Silver-Uranium System [1]

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The phase diagram of the system silver-uranium was constructed from data obtained by thermal analysis, metallographic examination, and X-ray diffraction. The system is characterized by a eutectic having a composition of approximately 5 weight percent of uranium occurring at 950° C, and a monotectic occurring at 1,132° C, and 0.23 weight percent of silver. The solid solubility of uranium in silver appeared to be between 0.1 and 0.4 weight percent at the eutectic temperature; no appreciable solubility of silver in uranium was noted. The temperatures of the gamma-beta and the beta-alpha transformation of uranium apparently were unaffected by silver.

1. Introduction

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

2. Previous Work

A survey of the literature showed that information on the constitution of the silver-uranium system was meager [1].[2] It has been reported that silver and uranium separated into two distinct layers on melting, with very little evidence of alloying [2] and were mutually insoluble. A eutectic was observed in the silver layer, and considerable loss of silver by evaporization was noted [2].

3. Preparation of Alloys

The base metals consisted of ~99.9 percent of uranium (Mallinckrodt Biscuit) and 999-fine silver. The alloys were prepared in beryllia crucibles in a high-frequency induction furnace under an atmosphere of purified argon [3].

It was observed from sectioned ingots prepared in the composition range of 30 weight percent of silver that silver and uranium separated into layers when molten (fig. 1). Chemical analysis of a number of ingots revealed that the silver layer consistently contained 4 to 5 weight percent of uranium. This factor was later used to advantage by taking the 4 to 5 weight percent of uranium alloy as a master alloy; other alloys were made by direct alloying. The melting characteristics of the system required that the temperature of charges consisting of primary uranium and silver be raised above the melting point of uranium in order to obtain alloying. The molten silver had a high vapor pressure and, at the melting temperature of uranium, a high loss of silver by vaporization was encountered.

Uranium was an effective deoxidizer of silver so that, as uranium oxide was rejected from the melt, this oxidation caused a loss of uranium from the silver-rich alloys on each subsequent melting or heat-treating operation. Analyses of the silver-rich alloys were made only for uranium and, as uranium oxide was included in the total uranium reported by this method, there is a possibility that sufficient uranium oxide was retained in the low-uranium alloys (<0.5 weight percent) to cause the results of the chemical analyses for uranium to be higher than the actual uranium content of the alloys. In view of the change of composition of the alloys caused by these factors during subsequent thermal studies, the reported compositions of the alloys (tables 1 and 2) were determined after examination rather than on the "as-cast" material.

TABLE 1. *Summary of thermal data obtained for silver uranium alloys*

Silver [a]	Thermal arrest				
	Liquidus	$\delta+L_2\rightarrow\delta$	$\delta+L_2\rightarrow\gamma+\delta$	$\gamma\rightarrow\beta$	$\beta\rightarrow\alpha$
wt-%	°C	°C	°C	°C	°C
100	961	------	------	------	------
99.99	959	958	------	------	------
99.98	959	------	------	------	------
99.97	957	954	------	------	------
99.95	956	954	------	------	------
99.85	956	955	------	------	------
98.30	959	------	950	------	------
95.70	------	------	949	770	658
0.23	1,135	------	952	764	661
.04	1,128	------	956	765	654
.035	1,133	------	942	766	650
0	1,133	------	------	762	653

[a] Compositions show the ratio of the component metals and do not reflect the impurities.

TABLE 2. *Summary of microscopic data obtained for silver-uranium alloys*

Uranium [a]	Number of phases observed—quenching temperatures, °C						
	As cast	600	700	800	900	950	955
wt-%							
0.01	1	1	1	1	1	1	1
.03	1	1	1	1	1	1	1
.1	1	1	1	1	1	1	1
.4	2	2	2	2	2	Fusion	Fusion.
1.7	2	2	2	2	2	------	Do.
1.8	2	2	2	2	2	Fusion	Do.
2.1	2	2	2	2	2	do	Do.
3.0	2	2	2	2	2	do	Do.
4.0	2	2	2	2	2	do	Do.
5.0	2	2	2	2	2	do	Do.

[a] Compositions show the ratio of the component metals and do not reflect the impurities.

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

[2] Figures in brackets indicate the literature references at the end of this paper.

