MASTER

Liquid Metal Fuel Constitution

1. The Solubility of Uranium in Bismuth

by

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ABSTRACT

High vacuum, high temperature equipment for rapid, accurate determinations of liquid metal solution compositions is described.

The solubility of uranium in bismuth has been re-determined over the temperature range 300 to 725°C with improved precision and temperature calibration.

Anomalous solubility effects in uranium-bismuth-graphite systems which could affect the operation of reactors containing graphite have been described.

INTRODUCTION

The need of a method for rapid, accurate sampling of liquid metal solutions occurs frequently in the study of liquid metal alloys. The problem is particularly important in reactor experiments where liquid metals are used as fuel carriers, coolants, and heat exchange media. Studies of the solubilities of fuel components, rates of dissolution of container materials, and solid-liquid surface reactions require that the changes in solution composition be followed as functions of time and temperature. In systems where solute

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components are increasing or decreasing with time and temperature such studies may involve equilibria or kinetics making it desirable to sample frequently and quickly.

The most suitable nuclear fuel for a liquid metal fuel reactor is a solution of uranium in liquid bismuth.⁽¹⁾ The solubility of uranium in bismuth has been investigated by several workers^(2,3,4,5,6). However, the results obtained in some cases differ by more than a factor of two, whereas reactor design considerations require precise ($\pm 2\%$) knowledge of this solubility. Recent improvements in analytical techniques and in equipment sensitivity have permitted a re-determination of the solubility with higher precision.

EXPERIMENTAL

Materials

1. Helium - Reagent grade tank helium was passed over a charcoal cold trap immersed in liquid air and then into a titanium chip tank held at 850°C. The final test of purity used was to pass the helium over polished uranium at 600°C at the rate of a liter per minute for 1 hour. If the surface of the uranium did not tarnish the gas was considered useable.

2. Bismuth - 99.999% bismuth (in which the principal impurities are usually Pb, Cu, Ni, Sn, Fe, Zn, Ag, and Cl) was deoxidized and dechlorinated by hydrogen firing at 600-700°C. Analyses for the trace impurities were carried out during the experiments since different batches of

bismuth had slightly different impurity levels.

3. Uranium - Various batches of high purity uranium were analyzed during the experiments. At no time did any of the impurities being investigated exceed 100 ppm in the pure metal. Since this was diluted by more than a factor of 10 in the solubility experiments, the uranium did not introduce impurities in excess of those generally present in the bismuth.

4. Graphite - "Graphitite* G" which was used in crucibles and samplers was degassed (and in some cases degassed and hydrogen fired) at 800°C before coming into contact with the liquid metal solutions.

5. Molybdenum - The molybdenum crucibles used in these experiments had been repeatedly contacted with uranium-bismuth solutions. Analyses during the experiments indicated that the only impurity introduced into the solutions was a small amount of Cu. Over a period of two weeks, the Cu content of one solution increased from 5 to 15 ppm.

Apparatus and Procedure

A high temperature, high vacuum system designed to permit the continuous rapid determination of liquid metal solution compositions is shown in Figure 1. The system is similar to that described previously⁽⁷⁾ but has been modified to give more precise temperature measurements and to permit mixing of the solution during the experiments.

* Obtained from the Graphite Specialties Corp., Niagara Falls, N.Y.

The apparatus consists of two vacuum chambers of 2 inch stainless steel tubing (A) separated by a ball or gate valve (B). The vacuum manifold is so arranged that either chamber can be evacuated or pressurized with purified H_2 or He independently of the other. The lower chamber, which passes through an 18" clamshell furnace (C), is sealed at the bottom by means of an "O" ring flange (D), which opens to admit or remove the crucible (E) used to contain the liquid metal. A Leeds and Northrup "Micromax" controller-recorder is used to control the temperature of the furnace. The upper chamber can be opened at the top at the Dresser coupling (F) to admit sampling devices, additives, bismuth, etc. These can be attached to the 1/2" sliding tube (G) which in turn can be lowered into the melt when the valve (B) is open by sliding through the Wilson seal (H) without contaminating the vacuum or purified gas atmosphere in the furnace chamber. The coil of copper tubing (I) permits vertical motion of the sliding rod.

The liquid metal is purified within the system by loading cold bismuth into a length of 1 1/4 inch diameter steel pipe whose lower end is sealed with a type 410 stainless steel filter. The pipe is then attached to the slide tube (G), admitted into the top chamber through the Dresser coupling (F), evacuated, and lowered into the furnace chamber. When the metal reaches the desired temperature, purified hydrogen is admitted to the system, passed through

the filter and up through the melt escaping via the exhaust burner (J). After one hour, the liquid metal is cooled to approximately 325°C to precipitate any iron and chromium that dissolved during purification. The system is then evacuated and purified helium is admitted through the coiled tube (I) forcing the liquid metal through the filter into the crucible (E). The empty firing tube is then pulled into the top chamber, the gate valve and necessary manifold valves are closed, and sufficient time is allowed for cooling. The Dresser coupling is opened, the tube removed, and a sampler placed on the end of the slide tube.

