Reactions of Uranium and the Platinide Elements.

III. The Uranium-Iridium System

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The phase diagram of the uranium-iridium system was constructed from data obtained by thermal analysis, metallographic examination, and x-ray diffraction. The system is characterized by five intermetallic compounds: U_3Ir, formed peritectically near 945 °C and decomposing eutectoidally near 758 °C; U_3Ir_2, formed peritectically near 1121 °C; UIr, melting congruently at about 1470 °C; UIr_2, formed peritectically above 1850 °C; and UIr_3, having a congruent melting point above 1950 °C. U_3Ir_2 has a solid state transition near 898 °C. One eutectic occurs at 914 °C at about 15 atom percent (a/o) iridium between uranium and U_3Ir; a second occurs between UIr and UIr_2 near 1450 °C; and a third occurs between UIr_3 and iridium at about 1950 °C. The solid solubility of iridium in gamma-uranium is about 5.5 a/o and of uranium in iridium is under 3 a/o. Iridium lowers the gamma-beta uranium transformation to about 681 °C and the beta-alpha transformation to about 565 °C.

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

1. Introduction

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

2. Previous Work

The compilation of the constitution diagrams of uranium and thorium alloys by Rough and Bauer [1][3] reported the existence of the intermetallic compound UIr_2 with the C15, $MgCu_2$, type structure. The summary by Hansen and Anderko [2] reported that β-uranium could be stabilized by the addition of 2 percent iridium. The supplement on binary constitution diagrams by Elliott [3] reported the existence of the UIr_3 compound with the cubic structure and also that the maximum solubility of iridium in uranium is

about 2 percent. The UIr_3 compound is isotypic with Cu_3Au, as reported by Dwight, Downey, and Conner [4].

3. Preparation of Alloys

The component metals consisted of uranium metal of about 99.9 percent purity (Mallinkrodt Biscuit) obtained from the Atomic Energy Commission and iridium powder of about 99.5 percent purity. A qualitative spectrochemical analysis of the powder by Hubbard at NBS showed that palladium, platinum, and osmium were present in the range of 0.01 to 0.1 percent and that rhodium was present in the range of 0.001 to 0.01 percent. Additional metallic impurities were estimated as follows: copper, iron, nickel, and silicon as 0.01 to 0.1 percent each; silver and magnesium as 0.001 to 0.01 percent each; and aluminum, calcium, and chromium as 0.0001 to 0.001 percent each. Prior to melting the powder was pelletized.

Some of the alloys in the range 0 to 24 atomic percent (a/o) Ir were prepared by induction melting under vacuum in beryllia crucibles. During induction melting of alloys containing above 6 a/o Ir, there usually occurred a violent reaction which was strong enough to eject some of the alloy from the crucible. For this reason the majority of the alloys above 6 a/o were prepared by arc melting which was carried out on a water-cooled copper hearth using a tungsten electrode and under a helium atmosphere; these alloys were

melted at least three times, being turned over and remelted after each solidification.

The specimens for microscopic analysis were mounted in an acrylic plastic and rough finished on a series of silicon carbide papers ending with a 600 grit paper. The specimens were then polished on lubricated laps with a series of diamond abrasives ending with 1μ and occasionally with $\frac{1}{4}\mu$ diamond paste.

The structures of most of the uranium rich alloys were revealed by electrolytic etching using about 30 Vdc and 10 A/cm² in an electrolyte containing 5 parts orthophosphoric acid, 8 parts ethyl alcohol and 8 parts ethylene glycol. Alloys of high iridium content were etched electrolytically using a 5 percent sodium cyanide electrolyte with 10 Vac and a current density of approximately 10 A/cm². Depending on the particular sample, the microstructures of the remaining alloys were revealed by several etching techniques with a variety of reagents. These included immersion in HNO_3 (60% by volume), electrolytic etching with hydrochloric acid in ethyl alcohol (1 : 9) at 10 A/cm², swabbing with aqua regia, and electrolytic etching with 10 Vdc and 1 A/cm² in a perchloric acid electrolyte (60% by volume).

