. Introduction

This report is one of a group concerned with the binary equilibrium diagrams of uranium with the individual elements of the platinide group, Group VIII of the periodic chart, conducted for the Atomic Energy Commission. These studies have resulted in a correlation among atomic radius, solid solubility, and the crystal lattice of the solvent which will be presented in the final report of this series. The data were obtained by thermal analysis, metallographic examination, and x-ray diffraction, which were combined to produce this proposed phase diagram.

2. Previous Work

Some information on the uranium-rhodium system appears in the compilation of the constitution diagram of uranium and thorium alloys by Rough and Bauer [1],[1] and includes some of that from the present study. No information on this system was included in the compilation by Hansen and Anderko [2], but various portions of this system have appeared in reports from the Argonne National Laboratory Metallurgy Division [3, 4, 5]. The recent compilation by Elliott [6] presents the uranium-rich portion of the diagram; this shows the existence of U_2Rh, URh, and also the URh_3 compound and the presence of a eutectic arrest at 867 ± 2 °C. The U_2Rh and URh compound were not detected, as will be presented in this paper. Apparently no complete diagram with supporting data has yet appeared in the published literature.

3. Preparation of Alloys

The alloys used in the study of this system were prepared by arc melting or by induction melting in beryllia crucibles. In general, the alloys of low rhodium content were made by induction melting, though arc melting was utilized in diluting certain alloys of low rhodium content. No evidence of contamination by beryllia was noted in the as-cast alloys or in those which had been later heated in a beryllia crucible for melting point determinations.

The rhodium was obtained as powder which was compressed into pellets for later melting. The powder was about 99.9 percent purity, and qualitative spectrochemical analysis of the material by E. K. Hubbard at NBS indicated the following metal impurities and their estimated amounts: 0.01 to 0.1 percent Fe, Ir, Pd, Pt; 0.001 to 0.01 percent Cu, Mg, Ni, Ru, Si, Sn; and 0.0001 to 0.001 percent Ag, Al, Ca.

The thermal analyses, metallographic preparation, and x-ray diffraction procedures were identical to those employed in the study of the uranium-ruthenium system [7]. Chemical analyses to confirm compositions of the alloys were made in the Analytical Chemistry Division at NBS by E. J. Maienthal [8].

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[1] Figures in brackets indicate the literature reference at the end of this paper.

4. Experimental Results

4.1. The Uranium Solid Solution Regions

The solid solubility of rhodium in the respective terminal uranium phases was determined principally by metallographic examination of quenched specimens but additional data on the solid solubility regions were obtained dilatometrically. The specimens utilized for subsequent heat treatment and quenching had received a preliminary homogenization for about 200 hr at 825 °C; the alloys were then sectioned and small specimens were sealed in high silica tubing under a partial pressure of helium.

Thermal analysis data of alloys of low rhodium content revealed that the addition of rhodium to uranium lowers the melting point of uranium and also depresses the uranium transformations. The thermal analysis data are listed in table 1 and plotted in figure 1.

The data show the decrease in liquidus for the alloys, and they also indicate that the gamma-transformation is lowered to an average of 683 °C and the beta-transformation to about 625 °C. These results are almost identical with the data for the uranium-ruthenium system presented previously [7]. The apparent solid solubility of rhodium in alpha-uranium is less than 0.5 a/o, since the alloy of 0.6 a/o rhodium exhibited the beta-transformation near the minimum temperature for the other alloys. The solid solubility of rhodium in beta-uranium is higher and on the order of 1 to 2 a/o as indicated by thermal analysis, though quenched specimens were used in determining the phase fields more closely.

Data on the uranium transformations had been obtained from dilatometric measurements [9] and summarized in table 2, and these confirmed the results from thermal analysis. Both sets of data indicated that the beta-alpha transformation had stabilized on cooling at 625 °C, which apparently is the eutectoid horizontal. Extrapolation to the intersection of the line connecting the uranium and the 0.36 a/o rhodium alloy transformation temperature with the line at 625 °C suggests that the rhodium solubility in the alpha phase is near 0.2 a/o.