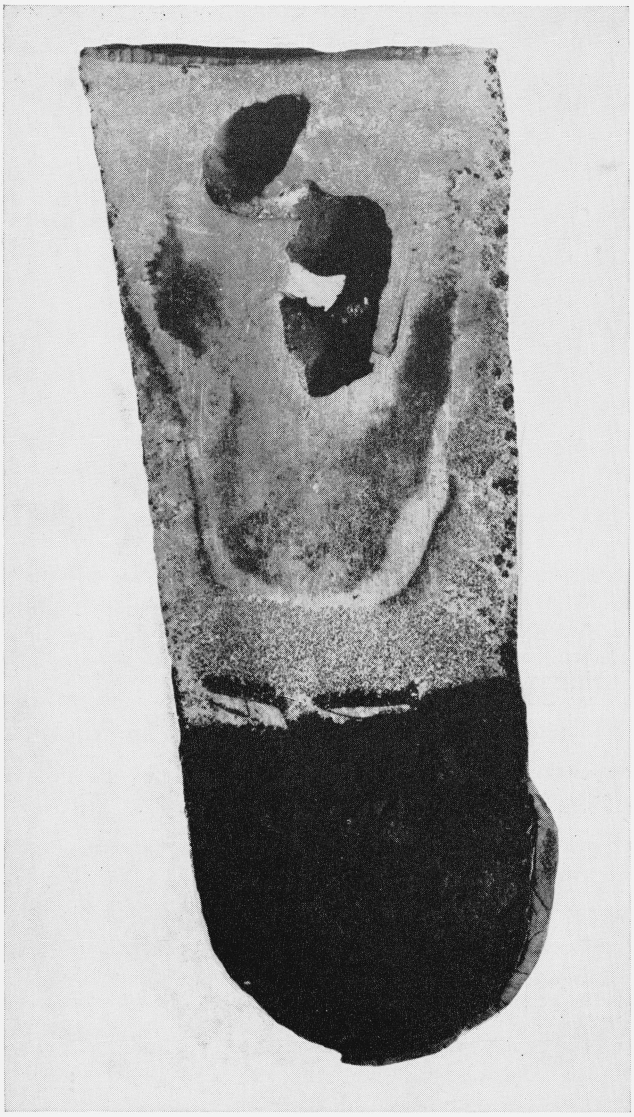

FIGURE 1. *Ingot containing 30 weight percent of silver showing the uranium (dark) and silver (light) layers.*

4. Experimental Procedures

4.1. Thermal Analysis

The thermal arrests were determined by time-temperature analysis, using a molybdenum-wound resistance furnace. The accessory apparatus included a program controller to maintain uniform heating and cooling rates and an electronic recorder to reproduce automatically the heating and cooling curves [4]. The thermal curves were obtained from specimens of approximately 50 g, which were heated and cooled at a controlled rate of 2° C/min with the furnace operating under an atmosphere of purified argon. The thermal arrests were derived from the cooling curves.

4.2. Microscopic Analysis

The specimens for microscopic examination were mounted in Bakelite, ground on a series of silicon-carbide papers, with the finishing paper of 000 grit, and finished either on a levigated alumina lap or electrolytically, using 70 v at 1½ amp, 3 to 6 immersions of 10-sec duration in an electrolyte of the following composition: 20 g of chromic acid; 30 ml of water, and 100 ml of glacial acetic acid.

In general, the structures of the silver-rich alloys were developed by swabbing with a modified chromic–sulfuric-acid solution [5] composed of 1 part of a concentrated stock solution (100-ml saturated solution of potassium dichromate in water, 2-ml saturated solution of sodium chloride in water, and 10-ml of concentrated sulfuric acid) in 9 parts of water. The silver-rich alloys developed a grayish coating and required a light polish on a alumina finishing lap after etching. The structures of the uranium alloys were developed electrolytically in a 10-percent chromic-acid solution, using 0.5 amp and 4 v at 25° C.

Specimens to be quenched were sealed under argon in high-silica glass tubes of 7-mm bore, homogenized for 8 days at 925° C, and furnace-cooled. The alloys were quenched in ice water, using the nickel-block technique, in the manner described for the titanium-uranium alloys [3].

4.3. X-ray Analysis

The specimens used for the microscopic studies were subsequently placed in an X-ray spectrometer and a chart obtained of the (Cu-Kα) X-ray diffraction lines at room temperature. By this method it was possible to identify the phases present in the alloys and correlate the X-ray and microscopic data.

5. Results

5.1. Thermal Data

The results of thermal analysis (table 1) were were obtained from the two terminal-alloy series (0 to 0.23 weight percent of silver and 0 to 5 weight percent of uranium). The alloys in the composition range 0.23 to 95 weight percent of silver separated into two layers during the thermal-analysis cycle, each layer having an analysis within the respective terminal-alloy composition range, as indicated above.

Thermal-analysis data of the silver-rich alloys (1 to 5 weight percent of uranium) showed consistent arrests in the vicinity of 950° C. Similar arrests were observed for the uranium-rich alloys; in these alloys a second arrest was observed at approximately 1,132° C. The uranium transformations were noted in all alloys and were apparently unaffected by silver.