The thermal analysis, heat treatments, and x-ray diffraction procedures were identical to those employed in the study of the uranium-ruthenium system [5].

4. Experimental Results

4.1. The Alloys of 0–24.7 a/o Iridium

The alloys of low iridium content are characterized by the existence of sluggish reactions. This sluggishness was apparent from the thermal analysis data; in many instances the uranium arrests were easily evident in the recording of the heating trace, but on the cooling cycle these arrests, particularly for the $\beta \rightarrow \alpha$ transformation, were rather weak. Repeated thermal analyses runs were made, and these included ones at different heating or cooling rates.

The presence of iridium in uranium has a significant effect upon the uranium transformations, depressing them considerably during a cooling process. The thermal analysis results for the 1.2 a/o iridium alloy will be useful in showing the effect of iridium upon uranium. This alloy had been premelted in a beryllia thermal analysis crucible prior to loading into the thermal analysis apparatus and the run was made under vacuum. The sample was heated at the rate of 3.8 °C/min on the first run; and the $\alpha \rightarrow \beta$ transformation began at 643 °C, the $\beta \rightarrow \gamma$ transformation began at 759 °C and melting started at 1100 °C, each arrest being very strong. The maximum temperature was 1217 °C. On cooling, at a rate of 3 °C/min, freezing started with a strong arrest at 1114 °C, the $\gamma \rightarrow \beta$ transformation began at 750 °C, also with a strong arrest, and the $\beta \rightarrow \alpha$ transformation gave a weak arrest at 536 °C. This thermal analysis run was repeated the following day under the identical conditions, the sample having remained in the furnace under

vacuum. The heating trace again showed three strong arrests, while the cooling trace exhibited two strong arrests plus a weak $\beta \rightarrow \alpha$ arrest.

In order to investigate the uranium transformations further, this same alloy was first reheated to above the $\alpha \rightarrow \beta$ transformation and then cooled. In this partial run, the $\alpha \rightarrow \beta$ transformation started at 631 °C on the heating cycle. The sample was heated to a maximum of 760 °C (no $\beta \rightarrow \gamma$ arrest was evident though it may have occurred) and was held above 675 °C for 2 hr and 10 min. The sample was cooled at 2.5 °C/min. On cooling, the $\beta \rightarrow \alpha$ arrest was of medium strength and was initiated at 542 °C. This sample was cooled to only 457 °C and was immediately reheated to above the $\beta \rightarrow \gamma$ transformation. On heating, the $\alpha \rightarrow \beta$ transformation started at 646 °C and the $\beta \rightarrow \gamma$ transformation started at 756 °C, with the maximum temperature being 861 °C. The sample was cooled at 0.8 °C/min and it was above 815 °C for 80 min. At this cooling rate, the $\gamma \rightarrow \beta$ transformation started at 751 °C and the $\beta \rightarrow \alpha$ transformation started at 560 °C.

These results indicate that iridium has a pronounced effect upon the uranium transformations and upon the $\alpha \rightarrow \beta$ transformation particularly. The hysteresis between heating and cooling of this 1.2 a/o iridium alloy is notable also, for in heating at the 3 °C/min rate the transformations occur at an average of 641 and at 758 °C and on cooling at 3 °C/min they occur at an average of 536 and 750 °C.
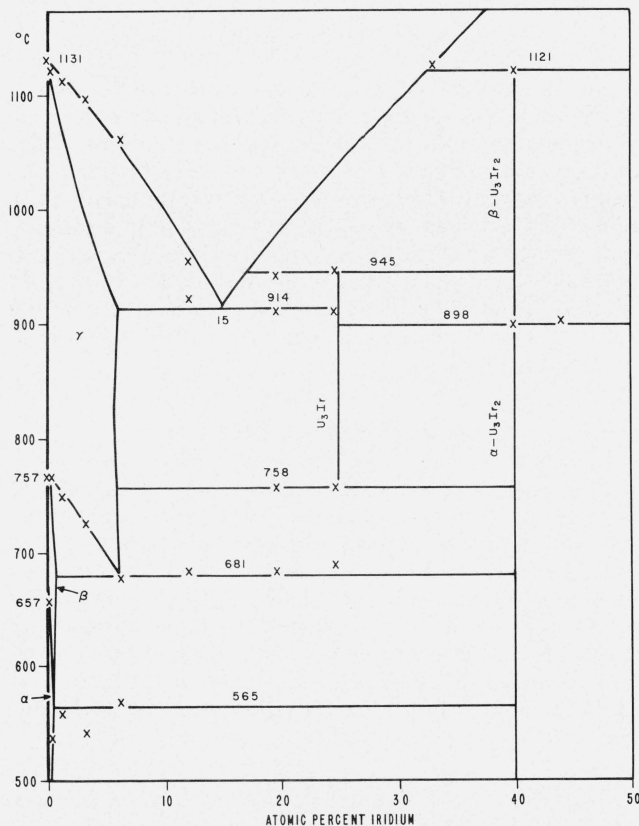