TABLE 1. *Thermal analysis results*, U-Rh

Alloys of 0–50.8 a/o Rhodium

	Arrests °C						
a/o Rh	Arrest	Arrest	Fusion	Eutectic	Arrest	$\gamma \rightarrow \beta$	$\beta \rightarrow \alpha$
0			1131			767	657
0.6			1107			746	630
1.7			1115			735	635
3.3			(above 960)			690	628
5.6			1049			673	624
10.8			1008		723	682	630
20.5			897	872	721	690	629
24.2				870	725	680	625
33.4			1000	865	725	685	626
36.6			1072	856	721	680	616
40.7				861	708	684	610
43.4		1156			719		
50.8	1440	1154					

TABLE 2. *Transformation in* U-Rh *alloys by dilatometric measurements* [9]

Alloy	Start of $\gamma \rightarrow \beta$, Cooling	Start of $\beta \rightarrow \alpha$, Cooling
Uranium	641 °C	758 °C
U–0.36 a/o Rh	611	754
U–0.77 a/o Rh	622	744
U–1.13 a/o Rh	624	738

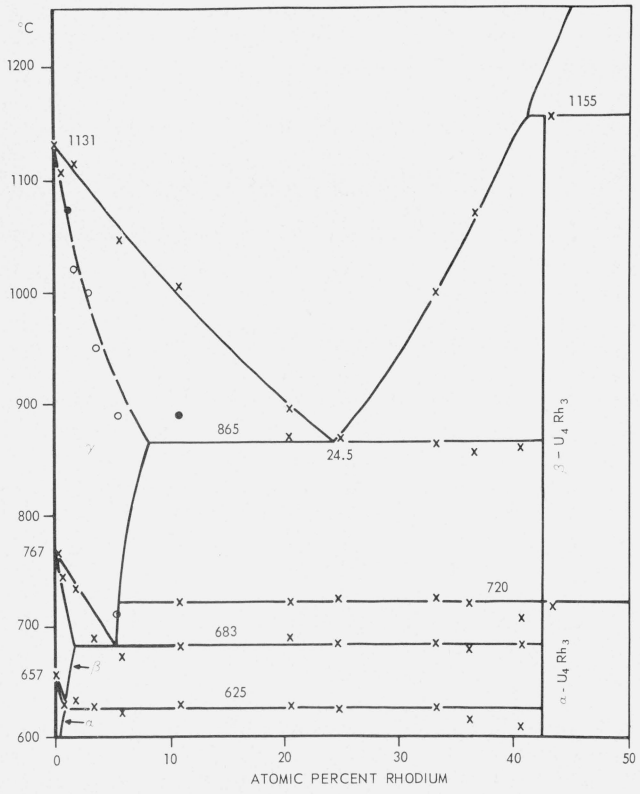


FIGURE 1. *Uranium-rich portion of uranium-rhodium system.*

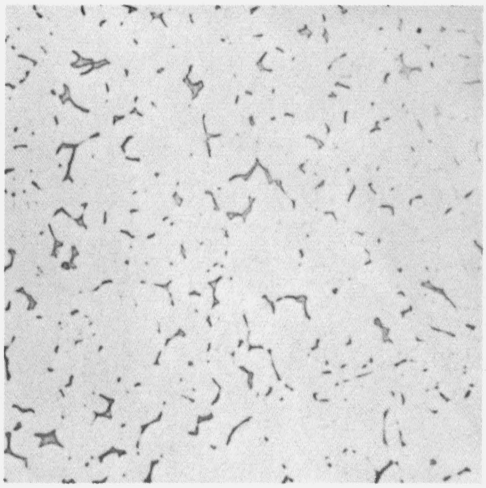
Quenched specimens were utilized for a more exact determination of the solid solution fields. The microstructures and the x-ray data confirmed the tentative conclusions from the thermal analysis data. The extent of the solid solubility of rhodium in alpha-uranium is quite limited, as indicated by a considerable amount of precipitate phase in the thermal analysis sample of 0.6 a/o rhodium. Quenched specimens of lesser rhodium content, due to small amounts of impurity precipitate, could not be determined unambiguously as single phase specimens. However, the accumulated data indicate that the maximum solid solubility of rhodium in alpha-uranium definitely is less than 0.5 a/o, and it is probably 0.2 to 0.3 a/o.