Two alloys (30 weight percent and 50 weight percent of silver) in the composition range of the liquid miscibility gap were prepared, and time-temperature cooling curves were determined on the

whole ingot. Arrests identical to those previously recorded for the uranium-rich terminal alloys were observed. The resultant ingots showed a sharp line of demarcation between a silver-rich and an uranium-rich layer. The layers were parted and reexamined by thermal analysis. Each layer developed arrests characteristic of the respective terminal-alloy series. The miscibility gap extended over the greater portion of the system. It was not possible to obtain liquidus determinations for compositions in excess of 5 weight percent of uranium because the alloys separated into two layers during thermal analysis. This indicated that the liquidus rose sharply from the eutectic to the monotectic temperature. On the basis of these observations, it was concluded that the composition range of the miscibility gap was determined to be approximately 0.23 to 94.5 weight percent of silver at the monotectic temperatures. The vapor pressure of silver greatly influenced the determination of the thermal arrests in the uranium-rich alloys. It was evident that silver had little effect on the thermal arrests of the uranium-rich alloys, and the temperatures used in the construction of the diagram were based on the values obtained for uranium.

5.2. Microstructures of the Alloys

In the study of the microstructures of these alloys (table 2), using the number of identifiable phases present as the criterion, it was revealed that the solubility of uranium in silver lies between 0.1 and 0.4 weight percent at room temperature, and little change in this value was observed between 25° C and 950° C.

A eutectic-like structure was observed in both the uranium-rich (fig. 2A) and the silver-rich (fig. 2B) alloys. Results of the microscopic analyses showed the eutectic composition to be approximately 5 weight percent of uranium and the monotectic composition to be approximately 0.23 weight percent of silver. In the composition range 0.4 to 5.0 weight percent of uranium, some evidence of fusion was observed at the edges of the specimens quenched from 950° C and complete fusion was observed at 955° C. This confirmed the eutectic temperature of 950° C as observed by thermal analysis.

5.3. X-ray Identification

X-ray diffraction charts were obtained, using the same surfaces of the specimens as were examined microscopically; the results of the X-ray and microscopic examination were then correlated. Only uranium and silver lines were observed for the alloys examined in this system.

6. Proposed Diagram

The thermal arrests, derived from the cooling curves, were obtained from "as-cast" alloys that were rapidly cooled from the liquid condition. Chemical analysis showed these ingots to be homogeneous from top to bottom. Since both silver and uranium were lost during the thermal analysis cycle, the reported alloy compositions are those determined from the chemical analysis of samples cut from the ingot (at the thermocouple tip) after thermal analysis.

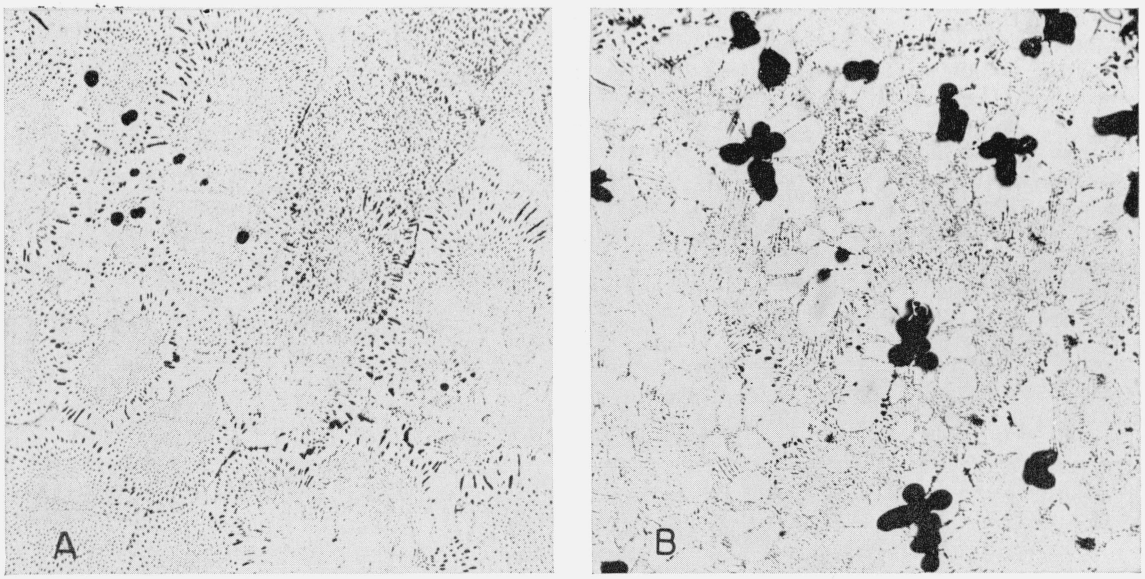

FIGURE 2. *As-cast alloys, showing characteristic eutecticlike structutes found in both the uranium-rich and the silver-rich terminal alloys.*

A, 4.5 weight percent of uranium, chromic-sulfuric etch. B, 0.07 weight percent of silver, electrolytic etch, 10-percent chromic acid. Magnification, X100.