FIGURE 1. *Uranium-rich portion of* U-Ir *system.*

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In additional thermal analysis runs, it was determined that the $\beta \to \alpha$ transformation shifted considerably with a change in cooling rate. The transformation started at 542 °C and was raised to 560 °C as the cooling rate was changed from 2.5 °C/min to 0.8 °C/min. A change in the cooling rate did not appreciably affect the $\gamma \to \beta$ transformation.

The above effects were noted in alloys of up to 12.0 a/o iridium. The thermal analysis results are given in table 1 and some data are presented in figure 1. These results show that the addition of iridium to uranium lowers the melting point of the alloy to a eutectic located near 15 a/o iridium and at a temperature of 914 °C. The $\gamma \to \beta$ uranium transformation is lowered gradually by the addition of iridium to a minimum near 681 °C, this horizontal being stabilized at this temperature by about 6 a/o iridium. The $\beta \to \alpha$ uranium transformation was most drastically affected. This particular transformation is rather sluggish on cooling, as evidenced by a minimum temperature of 538 °C for the 0.3 a/o iridium alloy and 536 °C for the 1.2 a/o iridium alloy. This behavior was not observed in the previous studies of the uranium-ruthenium [5] and uranium-rhodium [6] systems. Further additions of iridium raised the transformation temperature to near 565 °C. The transformation occurs at 570 °C in the 6.1 a/o iridium alloy and at 560 °C in a slowly cooled alloy of 1.2 a/o iridium, giving an average of 565 °C.

TABLE 1. *Thermal analysis results, U-Ir alloys*

		Reactions °C		
a/o Ir	Fusion	Arrest	$\gamma \to \beta$	$\beta \to \alpha$
0	1131		767	657
0.3	1121		766	538
1.2	1114		750	536 (cooled at 3 °C/min)
			751	560 (cooled at 0.8 °C/min)
3.1	1098		726	544
6.1	1061		679	570
12.0	955	922	685	
19.6	941	910	758	684
24.7	945	910	757	685
33.0	1126			
39.9	1121	898		
44.2		901		
51.3	1447			
60.2	1450			

Optical Pyrometer Measurements:
51.3 a/o Ir Melted at 1470 ± 20 °C
60.2 a/o Ir Melted at 1800
68.8 a/o Ir Not melted at 1850
75.3 a/o Ir Not melted at 1850
82.0 a/o Ir Not melted at 1830
95.1 a/o Ir Not melted at 1950
96.8 a/o Ir Not melted at 2075

The uranium transformations were less easily detected in the cooling curves as the iridium content increased to more than 12 a/o. The $\beta \to \alpha$ arrest in the 19.6 and 24.7 a/o iridium alloys on cooling were not readily apparent, but the heating curves for these alloys showed good arrests for the $\alpha \to \beta$ and the $\beta \to \gamma$ transformations. Despite the absence of the $\beta \to \alpha$ arrests the x-ray diffraction patterns and the thermal analysis heating curves showed that uranium is present at room temperature in alloys of up to 24.7 a/o iridium.