Additional quenched specimens aided in determining the boundaries between the higher temperature phase fields. Quenched specimens of the 0.77 a/o rhodium alloy gave only the alpha-uranium x-ray diffraction peaks. Metallographic examination indicated that the specimens contained two phases (alpha

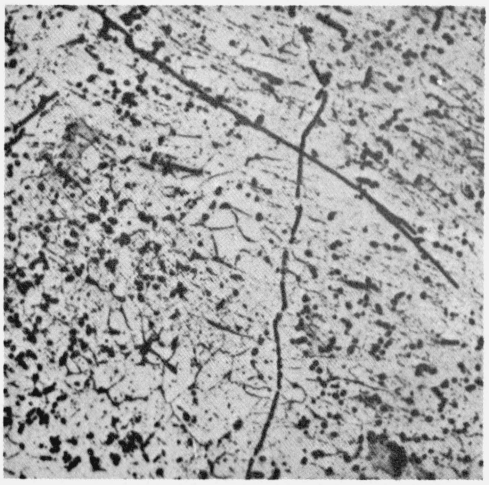
plus compound) at 625 °C, a single phase (originally beta) at 675 and 720 °C, two phases (beta plus gamma) at 737 °C, and a single phase from 760 to near 1105 °C at which melting appeared. In this particular alloy, beta-uranium could not be retained by quenching to room temperature; the conclusions of the presence of beta- or of gamma-uranium were based on the appearance and distribution of the phases in the etched specimens. The alloy of 1.1 a/o rhodium quenched from 726 °C had apparently been quenched from the $\gamma+\beta$ field (fig. 2a), and an apparent change in specimens quenched from 697 and 675 °C (fig. 2b, c) indicate that the beta-solvus passes between these two points. The data from the metallographic observations place the maximum solid solubility of rhodium in beta-uranium at about 1.5 a/o.

Some x-ray patterns indicated the presence of beta-uranium in quenching from the gamma region. The alloys of 1.7, 2.3, and 4.0 a/o rhodium quenched from the 950 to 1070 °C range each had beta-uranium in the x-ray pattern. In two other specimens, the 1.1 a/o rhodium alloy at 737 °C and the 1.8 a/o rhodium at 747 °C, beta-uranium was present. In no instance was the gamma-uranium pattern detected.

The maximum solubility of rhodium in gamma-uranium is less than 10.8 a/o for the 850 °C quenched specimen of this alloy was two phase (fig. 3a). The gamma-solvus is further outlined by the presence of



(a)



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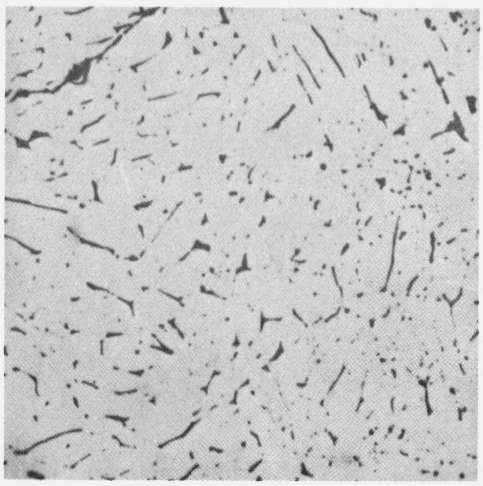


(c)

FIGURE 2. *Uranium-rhodium alloys.*

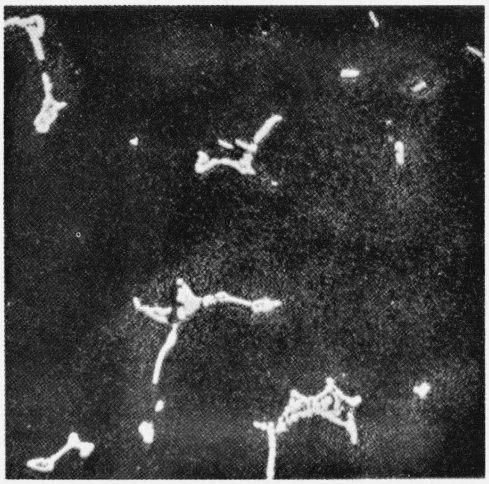
(a) Alloy of 1.1 a/o rhodium quenched from 726 °C, quenched from $(\gamma+\beta)$ region. Glycol etch. ×100.
(b) Alloy of 1.1 a/o rhodium quenched from 697 °C, quenched from β-region, showing cracks and impurities. Nitric acid etch. ×100.
(c) Alloy of 1.1 a/o rhodium quenched from 675 °C, quenched from $\beta+U_4Rh_3$ region. Glycol etch. ×100.

two phases in the 710 °C quenched specimen of 5.6 a/o rhodium (fig. 3b). The maximum solid solubility of rhodium in gamma-uranium is very close to 8 a/o. In addition, the gamma-uranium eutectoid composition is very close to 5.6 a/o rhodium. Specimens of this composition quenched from 600 and 670 °C (fig. 3c) were almost completely decomposition products, while the 710 °C sample was not (fig. 3b).