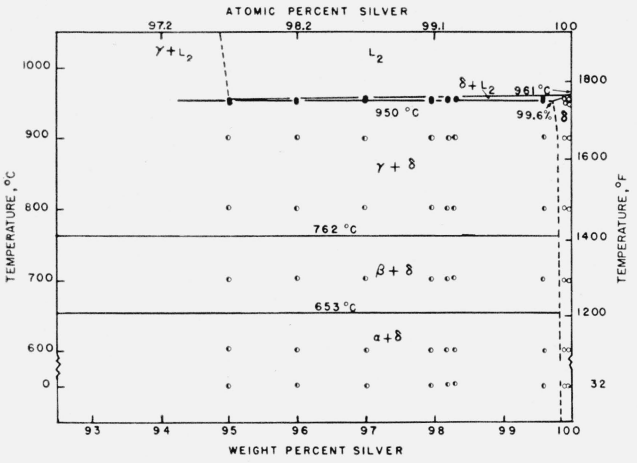

FIGURE 3. *Silver-uranium system, 94 to 100 weight percent of silver.*

Microscopic data: ○, one phase; ◐, two phase; ●, fusion.

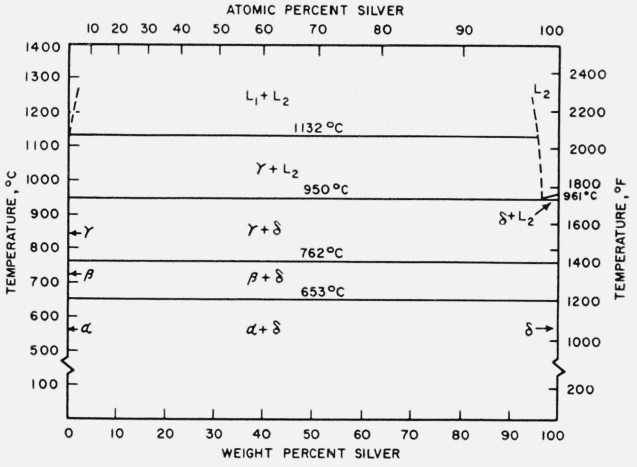

FIGURE 4. *Silver-uranium system.*

Thermal arrests were observed at about 950°, 762°, and 653° C in both the uranium and silver-rich alloys, and in the vicinity of 1,132° C in the uranium-rich alloys. Microscopic studies revealed a eutectic-like structure in both series of alloys. It was indicated that a monotectic occurred in the system at approximately 0.23 weight percent of silver and at the melting point of uranium; it was not possible to differentiate between the melting point of uranium and the monotectic temperature. In the silver-rich terminal alloys, fusion was noted at about 950° C in the composition range 0.4 to 5.0 weight percent of uranium (table 2), indicating a eutectic occurring at 950° C and approximately 5 weight percent of uranium. The microscopic studies of the quenched alloys used in the determination of the silver-uranium solvus were made on specimens that were heat treated prior to chemical analysis. It was well established that the solubility of uranium in silver is less than 0.4 weight percent at the eutectic temperature of 950° C (fig. 3). In evaluating the studies of the alloys in the composition range of less than 0.4 weight percent of uranium, it must be borne in mind that the uranium-oxide content of the alloy appears as uranium in the chemical analysis, and it is quite possible that the solubility may be even lower than reported. No intermediate phases or intermetallic compounds were observed in the system as a result of X-ray, thermal, or microscopic analysis.

7. Summary

The silver-uranium system (fig. 4) was constructed from data obtained by thermal, microscopic and X-ray analyses.

The important features of the system include: (a) A monotectic at 0.23 weight percent of silver and 1,132° C with a liquid miscibility gap extending from 0.23 weight percent to approximately 94.5 weight percent of silver. (b) A eutectic at approximately 5 weight percent of uranium and 950° C. (c) The solubility of uranium in silver appeared to be between 0.1 and 0.4 weight percent at the eutectic temperature while no appreciable solubility of silver in uranium was noted. (d) The gamma-beta and the beta-alpha transformations of uranium were apparently unaffected by silver.

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8. References

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