Sampling is accomplished by an inert sampler (graphite, pyrex, vycor, tantalum, molybdenum, etc.)*, which consists of a 1/2 to 3/4 inch diameter cylinder with a 30-40 μ pore-size frit. A vycor or pyrex sampler is shown in Figure 2. Several large holes are placed in the walls of the sampler above the filter to allow easy admission of the solution. A thermocouple sealed in a stainless steel tube, which in turn is placed in an inert (vycor) thermocouple shield tube, is placed directly above the filter. This arrangement permits the thermocouple to measure the liquid metal temperature directly at the exact time the sample is being taken. With this technique the solution temperature can be determined within $\pm 0.5^\circ\text{C}$. In practice, the sampler is preheated above the melt until the thermocouple reading corresponds to the expected melt temperature as determined by experience. It

* These do not react appreciably with the solute or solvent metals during the short (1/4 hour) contact time required during the sampling procedure.

is then immersed in the melt under vacuum and allowed to remain there until the thermocouple reading stays constant for 5 to 10 minutes. During this time the melt flows freely through the hole above the filter and surrounds the thermocouple shield but is prevented by surface tension from passing through the filter. Purified He is then admitted to the system pushing the solution through the filter into the evacuated sample chamber. The sampler is removed and solidified under He in the chamber above the gate valve B (Fig. 1). The entire Bi sample is dissolved for chemical analysis to eliminate effects due to segregation during solidification. The thermocouple is calibrated periodically by measuring the freezing point of bismuth.

With this equipment, stirring can be used for those systems that take long times to reach equilibrium. A cylinder whose lower end is sealed with a frit is placed on the slide tube with a vacuum tight adaptor. Purified helium is then admitted into the coiled tube (through a flowmeter), down through the slide tube and fritted cylinder and bubbled through the melt. Mechanical stirring can be accomplished by putting a propeller on the bottom of the thermocouple tube and turning the tube through the Wilson seal by a magnetic clutch or motor-gear mechanism. Generally, the errors introduced by the equipment are smaller than those due to the chemical techniques used in the solution analysis.

RESULTS AND DISCUSSION

The Solubility of Uranium in Bismuth

The solubility of uranium in bismuth is shown in Figure 3. The data were obtained from three separate pieces of equipment (identical to that shown in Figure 1), using pyrex, vycor and "Graphitite G" samplers, and vycor, "Graphitite G", and molybdenum crucibles. The solutions contained from 3 to 10% uranium by weight. It can be seen that there is no difference in the data obtained from the different sampling techniques or equipment. Equilibrium was checked by allowing various solutions to remain at temperature for times ranging from 3 hours to 17 days, and by taking samples on both cooling and heating cycles. No discernible differences were found with either of these techniques.

The thermocouple and temperature readings were checked by placing the sampler and thermocouple in the same position that they occupy during the sampling procedure while measuring the freezing point of the U-Bi solution. The freezing point determined in this way was found to be $271.3 \pm 0.3^\circ\text{C}$ which is in excellent agreement with the accepted value for the freezing point of bismuth.

The uranium solubility curve of Figure 3 can be approximated by the equations

$$\log_{10} (\text{ppm U}) = 6.585 - \frac{2240}{T} (\pm 2\%) \quad (300-480^\circ\text{C})$$

$$\log_{10} (\text{ppm U}) = 7.263 - \frac{2744}{T} (\pm 10\%). \quad (480-725^\circ\text{C})$$

For the lower temperature range, the precision obtained in these experiments is the same as that of the analytical techniques. The solid in equilibrium with the melt throughout the temperature range investigated is $\text{UBi}_2^{(5)}$.

Graphite Effects on the Solubility of U in Bi

No effects by container materials on the solubility of uranium were found when large excesses of uranium were present in the systems. However, when uranium in small excess of the saturation value at these temperatures was placed in graphite crucibles containing bismuth, precise, reproducible solubility curves were obtained that were considerably lower than those obtained in the former experiments. No such effects were found in molybdenum or vycor crucibles. Figure 4 shows some of the typical curves obtained using graphite crucibles. Several of these solutions have Mg present as a deoxidant and Zr as an inhibitor for uranium graphite reactions. Other work to be published by the authors has shown that Mg preferentially oxidizes before U and that Zr prevents U from forming carbides by reaction with graphite. It can be seen from the curves in Figure 4 that neither one nor both of these additives prevented the reduction of the uranium solubility. Furthermore, it was found that all the uranium originally added in these experiments could be driven back into solution at temperatures much higher than those corresponding to the normal saturation temperature. It appears that the reactions causing the apparent reduction

in uranium solubility do not permanently remove uranium from solution, but they may result in as much as 10 to 50% decreases in apparent solubility in these systems. The possibility of concentrating uranium in the graphite of the reactor core by these reactions could cause serious problems in the control and operation of the reactor. Further work is necessary for a more thorough understanding of the reactions in these systems.

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FIGURE TITLES

1. Liquid Metal Solubility Apparatus.
2. Liquid Metal Sampling Procedure.
3. The Solubility of Uranium in Bismuth.
4. Sparious Solubility Data Obtained from U-Bi Alloys with Low U Content Held in Graphite Crucibles.

SAMPLING PROCEDURE

PLEASE REFER TO NEG # 8-235-58