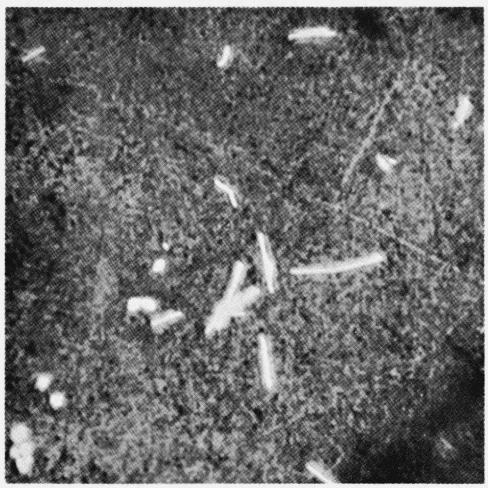
4.2. The Region of 0 to 50 a/o Rhodium

The addition of rhodium to uranium results in a lowering of the freezing point and a depression in the transformation temperatures (table 1). As mentioned above, the gamma-uranium transformation is lowered to near 683 °C and the beta-alpha transformation to about 625 °C. The eutectic composition, as determined from the trend of the freezing points is near 24.5 a/o rhodium and the eutectic temperature is at an average of 865 °C.

The thermal analysis data indicate a eutectic arrest in alloys of from 20.5 to 40.7 a/o rhodium. Confirmation of the eutectic was obtained from metallographic examination of specimens ranging from 24.4 to 40.7 a/o rhodium which had been held at 870 and at 853 °C for 25 hr. A set of four alloys were involved, and a considerable difference was found to exist in the microstructures of the alloys at 853 and at 870 °C (fig. 4a, b);



(a)



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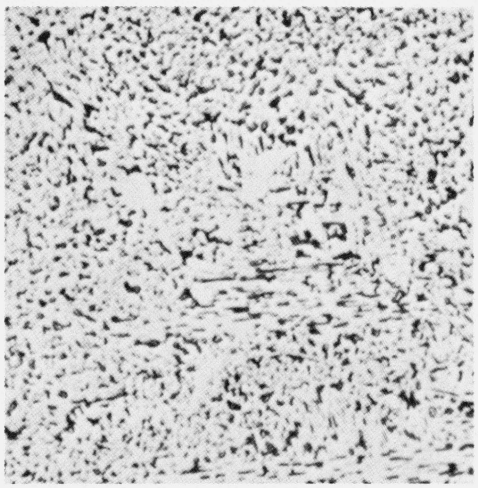

(c)

FIGURE 3. *Uranium-rhodium alloys.*

(a) Alloy of 10.8 a/o rhodium quenched from 850 °C with U_4Rh_3 and alpha-uranium (transformed from γ). Glycol etch. ×100.
(b) Alloy of 5.6 a/o rhodium quenched from 710 °C with U_4Rh_3 and alpha-uranium (transformed from γ). Glycol etch. ×100.
(c) Alloy of 5.6 a/o rhodium quenched from 670 °C showing γ-eutectoid decomposition into $\beta - U + U_4Rh_3$. Glycol etch. × 1000.

at the higher temperature fusion was evident. The alloy of 43.4 a/o rhodium was held at 935 °C for 90 hr with no evidence of fusion. In fact, this specimen was almost single phase following the thermal analysis (fig. 4c), which further indicates the existence of a compound near this composition. The detection of the uranium transformations during the heating and cooling traces of the thermal analysis charts in alloys of up to 40.7 a/o rhodium further establishes that the first compound adjacent to the uranium solid solution fields is between 40.7 and 43.4 a/o rhodium. In addition, x-ray diffraction patterns of alloys of 32.0 and 33.4 a/o rhodium after thermal analysis each contained the alpha-uranium peaks. No evidence of a compound at the U_2Rh [10] composition was found. This compound has been placed at the U_4Rh_3 composition (43.8 a/o rhodium). The presence of a reaction near 720 °C is the result of a solid-state transition within this phase; however, the heat treated and quenched specimens gave only one x-ray pattern, that for the room temperature structure. The x-ray *d*-spacings are listed in table 3. The presence of the thermal analysis reactions near 1155 °C in the 43.4 and the 50.8 a/o rhodium alloys are from the peritectic reaction of the U_4Rh_3 phase. No evidence of a eutectic was seen in specimens in this composition range, nor in alloys of up to near 57 a/o rhodium.

