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SAMPLING OF LIQUID METALS

by

I. O. Winsch, K. R. Tobias,
R. D. Pierce, and L. Burris, Jr.

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Chemical Engineering Division

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ABSTRACT

Methods and devices for obtaining both filtered and unfiltered samples of a metal solution containing insoluble material are described. Reasons why filtered samples are often necessary and precautions required during sampling are discussed. Evidence that establishes the reliability of the sampling methods described is presented.

I. INTRODUCTION

Determination of the concentration of a solute element in a saturated liquid-metal solution containing the equilibrium solid phase is often difficult. Such determinations are useful, for example, in locating liquidus lines of a phase diagram. A method sometimes used to obtain liquid phase samples that are free of the equilibrium solid phase is careful withdrawal of a portion of the supernatant liquid after allowing the solid or precipitated phase to settle for a long period of time while the temperature is maintained at a constant value. This procedure is laborious, time-consuming, and often somewhat unreliable, even when great care is exercised. Various methods of obtaining filtered samples of a liquid-metal phase in the presence of any precipitate material, for example, oxides or precipitated metal phases, have been developed at Argonne National Laboratory and constitute rapid, efficient means of securing highly reliable samples.

Various sampling techniques have been used at Argonne National Laboratory to sample unsaturated liquid-metal solutions and two-phase metal-metal and metal-salt solutions. Samples of immiscible phases are required in connection with the development of pyrochemical processes for recovery of uranium and plutonium present in discharged reactor-fuel materials. In these processes, molten halide salts and molten metal solutions consisting of various combinations of zinc, cadmium, and magnesium are used as processing media.^{1,2,3} Reliable sampling techniques have had to be developed for accurate determination of the distribution of solute elements between immiscible phases and for determination of process performance.

This report has been written in the belief that the sampling techniques developed at Argonne may be of interest and of use to others who require reliable samples of liquid-metal solutions.

II. SAMPLING TECHNIQUES

A. Filtered Samples

To obtain reliable samples of a liquid-metal or salt phase for determination of the concentrations of solutes in solution, it is necessary to exclude any solid phases that may be in suspension. This is especially important in the determination of liquidus lines of a phase diagram. In certain areas of the phase diagram, the equilibrium solute concentrations may be very low, and the inclusion of even small amounts of solid material would introduce large errors.

To overcome this problem, a sampling procedure was developed by which filtered samples were obtained. This was accomplished by filtering the solution under the action of a pressure differential through a plug of porous filter material (a filter frit) fitted into the end of a sample tube. The solution may be forced through the filter frit under pressure applied to the solution outside the sample tube or pulled through by vacuum applied through the sample tube. Because the solution may boil under the vacuum within the sample tube, forcing the solution through the filter frit by pressure is often preferable. The filter material, as well as that of the sample tube, should be inert to the solution being filtered.

At Argonne, sampling techniques and materials were improved in a normal evolutionary development. During this development, several different systems of interest in reactor-development fuel processing were investigated to develop information on process performance, distribution coefficients, solubilities, and oxide reductions. The solutions being sampled were generally zinc-magnesium solutions, which were employed at temperatures up to 800°C as process solvents for uranium and plutonium. The zinc-rich solutions are highly corrosive, being containable only in graphite, tantalum (with limitations), tungsten and certain of its alloys, and various ceramic materials. Initially, samples were obtained by filtering the solution through plugs of porous graphite of various porosities fitted into the open end of 6-mm-OD Vycor tubing. Figure 1 illustrates a method of preparing graphite plugs by coring them from a block of porous graphite. These plugs were then worked into the end of the Vycor sampling tubes to form a snug fit as shown in Fig. 2. Some early sampling units are shown in Fig. 3.

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Fig. 1. Preparation of Porous Graphite Plugs

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Fig. 2. Preparation of Vycor Sample Tubes for Obtaining Filtered Metal Samples

(Porous graphite plugs are inserted into end of tube as shown. End of plug is made flush with tube end by breaking off the protruding part of plug. Tubes on left have been coated internally with materials such as MgO , ThO_2 , or BN to prevent interaction of the molten metal sample with the Vycor tube.)

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Fig. 3. Vycor Tube Sample Units. (Tube on left has stopcock with evacuated tube, middle has rubber bulb, and right has syringe.)

It was subsequently discovered that the graphite was interacting with certain solutes, thereby resulting in low analyses for the samples. Moreover, magnesium when present reacted with the Vycor tubing, both inside and out, forming an interaction layer, which prevented easy recovery of the sample by breaking away the Vycor tubing. To prevent interactions with the Vycor tubing, protective coatings were applied to both the outside and inside of the Vycor tubes: to the outside, by flame-spraying a deposit of alumina; to the inside, by washes or slurries of MgO , ThO_2 , or BN in a volatile solvent, such as alcohol or acetone. The volatile solvent was later removed by heating, leaving a protective film of material on the inside. Open-end tubes, coated internally with thoria and externally with alumina, have been used successfully to obtain samples of molten uranium melts. However, not all of the difficulties with the Vycor sample units could be easily overcome, e.g., interactions with the graphite filters; occasional fracture of the graphite plugs, which resulted in contamination of the metal solution with carbon; and occasional breakage of the Vycor tubes, which resulted in gross contamination of the solution with silica.

