The Gold-Uranium System [1]

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The phase diagram of the gold-uranium system was constructed from data obtained by thermal analysis, metallographic examination, and X-ray diffraction. The system is characterized by two intermetallic compounds, one forming peritectically at 1,216° C and having an apparent composition of U_2Au_3, and the other melting congruently at approximately 1,450° C and having an apparent composition of UAu_3. There are two eutectics, one between UAu_3 and gold at 855° C and 87.5 atomic percent of gold, and the other between uranium and U_2Au_3 at 1,105° C and 10.5 atomic percent of gold. The solubility of uranium in gold appeared to be about 0.6 atomic percent at 855° C, and the solubility of gold in uranium was approximately 3.2 atomic percent at 1,105° C. Gold lowered the gamma-beta transformation temperature of uranium from 762° to 738° C, and the beta-alpha transformation from 653° to 647° C.

1. Introduction

The purpose of this investigation was to make a survey of the gold-uranium system and to develop the constitution diagram by correlation of thermal, X-ray, and microscopic data.

2. Previous Work

A survey of the literature [2] showed that prior information on the constitution of the gold-uranium system was meager. Metallographic studies of alloys having compositions of 5 to 12 atomic percent of gold have been reported.[3 4 5] The alloy containing 5 atomic percent of gold, in the "as-cast" condition, showed a definite two-phase structure, and the alloy having the composition of 12 atomic percent of gold, in the as-cast condition, showed particles of a gold-rich phase in a eutectic matrix. It was reported that some solubility of gold in alpha uranium was indicated.

3. Preparation of Alloys

The component metals consisted of uranium of about 99.9-percent purity (Mallinckrodt Biscuit) and 999-fine gold.[6] Most of the alloys were prepared in a high-frequency induction furnace under vacuum, using either beryllia or thoria crucibles.[7] The cold furnace was pumped to about 5 μ, and on melting, the pressure attained was about 200 μ. The alloys in the composition range 30 to 99 atomic percent of gold reacted with the beryllia crucibles to the extent that the beryllia adhered to the ingot, whereas the alloys in the range 0 to 30 atomic percent of gold slid free of the beryllia crucibles, giving no visual indication of a reaction of the alloy with the refractory. Subsequent metallographic examination (fig. 1, A) revealed that the alloys in the range 50 to 70 atomic percent of gold were partially oxidized, apparently from a reaction with the beryllia crucibles. This was later confirmed by observations during thermal analysis of the alloys in this composition range. These alloys were completely oxidized when beryllia crucibles were used, the resultant oxide mass containing pellets of practically pure gold. The use of thoria crucibles for the melting and thermal analysis of the alloys in this range of composition apparently avoided the oxidation of the alloys, although it was evident, on visual examination of the alloys, that a reaction between the alloy and the refractory had occurred. Metallographic examination of the thoria-melted alloys showed no evidence of the oxidation that was observed in the beryllia-melted alloys, but chemical analysis revealed that the thoria-melted alloys picked up as much as 1.6 weight percent of thorium. Subsequent melts of alloys in this composition range were made by arc-melting.

The exploratory series of alloys were made from a 50 weight-percent master alloy that, on microscopic examination, appeared free of oxide. Subsequent alloys were made by direct alloying. Chemical analyses were made for uranium on the as-cast alloys and the gold determined by difference. When visual evidence of attack on the crucible was observed or microexamination gave evidence of oxidation, analyses were made for both component metals. The compositions of the alloys used are given in table 1.