The solid solubility of iridium in alpha-uranium is extremely low, as indicated by the sharp depression of the $\beta \to \alpha$ transformation with the addition of 0.3 a/o iridium. At quench temperatures of 650 °C and below, the 0.3 a/o iridium specimens each contained a precipitate phase, presumably the adjacent compound, indicating that the maximum solid solubility of iridium in alpha-uranium is under 0.3 a/o.

The solid solubility of iridium in beta-uranium is also relatively low. The maximum solid solubility is on the order of 0.4 a/o, as determined from the metallographic appearance of alloys of 0.3 and 0.6 a/o iridium. The 0.3 a/o iridium alloy was probably single phase in the specimen quenched from 700 °C, though a small amount of a contaminant phase was visible. The alloy of 0.6 a/o iridium was definitely two-phase. The x-ray data revealed that beta-uranium could be retained to room temperature by quenching, although some had transformed to alpha-uranium. In some instances the beta-uranium peaks were present even though the sample had been quenched from the gamma-uranium solid solution field, as in the 1.2 and the 3.1 a/o iridium samples quenched from 1000 °C.

The solid solubility of iridium in gamma-uranium is relatively high being on the order of 5.5 a/o iridium. The presence of a very small amount of precipitate phase in the 6.1 a/o iridium alloy quenched from 910 °C indicates an upper limit of solid solubility. The intersection of the eutectic line near 914 °C with the solidus line, as determined from the appearance of fusion in quenched specimens of lower iridium content, placed the maximum solid solubility near 5.5 a/o iridium. The solidus line rises almost vertically from the minimum $\gamma \to \beta$ transformation temperature to intersect with the projected solvus line. The quenched specimens of 6.1 a/o iridium did not indicate that the solvus line had been crossed, since in each specimen a small amount of precipitate phase was present.

The alloys of 19.6 and of 24.7 a/o iridium content each had strong arrests near 945, 910, 758, and 685 °C. The arrest of 910 °C was determined to be the eutectic arrest and the 685 °C arrest was the $\gamma \to \beta$ eutectoid horizontal. The other two arrests are associated with the U$_3$Ir compound. The data for the uranium-rich alloys are assembled in figure 1.
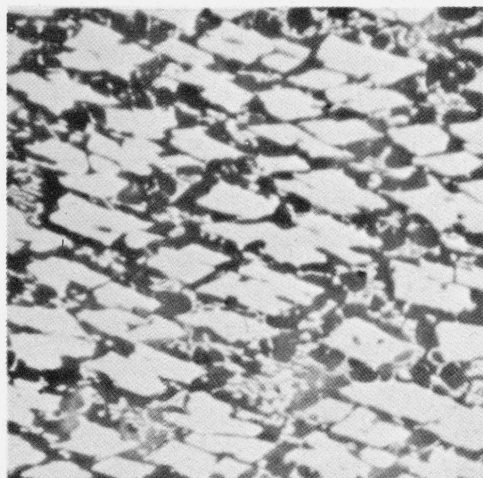
4.2. The U$_3$Ir Phase

The existence of the intermetallic compound at 25 a/o iridium was determined initially from extended heat treatments of an alloy of 24.7 a/o iridium. A series of alloys of 19.6 to 51.3 a/o iridium were heat treated at 820 °C for 65 hr. The specimen of 24.7 a/o iridium unexpectedly appeared to be almost a single phase. These samples had been sealed in silica tubing and were pulled from the furnace to cool in circulating air while still encapsulated. In order to confirm the existence of the U$_3$Ir phase the heat treatments were repeated using additional specimens; in each instance, once at 815 °C for 70 hr and again at 830 °C for 120 hr, the 24.7 a/o iridium alloy showed

a considerable change and was nearly single phase (fig. 2a, b). The alloys of 19.6 a/o and of 33.0 a/o iridium each consisted of two phases (fig. 2c, d) and each contained a phase whose x-ray diffraction pattern matched that of the 24.7 a/o iridium specimen. A compound in the ratio of three uranium atoms to one of the platinide elements had not previously been reported.