To avoid these difficulties, a change was made to tantalum frits and tantalum sample tubes, 0.25-in. OD with 10- and 20-mil thick walls. The frits were developed by the Kawecki Chemical Co. and were obtained in three porosities, coarse, medium, and fine (designated by Kawecki as C-1534, KL-308, and W-36, respectively). Porosities and other properties of the frits are given in Table I. Enlarged photographs of the three types of tantalum filter plugs are shown in Fig. 4. Photomicrographs of the three porosities are shown in Fig. 5. The fritted plugs (1/4 in. long) were inserted snugly into one end of tantalum tubes 4 to 6 in. in length by two methods. The frits fit easily into 10-mil wall tubing. Therefore, in the first method

TABLE I. Properties of Pressed-and-sintered Tantalum Filter Plugs

Property or Variable	C-1534 (Coarse)	KL-308 (Medium)	W-36 (Fine)
Particle sizes in starting tantalum powder (mesh)	20-60 (100%)	60-100 (25 to 38%) 100-200 (25 to 38%) 200-325 (10 to 25%) -325 (10 to 25%)	200-325 (1 to 2%) -325 (remainder)
Green density (g/cc)	6.0	7.8	8.3
Sintering temperature ($^{\circ}\text{C}$)	1750	1950	1750
Sintering time (hr)	0.5	0.5	0.5
Final density (g/cc)	6.1	8.1	9.6
Final dimensions	0.244 in. OD x 0.25 in.	0.224 in. OD x 0.25 in.	0.224 in. OD x 0.25 in.

Coarse Filter Plug
(No. C-1534)

Medium Filter Plug
(No. KL-308)

Fine Filter Plug
(No. W-36)

Fig. 4. Enlarged Photographs of Fritted Tantalum Filter Plugs. (All filter plugs have actual diameters of 0.224 in.)

Coarse-porosity Filter
(W-36)

Medium-porosity Filter
(No. KL-308)

Fine-porosity Filter
(C-1534)

Fig. 5. Photomicrographs of Cross Sections of Fritted Tantalum Filter Plugs. [1 Div. = 18.5μ (same enlargement for all micrographs).]

(used with 10-mil tubing), a rather deep circular indentation was first rolled into the tube slightly over 1/4 in. from the end to serve as a shoulder for the plug. The tube wall was then forced tightly against the plug by two rolled indentations opposite the plug (see Fig. 6). The blade of the tubing cutter used for rolling in the indentations was previously dulled to avoid cutting the tubing. In the second and superior method, the fritted plugs are forced into a 20-mil-wall tube by the device shown in Fig. 7. The tantalum

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Fig. 6. Manual Insertion of Fritted Tantalum Filter Plugs

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Fig. 7. Swaging Tool* Employed for Insertion of Fritted Tantalum Filter Plug

*Manufactured by the Imperial Brass Company.

tube is first fastened into position, the tube end is expanded slightly by means of a swaging die, and then the fritted plug is pressed into position. This device, a production swaging tool manufactured by the Imperial Brass Company with special dies, permits easy, reliable, and uniform insertion of fritted tantalum plugs into the sample tubes.

Short lengths of tantalum tubing were employed to reduce the expense of sampling. These short lengths were attached to steel extension rods, which extended from the tube above the melt out of the equipment as shown in Figs. 8a, 8b, and 8c or 8d. The methods of attachment consist, respectively, of driving the tube over a tapered end of the steel rod, of screwing a female plug pressed into the other end of the tube onto a steel rod, and of sliding the tube over the steel rod (after expanding the tube slightly with the swaging tool) and crimping it to the rod by the rolled indentations. The use of a 2.5° taper is recommended for attachment of the tube to a tapered rod. The tube does not hold to the rod well when greater tapers are used and is difficult to remove from the rod when lesser tapers are employed. The tapered-rod technique has worked reliably with 15- and 20-mil tubing but was not reliable (with a 2.5° taper) with 10-mil tubing.

With the assemblies shown in Figs. 8a, 8b, and 8c, solution was forced into the sample tube by external pressure on the solution surface; with that shown in Fig. 8d, solution was pulled through the frit by vacuum

applied through a capillary tube from small vacuum reservoirs (syringes, rubber bulbs, etc.). In two-phase systems, the lower phase may be sampled with the capillary tube sampler by blowing an inert gas through the frit as the tube is lowered into the lower phase; in the closed-tube techniques, the expansion of the inert gas out of the sample tube provides the same effect.

Fig. 8. Tantalum Tube Samplers for Obtaining Filtered Samples of Metal Solutions

Besides providing a filtering action, another important function of a frit in the tube end is to help prevent drainage of any sample liquid out of the tube when it is withdrawn from the solution. If such liquid is the solution remaining after crystallization of material out of solution, then large sampling errors can result. As a further precaution that none of the sample

drains out of the sample tube, the pressure outside the tube (or vacuum within) should be maintained until the sample has solidified.

