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# The Solubility of Columbium-1% Zirconium in Sodium by Activation Analysis

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## The Solubility of Columbium-1% Zirconium in Sodium by Activation Analysis

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The equilibrium solubility of the refractory alloy (Cb-1% Zr) in liquid sodium in the temperature range of 800° to 1380°C was determined under static, isothermal conditions. The standard comparator method of activation analysis was used to determine the columbium and zirconium content of the equilibrated sodium samples. The solubility ranges were estimated to be 0.25 to 250 ppm and 0.08 to 4 ppm by weight for columbium and zirconium, respectively.

### INTRODUCTION

This investigation was undertaken as part of a continuing program to establish the compatibility of various structural materials with liquid sodium. Solubility data are required to predict mass transfer rates for a specific heat transfer system and also to postulate the material transport mechanism. In the interest of more efficient electric power generating systems using a liquid metal as the working fluid and/or heat transfer medium, evaluation and test procedures for candidate container materials under simulated test conditions are required. A prime requisite of a solubility study is the development of a sensitive analytical scheme for the specific solute or solutes over a wide concentration range. In addition to the manifold objectives of the study so indicated, modification of the method employed here can be extended to the evaluation of similar systems, designed for high temperature applications in liquid metal technology.

### EXPERIMENTAL APPARATUS AND METHOD

#### Apparatus and Auxiliary System

The solubility apparatus, 2 inches in diameter and 3-1/4 inches long, is diagrammed in Fig. 1. With the exception of the molybdenum sampling crucible, the entire apparatus was made of the alloy material under test. An important design feature

of the apparatus is the off-center sampling port in the partitioning disc between the two compartments. Without this precaution, the liquid sodium, which is held back in the broad meniscus formed around the wall of the equilibration compartment due to surface tension effects, has low sampling yields. Both sampling ports had raised edges to minimize inclusion of particulate material in the melt. Prior to welding in a controlled atmosphere, the various components of the apparatus were chemically etched to a bright metallic lustre and finally cleaned with organic solvents.

The shell of the pressure furnace assembly (Fig. 2) was fabricated from a 5-foot length of 12-inch-diameter schedule-40 steel pipe with access flanges welded at each end. An alundum furnace core (4 inches I.D. and 3 feet long), wound with three molybdenum wire heaters, was suspended in a 304 stainless steel jig inside the pressure shell. Zirconia bubble insulation was used to fill the void space outside the alundum core.

#### Procedure

Approximately 20 to 25 grams of sodium were vacuum distilled from a nickel still into a pyrex glass receiver. The sodium was melted and filtered by differential argon pressures through a fine porosity pyrex glass frit at about 110°C into the solubility apparatus. The apparatus was sealed at the glass portion under an atmosphere of purified argon and removed from the distillation unit to an inert atmosphere welding box. The sodium transfer tube of the apparatus was then crimped and removed by fusion welding.

Titanium foil cladding was applied to all container surfaces exposed to the elevated

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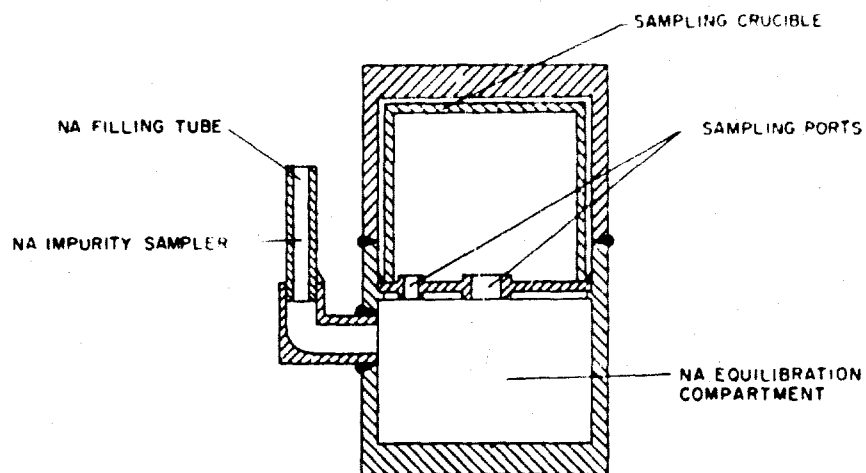