TABLE 1. *Composition of gold-uranium alloys*

Alloy	Uranium	Gold	Gold	Alloy	Uranium	Gold	Gold
	wt %	*wt %*	*Atomic %*		*wt %*	*wt %*	*Atomic %*
Au	0.	99.9	99.9	G29	44.7	55.3	59.9
G18	0.3	99.7	99.7	G1	49.0	51.0	55.7
G17	1.0	99.0	99.2	G33	49.5	50.5	55.2
G2	1.7	98.3	98.6				
G12	5.2	94.8	95.7	G11	64.1	35.9	40.3
				G10	68.2	31.8	36.1
G16	7.6	92.4	93.7	G31	76.4	23.6	27.2
G3	9.0	91.0	92.4	G9	80.2	19.8	23.0
G22	10.9	89.1	90.9	G30	89.7	10.3	12.2
G23	14.9	85.1	87.4				
G19	15.0	85.0	87.3	G8	90.2	9.8	11.6
				G15	94.8	5.2	6.2
G4	17.2	82.8	85.4	G13	96.9	3.1	3.7
G5	27.5	72.5	76.1	G7	97.9	2.1	2.5
G24	29.7	70.3	74.1	G14	99.2	0.8	1.0
G25	31.5	68.5	72.4				
G32	35.4	64.3	68.5	U	99.9	0	0
G35	38.9	61.1	65.5				
G6	39.4	60.5	65.0				

[1] Investigation sponsored by the Atomic Energy Commission at the National Bureau of Standards.

[2] R. W. Buzzard and H. E. Cleaves, J. Met. and Ceram. (TID65) **1**, 43 (1948).

[3] Battelle Memorial Inst. Report CT 2483 (Dec. 1, 1944).

[4] A. U. Seybolt, LA68 (CT) (Feb. 15, 1944).

[5] A. U. Seybolt, LA69 (June 21, 1944).

[6] Spectrochemical analysis of gold: 0.01 to 0.1 percent of Ag, 0.01 to 0.1 percent of Cu, 0.0001 to 0.001 percent of Fe, 0.0001 to 0.001 percent of Si, and <0.0001 percent of Mg, (all percentages by weight).

[7] R. W. Buzzard, R. B. Liss, and D. P. Fickle, J. Research NBS **50**, 209 (1953) RP2412.