The U_3Ir phase appears to be stable only between 945 and 758 °C as determined from thermal analysis data. Quenched specimens also revealed incipient fusion in specimens of 24.7 and 33.0 a/o iridium quenched from 950 °C. The phase also reacts rather slowly on heating; this was indicated by thermal analysis data where in a number of heating curves of the 19.6 and 24.7 a/o iridium alloys two strong arrests appeared on heating but only one strong arrest on cooling.
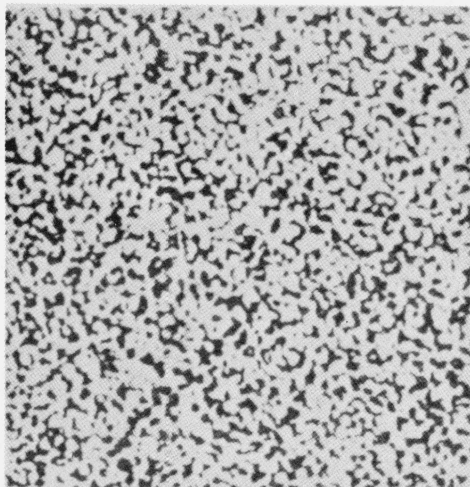
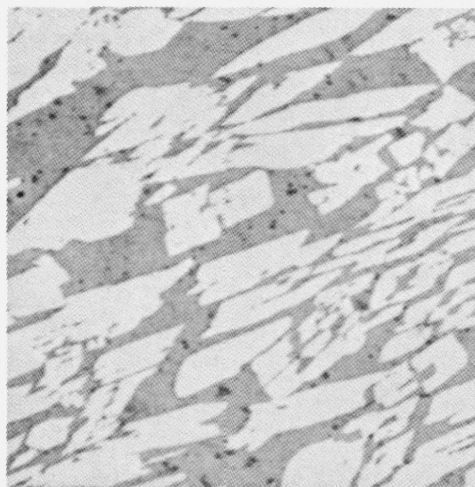The U_3Ir phase does not persist to room temperature. This is confirmed by a metallographic examina-

(a)
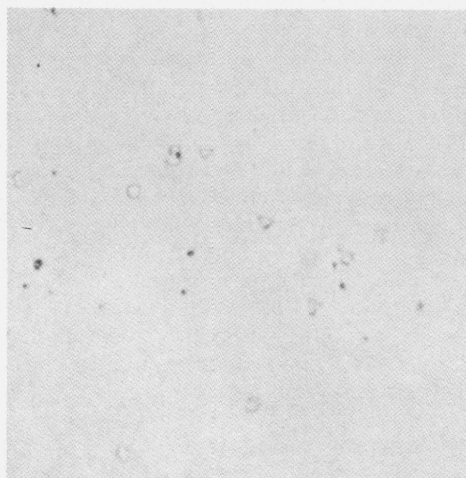
(b)

(c)

(d)

FIGURE 2. *Uranium-iridium alloys.*

a. As cast structure of 24.7 a/o iridium alloy. Unetched. X 100.
b. Alloy of 24.7 a/o iridium after 65 hours at 820 °C, predominantly the U_3Ir phase, with small areas of contamination. Starting material was the arc melted material (fig. 2A). Glycol etch. X 1000.
c. Alloy of 19.6 a/o iridium, after 65 hr at 820 °C. Etched in 5 percent HF. X 100.
d. Alloy of 33.0 a/o iridium, after 65 hr at 820 °C. Etched in 5 percent nitric acid in alcohol. X 100.

tion of the thermal analysis sample and of quenched specimen which consists of two phases; these phases were identified by their x-ray diffraction patterns as alpha-uranium, and the U_3Ir_2 phase. The characteristic x-ray pattern of the U_3Ir phase is given in table 2.

The x-ray patterns of the 19.6 and 24.7 a/o iridium alloys in the as cast (arc melted) condition were greatly different from that determined for the U_3Ir phase. It was subsequently determined that the predominant phase in the as cast condition was the U_3Ir_2 compound. The U_2Ir compound reported by Berndt and Dwight [7] was not detected.