Fig. 1 Solubility apparatus

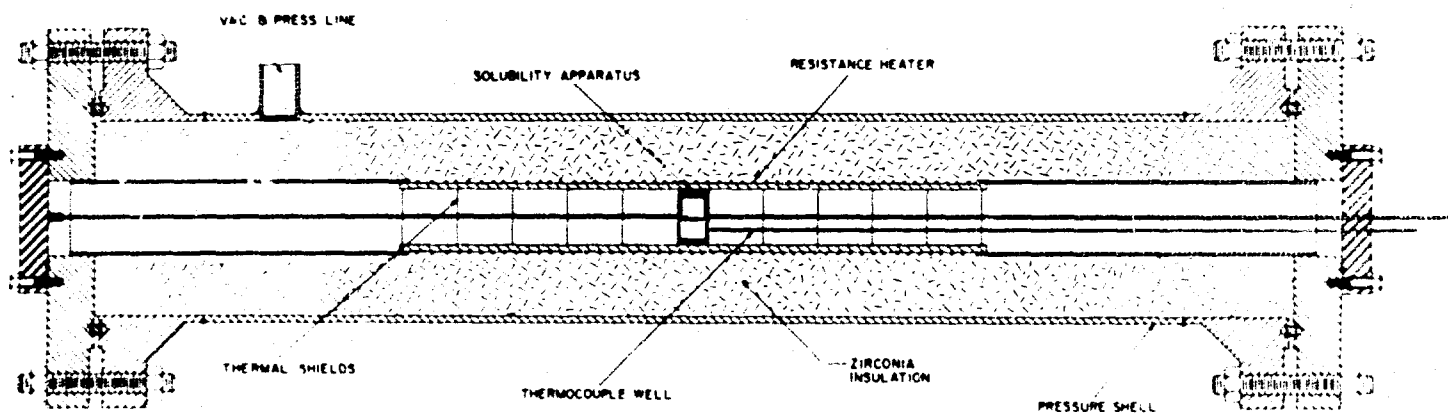


Fig. 2 Solubility furnace system

temperatures as additional protection against impurities in the argon atmosphere of the pressure furnace. The apparatus was positioned in the furnace core and the entire system sealed and evacuated. Argon, purified by passage through a molecular sieve and a heated titanium sponge column, was used to pressurize the system.

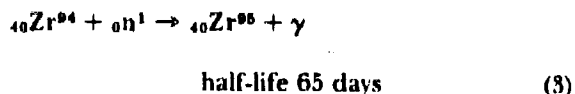
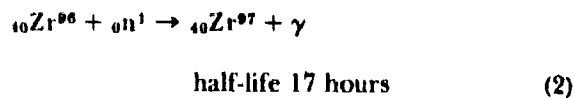
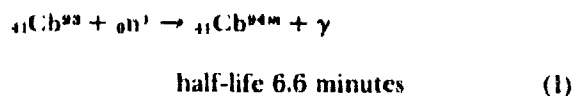
The temperature of the sodium was observed and controlled by a platinum/platinum-20% rhodium thermocouple in a platinum-20% rhodium well. As the temperature increased, the argon pressure of the furnace was adjusted to equal the estimated internal pressure of the solubility apparatus as a precaution against deformation or rupture. Mechanical stirring of the liquid sodium at infrequent intervals during the temperature equilibrium period was accomplished by oscillating the solubility apparatus through its axial linkage extending outside the furnace system. The axial rod protruding through a pressure type packing gland welded into one of the access flanges of the shell was also used to obtain a sample of the melt by 180-degree rotation of the solubility apparatus at the expiration of the temperature equilibrium period. Equilibrium was maintained for an additional 15 minutes after the inversion of the apparatus, to allow sufficient time for the sodium to drain into the molybdenum crucible. The furnace was allowed to cool to room temperature, the apparatus removed, and opened at the bottom of the molybdenum crucible chamber. The sampling crucible was removed and the sodium analyzed for columbium and zirconium.