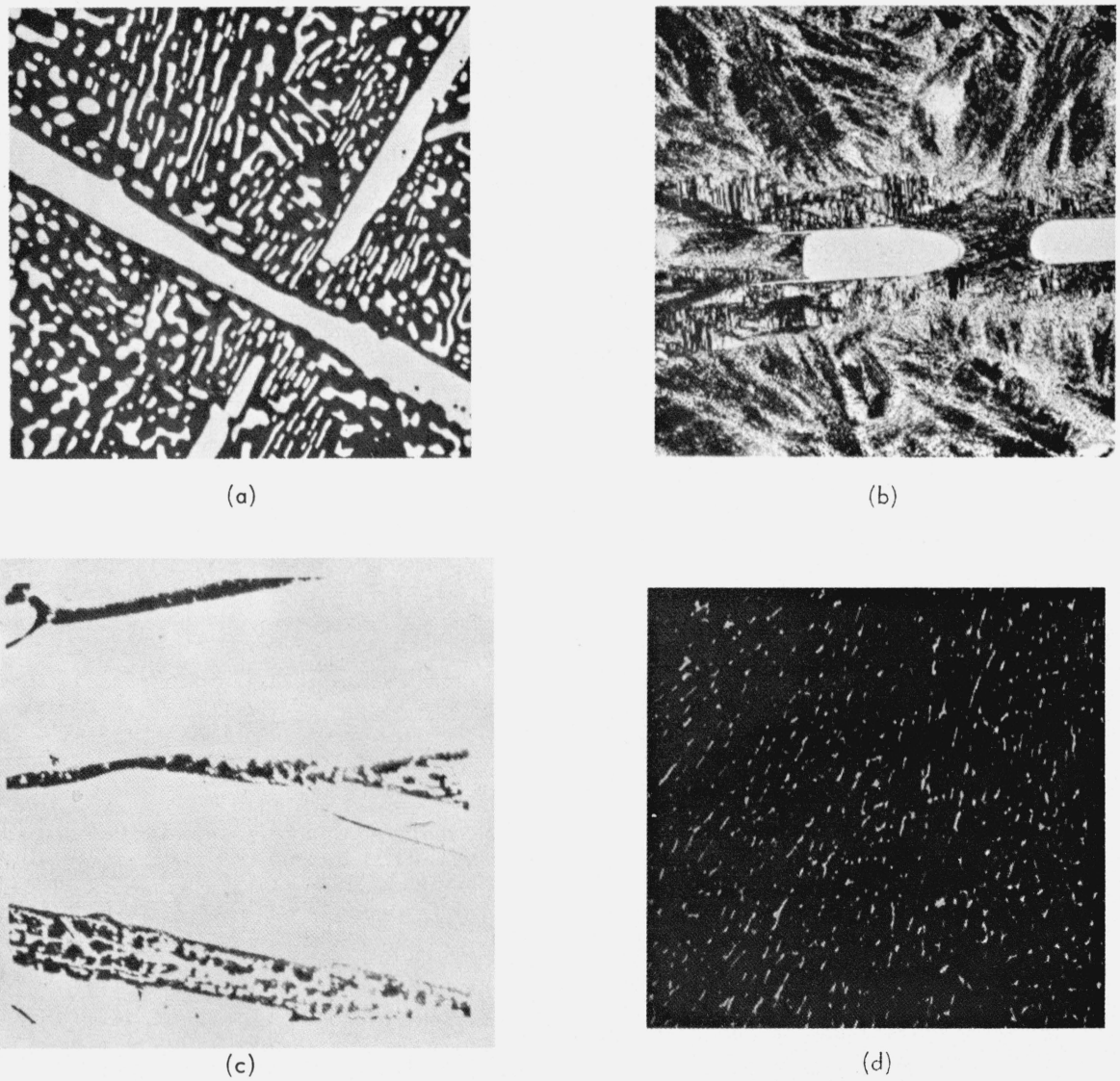

FIGURE 4. *Uranium-rhodium alloys.*

(a) Alloy of 24.2 a/o rhodium held at 853 °C for 25 hr. Glycol etch. ×100.
(b) Alloy of 24.2 a/o rhodium held at 870 °C for 25 hr. Glycol etch. ×100.
(c) Alloy of 43.4 a/o rhodium held at 935 °C for 90 hr. Glycol etch. ×50.
(d) Alloy of 57.4 a/o rhodium held at 935 °C for 90 hr. Nitric acid etch. ×100.

TABLE 3. *X-ray diffraction data, interplanar spacings*, U-Rh

U_4Rh_3		U_3Rh_4		U_3Rh_5	
d	*I*	*d*	*I*	*d*	*I*
3.17	vw	3.16	vw	2.62	m
2.66	m	2.46	w	2.44	w
2.60	vs	2.40	s	2.36	m
2.55	w	2.25	w	2.22	s
2.50	m	1.86	m	2.14	w
2.27	vw	1.73	s	2.12	w
2.22	w	1.51	w	2.04	m
2.16	w	1.39	m	1.92	m
2.06	vw	1.28	w	1.67	vw
1.82	w	1.26	m	1.49	w
1.80	s	1.14	m	1.44	vw
1.66	m	0.99	m	1.35	w
1.58	vw			1.31	m
1.56	vw			1.17	vw
1.53	w			1.14	vw
1.48	w			1.02	m
1.42	vw				
1.40	vw				
1.38	vw				
1.30	vw				
1.24	vw				
1.14	w				

Data derived from diffraction patterns, both chart and film, utilizing filtered Co and Cu radiation. Estimated relative intensities: vs—very strong; s—strong; m—medium; w—weak; vw—very weak.

4.3. The Region of 50 to 75 a/o Rhodium

X-ray diffraction patterns of the alloys between 50 and 57 a/o rhodium were obtained. One particular pattern became most strong in alloys near the 57 a/o rhodium composition. The alloy of 50.8 a/o rhodium was definitely two phase in all heat treated specimens but the alloy of 57.4 a/o rhodium was almost single phase. The combination of x-ray diffraction data and the metallographic examination of the specimens placed the compound at the U_3Rh_4 composition. The reaction observed near 1450 °C by thermal analysis and melting point determinations is apparently the peritectic reaction for this particular compound. The x-ray diffraction pattern for the U_3Rh_4 phase is listed in table 3.