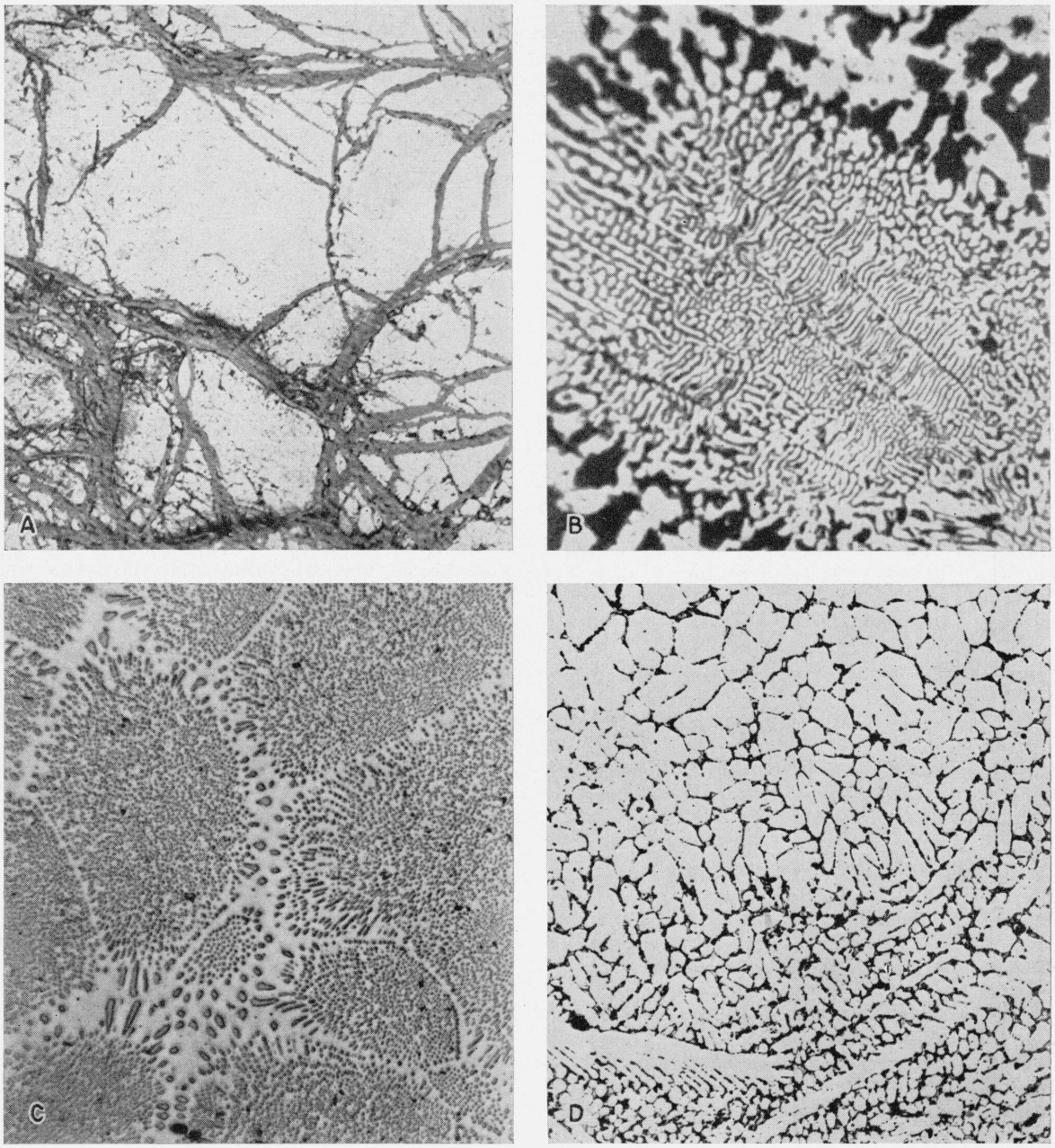

FIGURE 1. *Gold-uranium alloys.*

A. 65 atomic percent of gold alloy; inchoate oxidation (grey), U_2Au_3 (light), unetched. × 100.
B. 89.8 atomic percent of gold alloy; eutectic-type structure of gold phase (light) and epsilon (dark), 5 percent of KCN electrolytic etch. × 500.
C. 14.5 atomic percent of gold alloy, eutectic structure, containing excess delta (light) outlining grains, unetched. × 500.
D. 65 atomic percent of gold, epsilon phase (dark) outlining grains of delta, orthophosphoric acid plus acetic acid electrolytic etch. × 250.

4. Procedures

4.1. Thermal Analysis

Thermal arrests were determined by time-temperature analysis, in a molybdenum-wound furnace. In cases where an uncertainty of a thermal arrest existed, it was checked by differential analysis. The accessory apparatus included an air-operated controller to maintain uniform rates of heating and cooling and an electronic recorder to reproduce automatically the heating and cooling curves. The thermal curves were obtained from specimens of approximately 50 g, which were heated and cooled at controlled rates of 2 deg C/min, with the furnace operating under a vacuum of approximately 10 μ. The thermal arrests were derived from the cooling curves.

4.2. Microscopic Analysis

The specimens for microscopic analysis were mounted in Bakelite, ground on a series of silicon-carbide papers, with the finishing paper of 000 grit, and finished with levigated alumina either on a wet broadcloth lap or a dry paraffin lap. Excessive oxidation was encountered during the hot pressing of the Bakelite and on subsequent wet polishing of the alloys in the range 60 to 75 atomic percent of gold. These alloys were mounted in dental acrylic casting resin and dry polished.