Due to the apparent unaltered malleability of the Cb-1% Zr alloy after firing, the apparatus was readily opened with pipe cutters as a precaution against contamination of the melt by minute filings produced by other abrasive cutting procedures. Since the mechanical properties of the alloy were apparently unchanged by firing, three solubility apparatuses made of the same material were rewelded and successfully reused in subsequent experiments.

#### Analytical Procedure

Each sodium sample was reacted, diluted to volume, and an aliquot titrated to determine the sample size. The columbium and zirconium solutes were separated from the resultant aqueous solution nonisotropically using standard iron

carrier (10 mg). The ferric hydroxide scavenging efficiency for both columbium and zirconium was established quantitatively in preliminary tests on synthesized aqueous sodium solutions spiked with trace quantities of radioactive  $\text{Cb}^{95}$  and  $\text{Zr}^{95}$  fission product mixtures. The iron hydroxide was filtered and ignited to  $\text{Fe}_2\text{O}_3$  in which form the samples were irradiated in the NRL reactor and analyzed for columbium and zirconium activity respectively. The thermal neutron reactions of interest were the following:



Due to both the mode of decay of  $\text{Cb}^{94\text{m}}$ , principally (99%) by emission of a weak x-ray, and the nondestructive radiometric procedure used, uniformly thin samples of  $\text{Fe}_2\text{O}_3$  (0.26 mg/cm<sup>2</sup>) were required to minimize absorption losses in counting the x-rays. This was accomplished by the demountable centrifuge tube shown in Fig. 3. The cylindrical part was made of a 3-1/2-inch length of seamless stainless steel tubing (1-inch O.D., 3/32-inch wall), the inside of which was highly polished. A methyl alcohol slurry of finely divided one milligram amounts of  $\text{Fe}_2\text{O}_3$  was quantitatively transferred to the cell and a uniform deposit centrifuged onto the filter paper substrate. The methyl alcohol was carefully removed by siphoning with a micropipette and syringe. The deposit was partially dried to a paste like consistency and the cell dismantled to remove the mount intact. The mount was completely dried under an infrared lamp and permanently cemented down with collodion prior to irradiation. Unknown samples and columbium standards, identically prepared, were simultaneously irradiated in the reactor for 15 minutes. This is sufficient time for 75% of saturation activity of  $\text{Cb}^{94\text{m}}$  to be achieved. The irradiated  $\text{Fe}_2\text{O}_3$  deposits were nondestructively analyzed for  $\text{Cb}^{94\text{m}}$  activity by the technique of integral decay