4.3. The U_3Ir_2 Phase

The existence of the U_3Ir_2 phase was postulated on the evidence obtained from extended heat treatments of the alloys, including one of 39.9 a/o iridium. This specimen was heated at 820 °C for 65 hr and it consisted of one predominant phase upon metallographic examination. The x-ray data and the metallographic appearances of alloys adjacent to this composition indicated that the compound was placed at 40 a/o iridium.
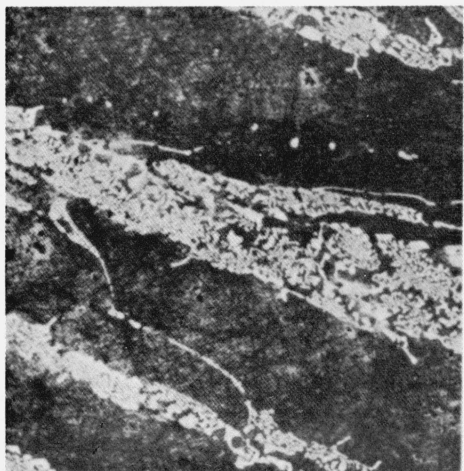
The thermal analysis data reveals that the formation
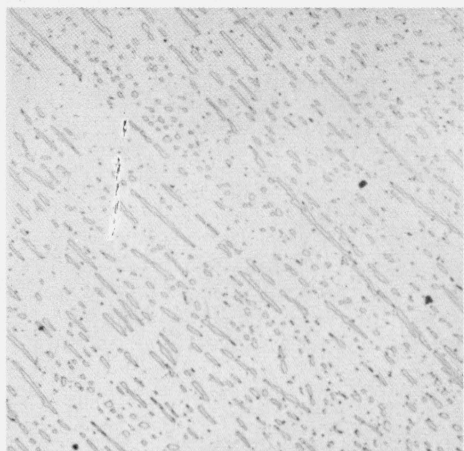
(a)
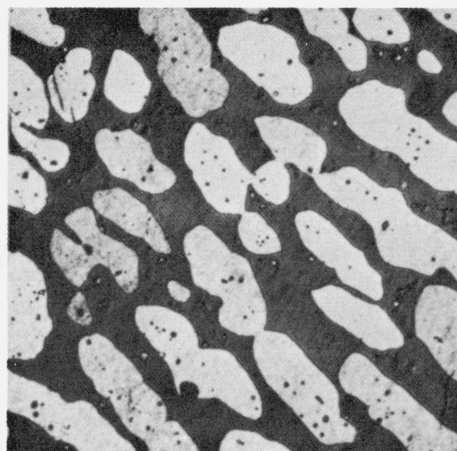
(b)

(c)
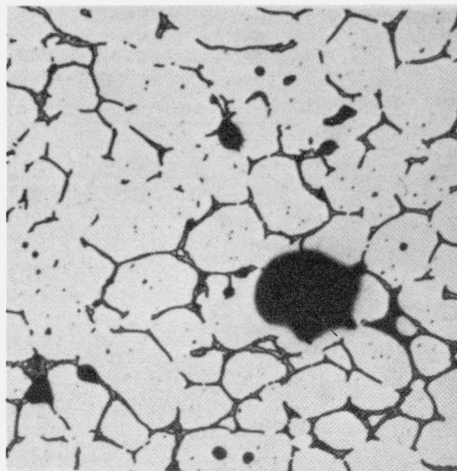

(d)

FIGURE 3. *Uranium-iridium alloys.*

a. Alloy of 39.9 a/o iridium after 93 hr at 915 °C. Modified glycol etch. X 100.
b. Alloy of 44.2 a/o iridium after 93 hr at 915 °C. Modified glycol etch. X 100.
c. Alloy of 51.3 a/o iridium, melted at 1450 °C. Etched electrolytically in 60 percent perchloric acid solution. X 100.
d. Alloy of 96.8 a/o iridium, heated to 2075 °C. Glycol etch. X 100.