In general, the structures of the uranium-rich alloys were developed by electrolytic etching in a chromic-acetic acid solution (100 ml of glacial acetic acid, 20 g of chromic acid, and 30 ml of water) by 2 to 4 immersions of 8-sec duration at 70 v and 10 amp/cm^2. The structures of the gold-rich alloys were developed electrolytically in a 5-percent solution of potassium cyanide by 2 to 4 immersions of 30 sec each at 4.5 v and 1 amp/cm^2. The structures of the alloys in the range of 45 to 75 atomic percent of gold were developed electrolytically in a solution containing 50 ml of orthophosphoric acid, 100 ml of concentrated sulfuric acid, and 100 ml of water by 2 to 4 immersions of 15-sec duration at 10 v and 10 amp/cm^2. This latter etching technique subsequently produced equally satisfactory results on alloys of all compositions and was used exclusively in the later stages of the investigation.

Specimens to be quenched were sealed under vacuum in 96-percent silica-glass tubes of 7-mm bore, homogenized for 8 days, and furnace-cooled. A homogenizing temperature of 825° C was used for gold-rich alloys, and 1,050° C for the uranium-rich alloys. The homogenized alloys were subsequently reheated and quenched in ice water. The nickel-block technique was used in the manner previously described.[8]

4.3. X-Ray Analysis

The specimens used for the microscopic studies were subsequently placed in an X-ray spectrometer, and the charts were obtained of the (Cu-Kα, or Co-Kα) X-ray diffraction maxima at room temperature. Powder patterns were used to supplement the spectrometer data. By this method it was possible to identify the phases present in the alloys and to approximate the alloy compositions at which the compounds appeared. These results were correlated with the thermal and microscopic data.

5. Results

5.1. Thermal Data

The results of the thermal analyses are given in table 2 and are also incorporated in the equilibrium diagram of figures 2 and 3. Additions of gold to uranium lower the melting point of uranium from 1,133° to 1,105° C at 10.5 atomic percent of gold, from which the liquidus temperature rises to a maximum in excess of 1,450° C at 75 atomic percent of gold; from the maximum the liquidus temperatures fall sharply to 855° C at 87.5 atomic percent of gold, and then rise sharply to the melting point of gold at 1,060° C.

The results of the liquidus determinations between 30 to 80 atomic percent of gold were subject to an error due to a reaction between the alloy and refractory. In this range of composition the alloys were very reactive in the liquid state, and during thermal analysis a reaction was noted between the alloys and the beryllia crucibles. Sometimes a reaction was observed when using thoria crucibles. With beryllia crucibles, the alloys showed a decided tendency to oxidize completely during the thermal-analysis cycle;

TABLE 2. *Summary of thermal data obtained for gold-uranium alloys*

Gold [a]	Thermal arrests					
	Liquidus	Peritectic	Eutectic	Solidus	$\gamma \rightarrow \beta$	$\beta \rightarrow \alpha$
Atomic %	°C	°C	°C	°C	°C	°C
99.9	1,060	------	------	1,060	----	----
99.7	1,056	------	------	985	----	----
99.2	1,052	------	853	----	----	----
98.6	1,044	------	855	----	----	----
95.7	980	------	858	----	----	----
93.7	981	------	854	----	----	----
92.4	955	------	853	----	----	----
90.9	888	------	859	----	----	----
87.3	959	------	856	----	----	----
85.4	997	------	856	----	----	----
76.1	>1,450	------	(b)	----	----	----
68.5	>1,360	(b)	------	----	----	----
55.2	(b)	1,222	(b)	----	(b)	648
55.7	1,376	(b)	1,105	----	(b)	646
40.3	(b)	1,212	1,108	----	739	647
36.1	(b)	1,215	1,107	----	738	646
27.2	1,262	1,218	1,105	----	736	647
23.0	1,265	1,218	1,106	----	736	646
12.2	1,200	------	1,105	----	736	648
11.6	1,163	------	1,105	----	739	648
6.2	1,116	------	1,105	----	737	646
3.7	1,115	------	1,105	----	739	646
2.5	1,122	------	------	1,107	737	652
1.0	1,132	------	------	1,116	739	647
0	1,133	------	------	1,133	762	653

[a] Analyses denote proportional ratio of components and do not reflect impurity.
[b] Arrest not determined because of controller failure.