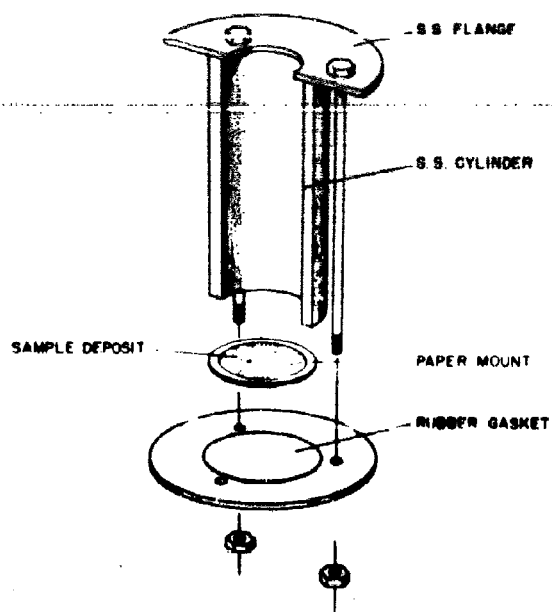


Fig. 3 - Demountable centrifuge tube

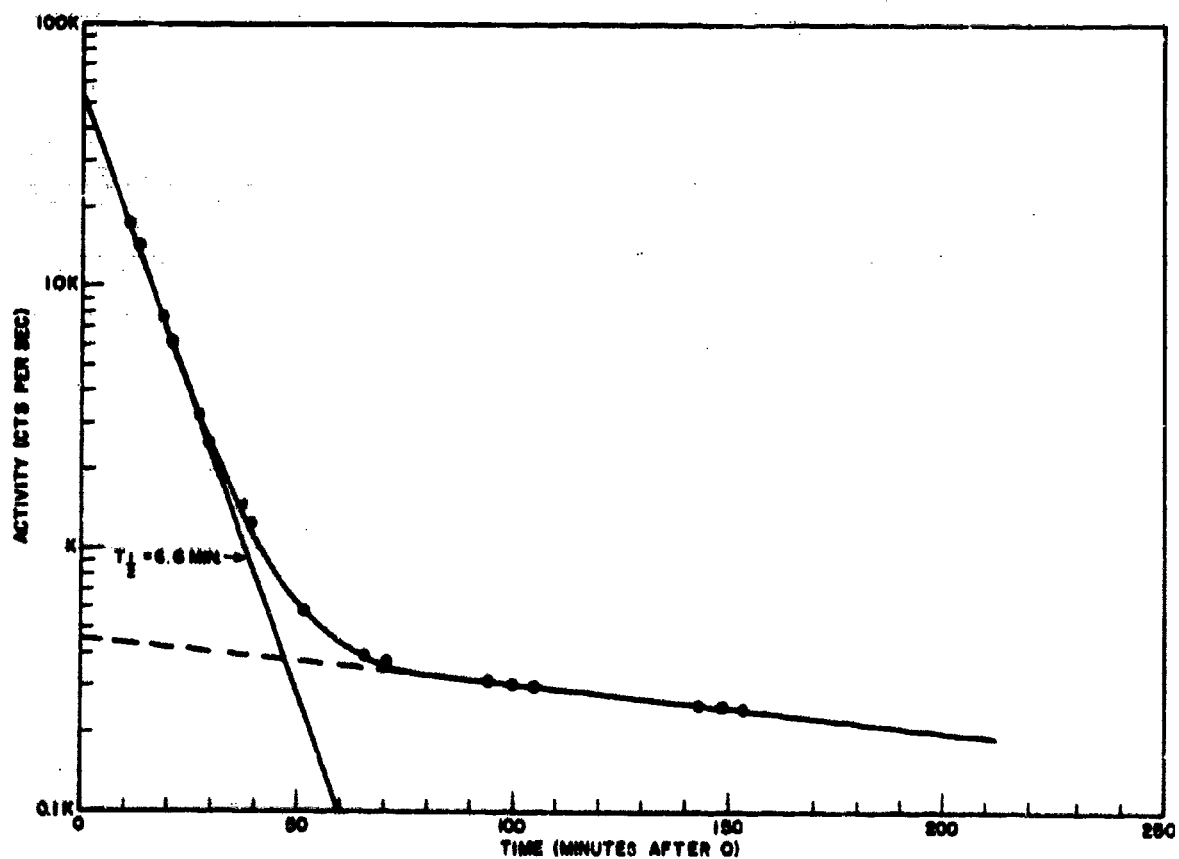


Fig. 4 - Composite decay curve and resolution

curve resolution, as the characteristic short half-life of 6.6 minutes did not allow sufficient time to effect a radiochemical separation from the extraneous activity.