Table 2. Characteristic x-ray patterns for U–Ir compounds

U–Ir		α–U₃Ir₂		β–U₃Ir₂		UIr	
d	I	d	I	d	I	d	I
2.87	vw	2.73	m	2.79	vw	2.90	vw
2.73	vw	2.62	s	2.69	vw	2.52	s
2.70	vw	2.44	m	2.54	vw	2.31	vw
2.62	w	2.31	w	2.49	vw	1.82	m
2.59	w	2.22	s	2.42	s	1.62	w
2.55	s	1.92	w	2.36	m	1.49	w
2.43	vw	1.64	vw	2.12	vw	1.43	w
2.33	s	1.59	vw	2.04	vw	1.41	w
2.30	m	1.56	m	1.88	m	1.39	s
2.13	m	1.49	m	1.86	vw	1.15	m
2.08	w	1.39	s	1.77	m	0.97	w
1.93	vw	1.37	m	1.53	m		
1.54	w	1.28	w	1.43	vw		
1.52	m	1.19	w	1.42	vw		
1.48	w	1.15	s	1.31	m		
1.39	w			1.27	m		
1.37	m			1.23	m		
1.33	m			1.16	w		
1.27	w			1.00	vw		
1.24	m			0.95	vw		
1.18	w						
1.12	w						
0.92	w						

temperature of this compound is near 1121 °C. In addition, thermal analysis of alloys from 33.0 to 44.2 a/o iridium (fig. 3a, b) also revealed the presence of a reaction horizontal at about 898 °C. This arrest is due to a solid-state transformation of the U₃Ir₂ compound as revealed by the changed x-ray diffraction pattern for a specimen held at 915 °C for 93 hr as opposed to one held at 820 °C for 65 hr. The x-ray diffraction data are presented in table 2.

4.4. The UIr Phase

The alloy of 51.3 a/o iridium in the as cast condition contained only a small amount of a second phase, present as eutectic. The melting point of this alloy was determined by optical pyrometer measurements to be 1470 ± 20 °C, from two melting point readings of 1450 and 1490 °C (fig. 3c). In addition, thermal analysis of this alloy gave only one arrest, near 1447 °C. The thermal anaylsis run of the 60.2 a/o iridium alloy had one arrest only, near 1450 °C, while its melting point from optical pyrometer measurements was determined to be at 1800 °C. Thus it was concluded that a eutectic horizontal is located at 1450 °C and that the melting point of the UIr compound is 1470 °C. The metallographic appearances of the 51.3 a/o iridium specimens was not significantly changed by various heat treatments and quenches.

The x-ray diffraction pattern for this phase (table 2) was detected in the diffraction charts for alloys of from 44.2 to 60.2 a/o iridium. The metallographic appearances of the alloys in this range showed decreasing amounts of a second phase as the 50 a/o iridium composition was approached, and the specific x-ray diffraction peaks became more definite also.

4.5. The UIr₂ Phase

The existence of the UIr₂ phase (66.67 a/o iridium) was reported by Heal and Williams [8]; this compound has the face centered cubic lattice, $a = 7.4939$. The information on this compound was useful in determining that no compound existed between the UIr and the UIr₂ phases. This was confirmed by the fact that the specimens of 60.2 a/o iridium always exhibited the x-ray diffraction peaks of these two particular phases.

The melting point of this compound is above 1850 °C as determined by optical pyrometer measurements. The compound apparently is formed peritectically, because no evidence of eutectic was present in the alloy of 68.8 a/o iridium for the various heated specimens.

4.6. The 75–100 a/o Iridium Region

This particular portion of the phase diagram was determined through the use of alloys of 75.3, 82.0, 95.1, 96.8, and 100 a/o iridium. The UIr₃ compound has the face centered cubic structure, $a = 4.023$, as reported by Dwight et al. [4].