[8] R. W. Buzzard, R. B. Liss, and D. P. Fickle, J. Research NBS **50** 209 (1953) RP2412.

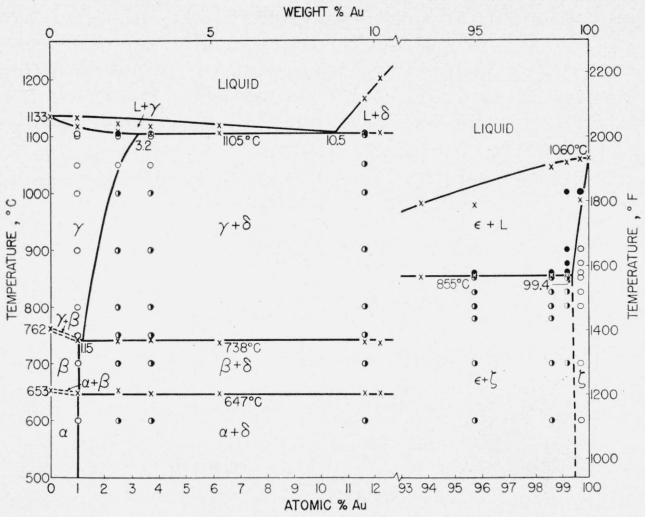

FIGURE 2. *Gold-uranium system, 0 to 12 and 93.0 to 100 atomic percent of gold.*

×, thermal arrests. Microscopic data: ○, one phase, ◑, two phase; ●, fusion.

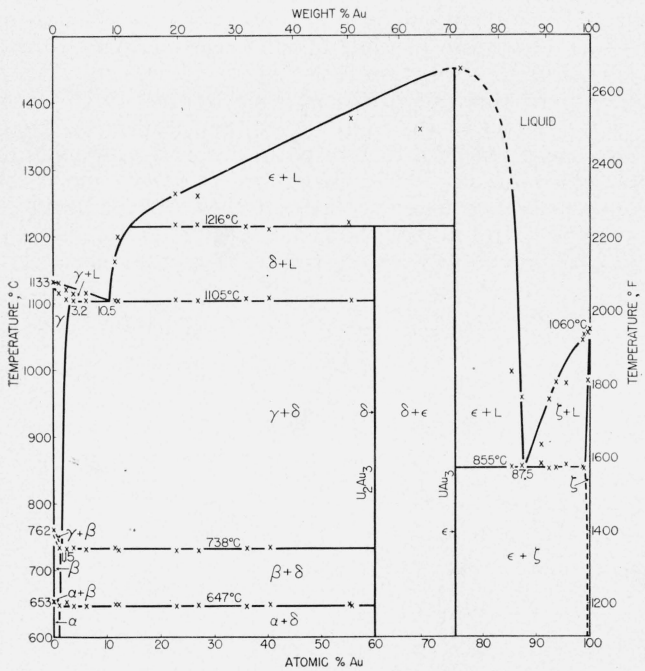

FIGURE 3. *Gold-uranium system.*

×, thermal arrests.

the oxidized mass apparently consisted of uranium oxide that was interspersed with pellets of practically pure gold. The thermal arrests reported were obtained from alloys tested in thoria crucibles and represent the arrests observed on material that appeared, on subsequent metallographic examination, to be of homogeneous oxide-free metal. The alloy having a composition of 76.1 atomic percent of gold apparently did not melt at 1,450° C; this was the limiting maximum temperature of the thermal-analysis furnace. Liquidus arrests reported above 1,300° C are approximations, as the characteristics of the furnace did not permit accurate determinations in excess of 1,300° C.

Thermal analysis of the alloys in the composition range 20 to 60 atomic percent of gold showed a consistent arrest in the vicinity of 1,216° C, which indicated a temperature horizontal in this range of composition. A second temperature horizontal was observed in the range of 3.7 to 60 atomic percent of gold in the vicinity of 1,105° C.