The pressure differential required to move solution through the frit is dependent on the solution properties, the porosity of the frit, and the wetting of the frit by the solution and must be determined by experiment. Normally, a sample can be obtained in about 2 min (including preheating of the sample tube above the melt and pressurizing the furnace) with a pressure differential of 10 to 20 psia.

Fig. 9. Lock Assembly for Obtaining Samples within Furnace Containing an Inert Atmosphere

Generally, the solution to be sampled is within a furnace chamber in which a high-purity inert atmosphere is maintained. To prevent contamination of the inert atmosphere with air, the sampling device must be inserted through a lock similar to that diagrammed in Fig. 9. The lower valve should be a plug or ball valve in order to make available a straight-through opening having the same diameter as the pipe to facilitate the passage of the sample tube.

Because segregation of solute in the sample may occur as it is cooled, the entire sample must be used for analysis. Two methods may be used for removing the sample: (1) the thin-wall tubing may be peeled away from the sample, as shown in Fig. 10, or (2) the entire sample may be dissolved out of the tubing. The first procedure is the more facile. When

Fig. 10
Removal of Filtered
Sample by Peeling
off the Tantalum
Sample Tube

the dissolution procedure is employed, it is necessary to insure that all of the sample is included and that all of the precipitate phase is excluded. This is accomplished by cutting off and discarding the outer half of the filter plug before the sample is dissolved out of the tantalum. The tantalum sample tubes may be reused until they become too short; however, often the portion containing the sample is sacrificed by cutting it into short lengths to enhance the dissolution rate of the sample.

That reliable solution samples are obtained by the above techniques is shown by the solubility data for plutonium, uranium, and thorium in zinc given in Fig. 11.^{4,5,6} The effectiveness of a filter in removing insoluble material is illustrated by Fig. 12. Even at low temperatures, where the solubility of a particular solute is low and most of it has been precipitated from solution, the solubility data lie closely along a line that is fairly well established by higher temperature data. Similar data have been obtained for many solute elements in zinc, magnesium, cadmium, and other systems.⁶⁻¹⁶ All of the sampling operations required to produce solubility data of the type shown in Fig. 11 can be accomplished in a relatively short time (~8 hr) under both ascending and descending temperature conditions. However, in some systems, longer times may be required for equilibrium at each condition before sampling of the melt.

Fritted filter materials of a variety of metals can be obtained for meeting the requirements of particular sampling situations. Stainless-steel filters of Types 304, 309, 316, 347, 410, 430, and 446 in thicknesses

of 1/16 to 1/4 in. may be obtained commercially in a number of porosities. Stainless steels may be used for sampling alkali, alkaline earth, and cadmium metal solutions. Fritted filters of nickel, Monel, platinum, gold, silver, and tungsten are also available. The pore size of a filter is given in microns. The "mean pore size" is a value calculated on the basis that half the flow area is provided by pores larger than the mean, and half by pores smaller than the mean. The most commonly used frits have mean pore sizes of 20 and 35 microns.

Fig. 11. Solubility of Thorium, Uranium, and Plutonium in Zinc

B. Unfiltered Samples

In some circumstances, unfiltered samples are necessary or will suffice. Generally, when a

Fig. 12. Enlarged Cross-sectional View of Filter after Sampling.
 [1 Div. = 9.25μ (same enlargement for both micrographs).]

sample does not have to be filtered, some form of bucket sampler is used to insure that there will be no loss of supernatant liquid or mother liquor. Variations of the bucket-type samplers are numerous. For example, if only one phase is present, or if the upper phase of a two-phase system is to be sampled, a simple device such as that shown in Fig. 13a will suffice.

Fig. 13. Samplers for Obtaining Unfiltered Samples of Metal Solutions

blowing an inert gas through the capillary while the tube is being lowered through the upper phase. Through practice, the size of the vacuum source and the initial pressure in the vacuum source can be adjusted to give the desired sample size.

More sophisticated devices, which allow use of the same extension rods used for filtered samples, are shown in Figs. 13b and 13c. Figure 14 shows a tantalum bucket sampler, used for zinc-magnesium solutions. Figure 15 illustrates a bucket sampler that had been successfully used for sampling uranium melts. The most reliable sampler is the capillary tube type, since a sample can be drawn through the holes regardless of whether the liquid being sampled wets the sampler. The lower phase of a two-phase system can also be sampled with the capillary-tube sampler by

108-8416

Fig. 14. Preparation of Bucket-sample Tube

Fig. 15

Graphite Bucket Sampler

After a preliminary heat-up period (~1 min) above the melt, a bucket sample can be obtained in a period of ~5 sec as contrasted with about a minute (exclusive of preheating time) for filtered samples. Consequently, the opportunity of reaction between the melt or sample and the sample tube is greatly reduced.

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