The UIr₃ phase is the compound adjacent to the iridium solid solubility field. Only the iridium and the UIr₃ diffraction peaks were observed in the x-ray patterns of alloys in the 75.3–100 a/o iridium range. The melting point of the UIr₃ phase is apparently above 1850 °C, for no evidence of fusion of this phase was found in an examination of a specimen of 75.3 a/o iridium heated to this temperature. In addition, the alloy of 82.0 a/o iridium was heated to 1830 °C with no evidence of fusion. The maximum temperature
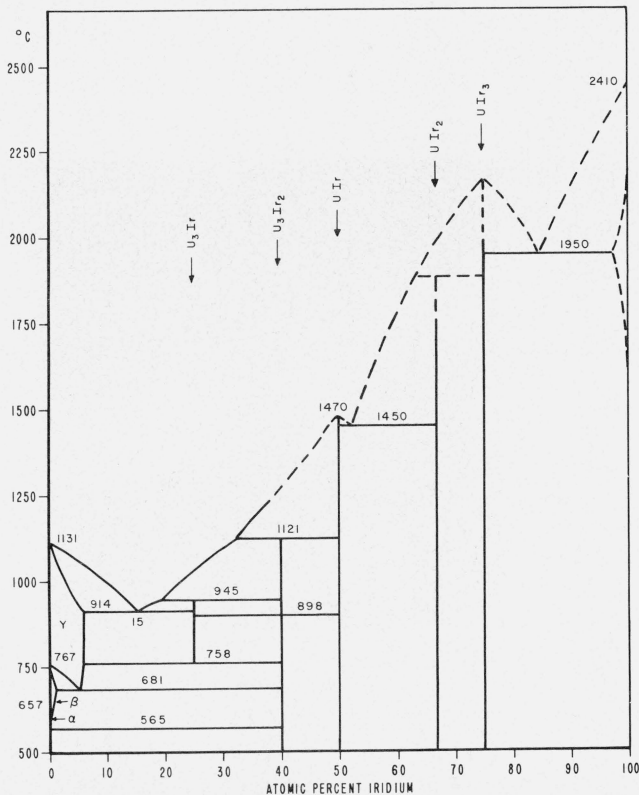

FIGURE 4. The uranium-iridium system.

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attained for this series of specimens was 2075 °C for the 96.8 a/o iridium alloy; the sample had not visibly melted and it was still two phase, though some grain growth had occurred and certain areas showed evidence of fusion (fig. 3d). In the 95.1 a/o iridium alloy heated to 1950 °C, fusion was also found and evidence of eutectic areas were noted. It seems likely that UIr_3 melts congruently and that a eutectic horizontal exists at about 1950 °C.

The solid solubility of uranium in iridium is quite low and is certainly under 3 a/o since the 96.8 a/o iridium alloy was two phase after being heated to 2075 °C. The x-ray diffraction patterns of alloys of over 95 a/o iridium showed practically no shift of the iridium peaks in the various heat treated specimens.

5. Summary

The liquidus for uranium-iridium consists of a eutectic between uranium and U_3Ir near 15 a/o iridium and 914 °C, from whence it rises to a maximum at the melting point of the UIr phase at 1470 °C, decreases slightly to the eutectic at 1450 °C between UIr and UIr_2, rises to the melting point of the UIr_3 phase which is probably at some temperature above 2000 °C and then to a postulated eutectic near 1950 °C between UIr_3 and iridium (fig. 4). The U_3Ir phase is formed peritectically at 945 °C from U_3Ir_2 and it decomposes at 758 °C into γ-uranium and U_3Ir_2. U_3Ir_2 is formed peritectically from UIr at 1121 °C and is stable to room temperature though it has a solid-state transformation at 898 °C. UIr melts congruently at 1470 °C, UIr_2 is believed to be formed peritectically from UIr_3, and UIr_3 is believed to have a congruent melting point.

Iridium depresses the $\gamma \rightarrow \beta$ uranium transformation to 681 °C and depresses the $\beta \rightarrow \alpha$ transformation to 565 °C. The maximum solid solubility of iridium in γ-uranium is 5.5 a/o, in β-uranium is about 0.5 a/o, and in α-uranium is less than 0.3 a/o. The solid solubility of uranium in iridium is less than 3 a/o.

6. References

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