The gamma-beta transformation temperature of uranium was lowered by gold from 762° to 738° C. This value was constant for alloys containing 1 to 60 atomic percent of gold. The beta-alpha transformation temperature was similarly lowered from 653° C to the constant value of 647° C for the same alloys.

In the gold-rich alloys (75 to 99 atomic percent of gold) a consistent arrest occurred at 855° C. This together with the lowering of the melting point of gold to a minimum at 855° C at 87.5 atomic percent of gold by additions of uranium, was indicative of a eutectic transformation occurring in this composition range.

No solid-phase reactions were noted below 1,216° C in the composition range 60 to 75 atomic percent of gold, but it should be noted that only one alloy was examined in this composition range. No indication of the eutectic arrest was observed in the alloys containing 1.0, 2.5, and 99.7 atomic percent of gold.

5.2. Microstructures of the Alloys

In the study of the microstructures of the gold-uranium alloys a eutectic structure was observed in the range 75 to 99 atomic percent of gold (fig. 1, B). In the range of 75 to 87.5 atomic percent of gold a second phase appeared in increasing proportions as successive increments of uranium were added to the alloys. This second phase was optically isotropic under polarized light, and therefore it was concluded that this phase was not uranium. The alloy became increasingly brittle as the uranium content was raised—an indication of an intermetallic compound. Similarly, in the uranium-rich alloys in the range 2.5 to 60 atomic percent of gold two phases were observed. One phase consisted of a typical eutectic structure (fig. 1, C). The second phase was optically anisotropic and therefore differed from the second phase observed in the gold-rich alloys. This was indicative that at least two intermetallic compounds existed in the system.

A two-phase structure (fig. 1, D) was observed in the range 60 to 75 atomic percent of gold. One phase was identified as that common to the gold-rich alloys, and the second as that common to the uranium-rich alloys. From this evidence it was concluded that apparently only two intermetallic compounds exist in the gold-uranium system.

The identifiable phases observed in the microstructures of quenched alloys (table 3) were used in the determination of the uranium and gold solvus. The maximum solubility of uranium in gold was found

TABLE 3. *Microscopic analysis of gold-uranium alloys*

SS, solid solution; 2, two-phase structures; F, fusion.

Quench temperature	Typical microstructure—atomic percent of gold				
	1.0	2.5	3.7	11.6	23.0
	URANIUM-RICH ALLOYS				
°C					
1,105	SS	F	[a] SS	2	2
1,100	SS	SS	[a] SS	2	2
1,050	SS	SS	[a] SS	2	2
1,000	SS	2	2	2	2
900	SS	2	2	2	2
800	SS	2	2	2	2
750	SS	2	2	2	2
700	SS	2	2	2	2
600	SS	2	2	2	2

Quench temperature	Typical microstructure—atomic percent of gold			
	95.7	98.6	99.2	99.7
	GOLD-RICH ALLOYS			
°C				
1,000	----------	----	F	F
900	----------	----	F	SS
875	----------	----	F	SS
860	F	F	F	SS
855	F	F	----	----
850	2	2	2	SS
825	2	2	2	SS
800	2	2	2	SS
780	2	2	----	----
700	2	2	2	SS
600	2	2	----	SS

[a] According to thermal data these structures should be two phase; undoubtedly, the second phase was not developed by the metallographic technique used.

to be in the range 99.2 to 99.7 atomic percent of gold. The solubility of gold in alpha and beta uranium was found to lie between 1.00 to 2.5 atomic percent of gold. The microstructures indicated that the solubility of gold in gamma uranium was in the vicinity of 3.7 atomic percent of gold. The plot of the thermal-analysis data, however, located this at 3.2 atomic percent of gold.

5.3. X-ray Data

The X-ray diffraction patterns were obtained from the same surfaces that were used for the metallographic examinations, and the data obtained were correlated with the microstructures. The alloys quenched from the gamma field were identified by the alpha-uranium lines (transformed gamma). All the alloys in the range 1.0 to 59.9 atomic percent of gold gave diffraction patterns characteristic of the alpha uranium and a second phase (delta); in the range 65.0 to 74.1 atomic percent of gold a typical two-phase pattern was observed characteristic of delta and a second phase (epsilon); and the alloys containing in excess of 76 atomic percent of gold gave diffraction patterns typical of epsilon and gold.