An x-ray photomultiplier tube, employing a 0.080-inch-thick NaI(Tl) scintillation crystal, was used for counting purposes. A beryllium filter (1470 mg/cm<sup>2</sup>) was interposed between the detector and sample to screen out the interfering beta activity in the Fe<sub>2</sub>O<sub>3</sub>. The sensitivity of the thin scintillation crystal to highly penetrating gamma rays is negligible due to its inefficient stopping power, thus rendering a counting system almost exclusively for weak x-rays. The samples were alternately counted at frequent intervals for short periods of time initially (1.5 minutes) and variably longer times as the x-ray intensity diminished. The integral decay activity was permanently recorded by feeding the output of a count-rate meter to a strip-chart recorder. Knowing both the starting time of the counting

period and the chart speed of the recorder, the count rate of the sample at any time after removal from the pile is accurately determined from the curves traced. The activities of the samples were followed for 3 to 4 hours after the 6.6-minute  $\text{Cb}^{99m}$  activity had decayed, to determine the exact amount of extraneous activity to be subtracted from the composite decay curve. Figure 4 shows a typical decay curve produced by this technique and its resolution. The decay curves were readily resolved and the principal component was shown to decay with a 6.6-minute half-life, characteristic of  $\text{Cb}^{99m}$ . The counting reproducibility of  $\text{Cb}^{99m}$  by this radiometric procedure is attested to by the graph in Fig. 5.

The limit of sensitivity for detection of columbium by this analytical method was approximately 2 micrograms, which was also the estimated amount of columbium found in a blank determination of an iron scavenger sample. Considering the average sodium sample analyzed (15 grams),

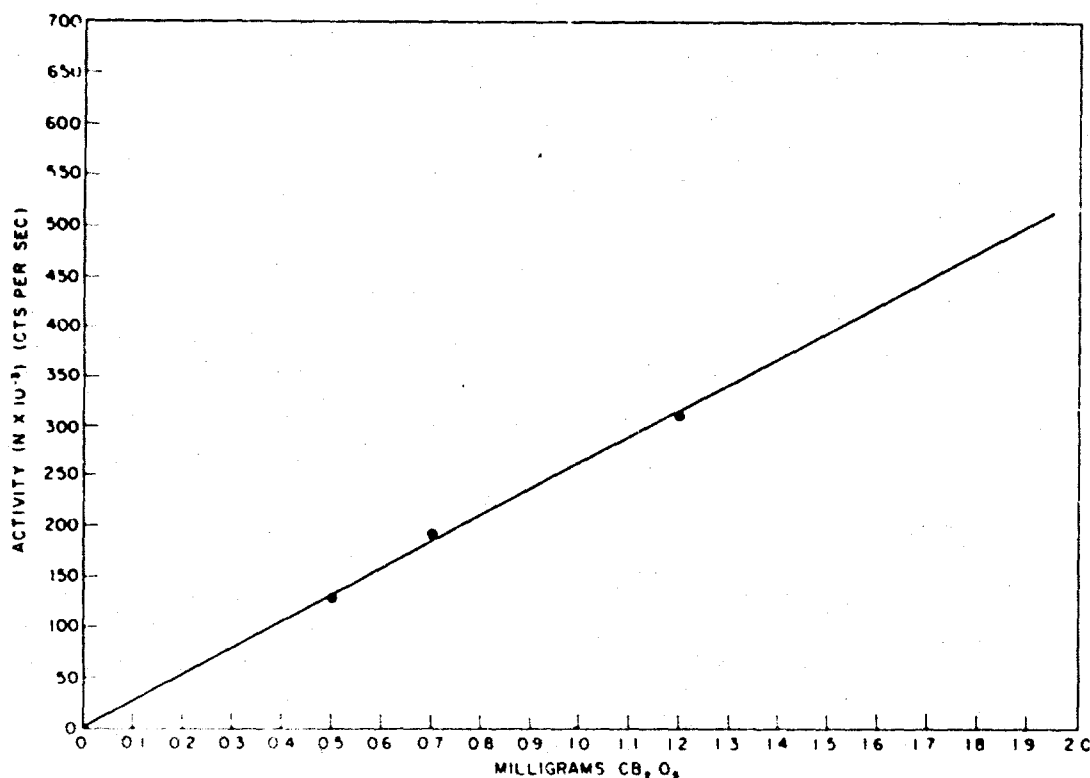


Fig. 5.  $\text{Cb}^{99m}$  count rate reproducibility.

the low limit of detectability of columbium in this study was about 0.1 ppm by weight.