An additional compound at 62.5 a/o rhodium, U_3Rh_5, is formed in this region. This particular phase was detected by x-ray diffraction in alloys between 62.5 and 74.5 a/o rhodium, and the diffraction pattern is given in table 3. The alloy of 62.5 a/o rhodium was heated by induction and it appeared to react near 1550 °C and to be wholly molten at about 1600 °C. Other alloys of higher rhodium content had melting points which tended toward a maximum near 1700 °C at the 75 a/o rhodium composition. The melting point determinations for alloys of from 60.7 to 74.9 a/o rhodium are listed in table 4, and these data indicate that the U_3Rh_5 compound forms peritectically at about 1550 °C.

TABLE 4. *Melting point determinations*

Alloys of 60.7 to 74.9 a/o Rhodium

a/o Rh	Optical pyrometer reading, °C
60.7	1450
62.5	1550 (reaction)
62.5	1600 (molten)
69.8	1675
74.9	1690

X-ray patterns from powder filed from the as-cast (arc melted) alloys of 60.7 and 74.9 a/o rhodium exhibited lattice spacings of approximately 4.00 Å; these were identified as a cubic phase, $AuCu_3$ type. These data compare well with the values for the URh_3 phase $a=3.992$, as reported by Ferro [11] and $a=3.991$ Å, as reported by Dwight, Downey, and Conner [12]. However, upon heat treatment and the attaining of chemical equilibrium of the 60.7 a/o rhodium alloy, this phase gradually disappeared, and it was retained only in homogenized alloys of greater than 62.5 a/o rhodium.