In the region 1 to 60 atomic percent of gold, the X-ray diffraction charts were analyzed and compared; the diffraction peaks of uranium were determined by comparison with known alpha-uranium peaks.[9] The remaining unassigned peaks were attributed to a second phase (delta); the intensities and number of the delta peaks increased as the percentage of gold increased, whereas the intensities and number of the alpha-uranium peaks gradually decreased. However, the alloy containing 65.5 atomic percent of gold gave a diffraction pattern consisting of the peaks attributed to the delta phase plus weaker peaks later considered to be from the epsilon phase. Similarly, in the region 75 to 99 atomic percent of gold, the strength of the known gold peaks decreased with increasing amounts of uranium, though no peaks attributable to uranium itself were detected; the unknown peaks of this series of alloys were considered to be from a second phase (epsilon). The pattern from the alloy containing 76.1 atomic percent of gold consisted almost entirely of epsilon peaks. By such a comparison of intensities of known and unknown peaks, the composition of the delta phase was estimated to be 60 atomic percent of gold with the formula U_2Au_3, and the pure epsilon phase was estimated to consist of 75 atomic percent of gold with the formula UAu_3.

The known *d*-spacings for gold at room temperature were not changed appreciably by additions of

TABLE 4. *Interplanar spacings of compounds* [a]

Uranium plus delta at 55 atomic percent of gold	Delta spacings (most probable values)	Delta plus epsilon at 69 atomic percent of gold		Epsilon spacings (most probable values)	Epsilon at 76 atomic percent of gold		Epsilon plus gold at 85 atomic percent of gold
		Powder	Solid		Powder	Solid	
A	*A*	*A*	*A*	*A*	*A*	*A*	*A*
----------	----------	---- ----	3.117	3.059	3.068	3.033	3.121
----------	----------	---- ----	---- ----	2.513	2.524	2.513	2.524
[b] 2.484	2.490	2.451	2.485	---- ----	---- ----	---- ----	---- ----
----------	----------	---- ----	---- ----	2.451	2.451	2.445	2.451
2.369	2.382	2.372	2.387	2.377	2.377	2.387	2.382
----------	----------	---- ----	---- ----	---- ----	---- ----	---- ----	[c] 2.352
----------	----------	---- ----	---- ----	2.308	2.308	2.308	2.308
[b] 2.274	----------	---- ----	---- ----	---- ----	---- ----	---- ----	---- ----
----------	----------	---- ----	---- ----	2.152	2.152	2.161	2.144
----------	----------	---- ----	---- ----	----	----	----	2.051
2.055	2.061	---- ----	---- ----	----------	----	----	----
1.880	1.892	1.889	1.888	----------	----	----	----
1.714	1.721	1.712	1.716	1.716	1.719	1.714	----
----------	----------	----	1.559	1.551	1.551	1.553	1.550
[b] 1.536	----------	---- ----	---- ----	----------	----	----	----
----------	----------	---- ----	---- ----	----------	----	----	[c] 1.443
----------	----------	1.391	1.393	1.385	----	----	----
[b] 1.385	----------	---- ----	---- ----	----------	----	----	----
----------	1.374	1.373	----	----------	----	----	----
----------	----------	1.360	----	----------	----	----	1.352
1.304	1.305	1.300	1.304	1.304	1.309	1.309	----
----------	----------	---- ----	---- ----	1.283	1.283	1.284	1.283
[b] 1.241	----------	---- ----	---- ----	----------	----	----	----
----------	----------	---- ----	---- ----	----------	----	----	[c] 1.231
----------	----------	1.188	1.192	1.188	1.188	1.188	----
----------	----------	---- ----	---- ----	----------	----	----	[c] 1.179
----------	----------	1.072	1.072	1.071	----	----	----
1.028	1.032	1.029	1.039	----------	----	----	----
----------	----------	---- ----	---- ----	----------	----	----	[c] 1.021
----------	----------	0.945	0.944	0.944	----	0.953	----
----------	----------	---- ----	---- ----	.935	0.935	.933	----
----------	----------	---- ----	---- ----	----------	----	----	[c] 0.832

[a] Calculated from the 2θ values. [b] Uranium. [c] Gold.