The remainder of the iron scavenger as  $\text{Fe}_2\text{O}_3$  (9 mg Fe) from a typical solubility experiment, along with a prepared zirconium standard, was irradiated for one hour in the NKL reactor and radiochemically analyzed for zirconium activity. The irradiated samples were chemically dissolved, and the zirconium activity separated isotopically from the extraneous activity by precipitation with mandelic acid (1). After rigorous purification of the separated zirconium samples by radiochemical procedures, the samples were counted in the form of  $\text{ZrO}_2$  by a thin-window gas-flow beta counter. Counting was started after sufficient time (~9 hours) had elapsed for the  $\text{Cb}^{97}$  daughter activity of  $\text{Zr}^{97}$  to reach equilibrium. An aluminum filter ( $112 \text{ mg cm}^{-2}$ ) was interposed between the sample and counter to eliminate the beta activity of the 65-day half-life  $\text{Zr}^{96}$  isotope. This precaution was taken mainly because the principal zirconium activity induced by thermal neutron irradiation is the 17-hour half-life  $\text{Zr}^{97}$  isotope, and also the half-life criterion was used to characterize the radioactivity. The activities, of the purified zirconium samples, were followed for at least 120 hours after irradiation and are shown in Fig. 6 to decay typically with a 17-hour half-life.

The limit of measurement by this method was estimated as 1 microgram of zirconium. In view of the average sodium sample size (15 grams) analyzed, the low limit of detectability was 0.06 ppm by weight of zirconium. A blank determination on the iron scavenger for zirconium was negative.

## RESULTS AND DISCUSSION

The results of the solubility experiments are compiled in Table 1. The data indicate equilibrium conditions to be established within approximately eight hours.

Semilog plots of the concentrations of columbium and zirconium versus the reciprocal of the absolute temperature for the eight hour equilibrium temperature experiments are shown in Fig. 7. The solubility values of both constituents, as determined in the low temperature experiment, appear to be a factor of approximately 10 too high to be consistent with the higher temperature values. The source of this irregularity

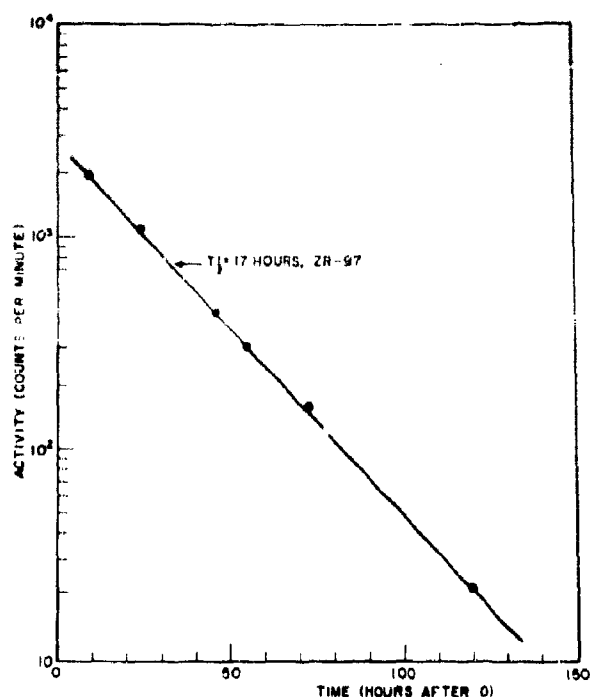


Fig. 6 — Decay curve of separated zirconium

TABLE 1  
The Effect of Exposure Time on the Solubility of Cb-1% Zr Alloy in Sodium