5. The Region of 75 to 100 a/o Rhodium

The liquidus determinations for alloys of compositions between 75 and 100 a/o rhodium showed an obvious depression to an apparent eutectic composition. Alloys of less than 75 a/o rhodium were tending toward a maximum, and the melting point of the 74.9 a/o rhodium alloy was at 1690 °C, while the alloy of 79.7 a/o rhodium had a melting point of 1570 °C. These data indicate that the URh_3 compound melts congruently at approximately 1700 °C. The data from thermal analysis and from the melting point determinations are listed in table 5.

TABLE 5. *Thermal data, rhodium-rich alloys*

Alloys of 75–100 a/o Rhodium

A. Thermal analysis

a/o Rh	Thermal arrests, °C
84.0	1467
89.3	1393

B. Melting point determinations

a/o Rh	Melting point, °C
74.9	1690
79.7	1570
88.2	1500
89.3	1505
95.4	1750
97.8	1850

The eutectic composition, as determined from the liquidus information for the alloys, is located near 87 a/o rhodium, and the eutectic temperature is near 1400 °C. The thermal analysis chart of the 89.3 a/o rhodium sample showed a strong reaction at 1393 °C, which fits closely with the other data, and this temperature has been taken as the eutectic temperature.

The solid solubility of uranium in rhodium is between 2.3 and 4.6 a/o uranium. The alloy of 97.7 a/o rhodium which had been heated for 20 min at 1600 °C was single phase while the alloy of 95.4 a/o rhodium was not. The diffraction patterns of these alloys showed broad peaks which prevented an accurate determination of the lattice spacings. The maximum solid solubility of uranium in rhodium is believed to be about

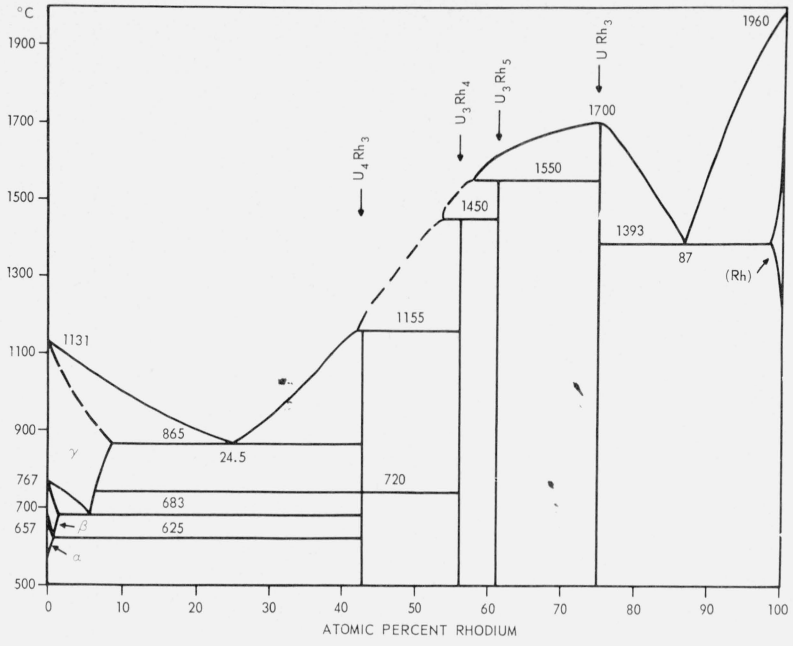

FIGURE 5. *Uranium-rhodium system.*

3 a/o. The complete diagram for this system is presented in figure 5.

6. Summary of the Uranium-Rhodium System

The addition of rhodium to uranium results in the depression of the liquidus to a eutectic near 24.5 a/o rhodium and an average temperature of 865 °C; it also lowers the gamma-uranium transformation to about 683 °C and the beta transformation to near 625 °C. The U_4Rh_3 compound is formed peritectically from liquid and U_3Rh_4 at about 1155 °C, with a solid-state transformation at about 720 °C. The U_3Rh_4 compound is formed peritectically from liquid and U_3Rh_5 at about 1450 °C, and U_3Rh_5 is formed peritectically from liquid and URh_3. The URh_3 compound melts congruently near 1700 °C. URh_3 and rhodium react to form the eutectic mixture near 87 a/o rhodium and 1393 °C.

The maximum solid solubility of rhodium in gamma-uranium is near 8 a/o, in beta-uranium is about 1.5 a/o, and in alpha-uranium is about 0.2 a/o. The solid solubility of uranium in rhodium is about 3 a/o.

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