[9] C. W. Jaco and B. E. Warren, J. Am. Chem. Soc. **59**, 2588 (1937).

uranium, nor were the *d*-spacings of alpha uranium changed by additions of gold. No appreciable solid solubility of either compound was detected. The interplanar spacings of the compounds (table 4) were determined, but the crystal structures of the compounds were not ascertained.

Powder methods of X-ray analysis were not completely successful owing to the high affinity of the compounds for oxygen. The microstructure of the alloy having a composition of 76.1 atomic percent of gold consisted almost entirely of the epsilon phase; the sample was so brittle that minute pieces (approximating a powder sample) were scraped off the ingot, sieved, and used as a powder sample. The many weak peaks obtained indicated a compound of low symmetry.

6. Proposed Diagram

The thermal arrests, derived from the cooling curves, were obtained from as-cast alloys that were cooled rapidly from the liquid condition. Chemical analysis showed these ingots to be homogeneous from top to bottom. Thermal arrests were observed at about 1,216°, 1,105°, 738°, and 647° C in most uranium-rich alloys (0 to 60 atomic percent of gold) and at about 855° C in most gold-rich alloys (75 to 100 atomic percent of gold); in the range of 60 to 75 atomic percent of gold, no thermal arrests were noted below 1,216° C. Metallographic studies revealed a eutectic-like structure in both the uranium-rich and gold-rich alloys and a two-phase structure in the range 60 to 75 atomic percent of gold. Both X-ray and metallographic analysis indicated the existence of two compounds having apparent compositions of U_2Au_3 (delta) and UAu_3 (epsilon). The reaction horizontal observed by thermal analysis at 1,216° C is peritectic in nature, denoting the formation of the delta phase by this reaction.

In the gold-rich alloys, correlation of the metallographic and thermal analysis data indicated a eutectic at 855° C and approximately 87.5 atomic percent of gold. Similarly, in the range 4 to 60 atomic percent of gold, correlation of metallographic and thermal-analysis data indicated a eutectic at 1,105° C and approximately 10.5 atomic percent of gold. The solubility of gold in uranium was established by correlation of metallographic and thermal data at approximately 3.2 atomic percent at 1,105° C, and the solubility of uranium in gold was established at approximately 0.6 atomic percent at 855° C (figs. 2 and 3). Two compounds, having the apparent compositions of 60 and 75 atomic percent of gold, were identified in the system. The compound at 60 atomic percent of gold was formed peritectically at 1,216° C, and the compound at 75 atomic percent of gold was congruent melting, with a melting point in excess of 1,450° C.

7. Summary

The gold-uranium system (fig. 3) was constructed from data obtained by thermal, microscopic, and X–ray analyses.

The system is characterized by (a) two eutectics, one occurring at 1,105° C and a composition of 10.5 atomic percent of gold, and the second at 855° C and 87.5 atomic percent of gold, and (b) two intermetallic compounds, one formed peritectically at 1,216° C having an apparent composition of 60 atomic percent of gold, and the second melting congruently in excess of 1,450° C, having an apparent composition of 75 atomic percent of gold. The solubility of uranium in gold appeared to be between 0.3 to 0.6 atomic percent at 855° C, and the solubility of gold in uranium was approximately 3.2 atomic percent at 1,105° C. The gamma-beta transformation temperature of uranium was lowered from 762° to 738° C and the beta-alpha transformation temperature was lowered from 653° to 647° C by gold.

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