| Temperature (°C) | Cb Solubility (ppm) | Zr Solubility (ppm) | Temperature Equilibrium Time (hours) |
|------------------|---------------------|---------------------|--------------------------------------|
| 802              | 178                 | 1.72                | 2                                    |
| 1185             | 12                  | 2.40                | 2                                    |
| 803              | 17.9                | 0.77                | 8                                    |
| 1008             | 7.5                 | 0.57                | 8                                    |
| 1181             | 35.2                | 0.97                | 8                                    |
| 1380             | 243                 | 3.60                | 8                                    |

is indeterminable from a number of standpoints. Mechanical as well as chemical phenomena may contribute to this anomaly. Fine particulate entrainment in the sampling or apparatus opening procedure and/or chemical interaction of impurities originating from either the liquid sodium and the alloy metal or both are possible explanations.

The magnitude and effect of oxide and hydroxide impurities in the liquid sodium on

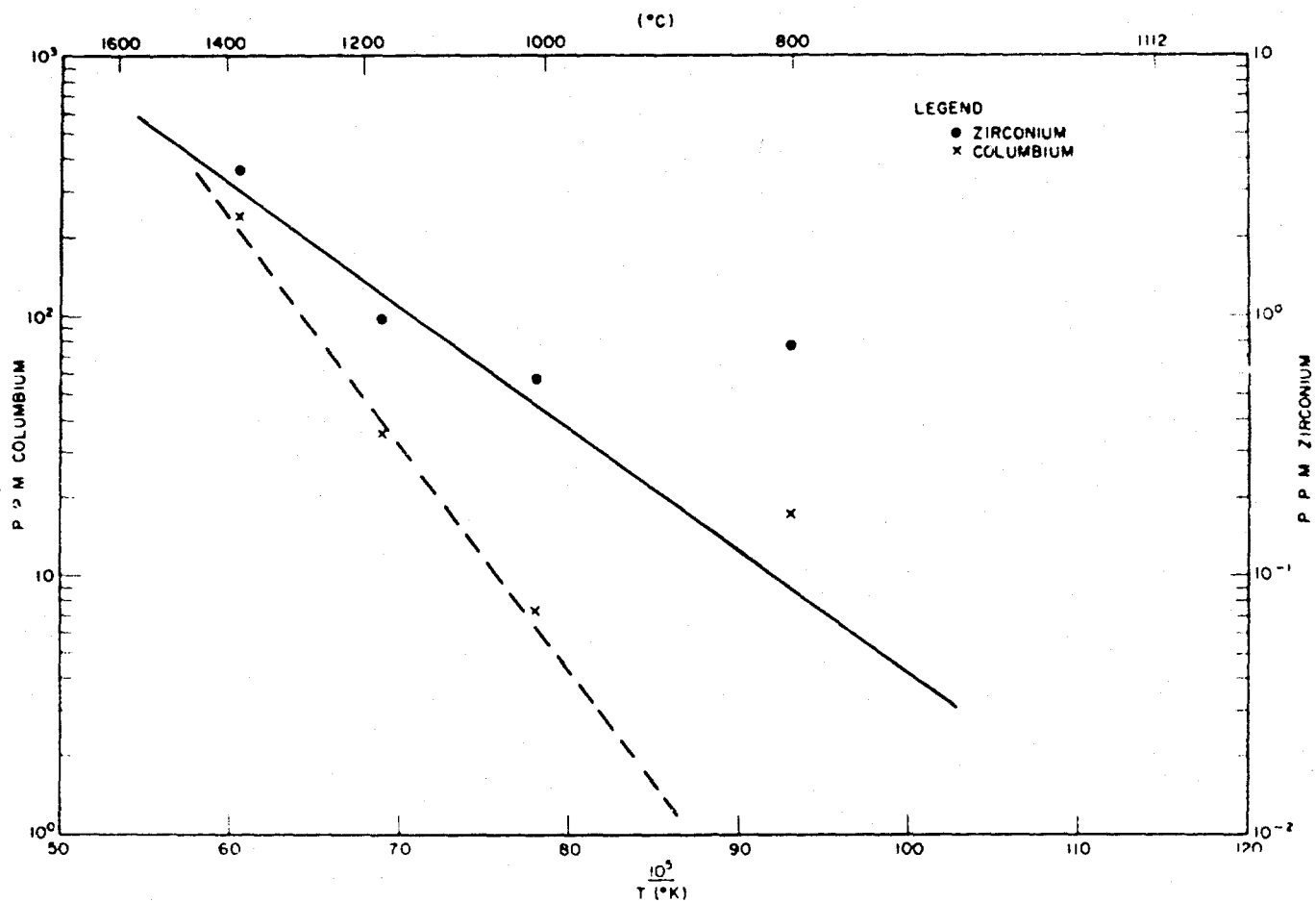


Fig. 7. Solubility of U-10% Zr alloy in sodium.

solubility were not established in this study. Inadequate precautions were taken to remove sodium samples for analysis without additional contamination from the solubility apparatus at the end of a run. Double oxide salt formation (2) between sodium monoxide and various metal oxides and its subsequent solubility in the bulk sodium liquid has been postulated as a solubility mechanism in such systems in the past. Recent studies (3,4) investigating the effect of oxide and hydroxide impurities in liquid sodium on the solubility of container materials, have revealed orders of magnitude increases in solubility measurements with increasing impurity levels. In consideration of the low concentration ranges observed and the unknown impurity level of the liquid sodium system, the increased solubility effect evidenced at 803°C is not unreasonable.

The apparent increase in solubility of both constituents to approximately the same extent, in the perspective of the aforementioned factors, appears to be genuinely significant and noteworthy.

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| <p style="text-align: center;">UNCLASSIFIED</p> <p style="text-align: center;">U.S. Naval Research Laboratory, Report 6051.<br/> <b>THE SOLUBILITY OF COLUMBIUM-1% ZIRCONIUM IN SODIUM BY ACTIVATION ANALYSIS</b>, by T.A. Kovacina and R.R. Miller. 8 pp. and figs., March 20, 1964.</p> <p>The equilibrium solubility of the refractory alloy (Cb-1% Zr) in liquid sodium in the temperature range of 800° to 1380°C was determined under static, isothermal conditions. The standard comparator method of activation analysis was used to determine the columbium and zirconium content of the equilibrated sodium samples. The solubility ranges were estimated to be 0.25 to 250 ppm and 0.08 to 4 ppm by weight for columbium and zirconium, respectively.</p> <p style="text-align: center;">UNCLASSIFIED</p> | <ol style="list-style-type: none"> <li>1. Refractory materials – Solubility</li> <li>2. Columbium alloys – Solubility</li> <li>3. Zirconium alloys – Solubility</li> <li>4. Liquid sodium – Solubilizing effects</li> </ol> <ol style="list-style-type: none"> <li>I. Kovacina, T.A.</li> <li>II. Miller, R.R.</li> </ol> | <p style="text-align: center;">U.S. Na<br/> <b>THE SOLUBILITY OF COLUMBIUM-1% ZIRCONIUM IN SODIUM BY ACTIVATION ANALYSIS</b>, by T.A. Kovacina and R.R. Miller. 8 pp. and figs.</p> <p>The equilibrium in liquid sodium is determined under comparator method the columbium and zirconium content of the equilibrated sodium samples. The solubility ranges were estimated to be 0.25 to 250 ppm and 0.08 to 4 ppm by weight for columbium and zirconium, respectively.</p> |
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