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SOLUBILITY STUDIES IN ALKALI METALS

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SOLUBILITY OF REFRACTORY METALS AND ALLOYS IN ALKALI METALS

FIRST QUARTERLY REPORT

MARCH 3, – MAY 28, 1966

By

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Prepared for
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
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SOLUBILITY STUDIES OF REFRACTORY METALS AND ALLOYS IN ALKALI METALS

by

R. L. McKisson and R. L. Eichelberger

I. INTRODUCTION

The purposes of this program are to better understand the fundamentals of the solubilities of refractory metals and alloys in liquid alkali metals, and to develop data to assist in the formulation of corrosion-resistant alloys required for systems employing alkali metal coolants. The materials of particular concern in this program are the refractory alloys T-111, ASTAR-811C, and Cb-1Zr, the elements Nb, Ta, W, Re, and Mo, to which a nominal $\frac{1}{4}$ weight percent of Zr has been added as a gettering agent, and the pure elements Zr and Hf. The solubilities of these alloys and elements will be measured in purified liquid potassium. In addition, an exploratory study of the solubility of tantalum in filtered lithium will be made. The solubility tests will be made in the alkali metals at temperatures ranging from 900°C to 1600°C, and, where possible, an analysis of the thermodynamics of the solution process will be made.

It is the goal of this study to develop solubility and rate of solution data for well-characterized experimental systems, in which the number and ranges of complicating variables are minimized, in the hope that such data will not only further the understanding of these processes in alkali metal systems, but will also be of use in the materials selection and design of space electrical power system components.

II. SUMMARY

The contract for the construction of the new 1600°- 1800°C furnace has been let, and, unless there are unexpected delays in the delivery of the special refractory materials required for its construction, the furnace is scheduled to be delivered in the next quarter.

All materials except the special Re-$\frac{1}{4}$%Zr alloy have been ordered and/or have been delivered.

The welding of the crucible-to-collector joints between Cb-1Zr and Mo-$\frac{1}{2}$Ti, and between T-111 and Cb-1Zr, has been successfully and readily done using the electron beam welder.

III. TECHNICAL PROGRAM

General

The overall objective of the program is to develop an understanding of the solubility processes. To this end, the present program has the more limited immediate goal of investigating the solution behavior of gettered alloys in highly purified potassium. In the previous program (Contract NAS3-4163), a technique was developed for the production of ultra-pure potassium, i.e., potassium metal having 3.5 ppm O and less than 20 ppm of detectible metallic impurities. The solubilities in this material of triple-pass zone-refined refractory metals were measured, and, in spite of the rather extreme measures taken to use highly purified materials, and non-contaminating handling techniques, the results were difficult to understand in the light of theoretical estimates of the expected solubility values. Similar difficult-to-explain findings have been reported by Swisher (1), who found that his solubility results were apparently affected by the kind of collector material he used, and that a collector material containing an element with a strong oxygen affinity gave lower solubility results than one with a weaker oxygen affinity.

In the recent work at Atomics International, it was found that the apparent solubility of niobium (columbium) from a Cb-1Zr alloy solute was about one tenth that of niobium from a triple-pass zone-refined single crystal solute (3). Similar sorts of results have been noted in other laboratories in that gettered alloys in sealed alkali metal capsules and loops have almost invariably shown lower corrosion rates than have the corresponding ungettered materials. As a result of this sort of observation, the suggestion has been made that the gettered alloys show low metal solubilities because their effective oxygen contents are very low, and that even a few ppm oxygen such as is found in highly purified pure metals is enough to cause an appreciable increase in the apparent solubility of the metal. That oxygen may play such a role is perhaps exemplified by a comparison of the apparent solubilities of iron in potassium as measured by three laboratories. Table I shows the measured values at 1000°C for three purity levels of iron. Although one cannot be certain that the variation in oxygen content of the iron is the only cause of the differences, it cannot be discounted as a very likely cause.

If, then, the oxygen content of the solute metal does play a major of controlling role in the observed solubilities, the presence of a modest amount of a strong oxygen gettering metal should markedly reduce the observed solubilities of refractory metals.

TABLE I

Comparison of Iron Solubility Values in Potassium at 1000°C

Iron Description	O Content of Fe	O Content of K	Observed Solubility, ppm	Reference
Armco	510	20	1000	(1)
Puron	400	9 - 22	380	(2)
Triple-pass Zone-refined	<8	14	115	(3)

The testing of this thesis is one of the immediate goals of this program. To this end, the materials to be tested are all "gettered" alloys. Three of them are the 'normal' alloys, T-111, Cb-1Zr, and ASTAR-811C [Ta-8W-1Re-1Hf-0.025C]. Five of the solutes are elements to which a nominal ¼% of zirconium is added to act as the getter. These are Nb (Cb), Ta, Mo, W, and Re. The two remaining solutes are the pure getter metals Zr and Hf.

High Temperature Furnace

A purchase order for the furnace has been placed with Centorr Associates, Inc. of Suncook, New Hampshire. Sets of drawings which show the basic design of the furnace and details of some of the more critical design features have been submitted by Centorr for approval. Approval to proceed has been given with certain reservations with respect to design details. These reservations and means of handling them have been specified. At present, the most serious problem in the construction of the furnace is that of the rather long delivery times of the special refractory metals which are required to ensure that the furnace have a long use life at 1600°C.

The furnace has a clam-shall design with the front half hinged to swing forward to allow the test capsule to be swung about a horizontal axis out of the heat zone, and to seat into a water-cooled copper strap quench device. The furnace shell is water-cooled, and packs of tantalum radiation shields are used to reduce the power requirements of the unit. Its nominal test operating temperatures is 1600°C, although the power supply and the materials of construction have been selected to permit operation at 1800°C, if it is deemed necessary.

The sample capsule seats into a cup and is supported in place in the furnace hot zone on a T-111 alloy column which in turn is mounted on the T-111 alloy shaft at the bottom of the furnace proper. Thus, the rotation of this shaft moves the sample capsule from its test position in the furnace hot zone to a position below the furnace, at which position the quench device is located. This arrangement is quite similar to that used previously, and described in the final report (3).

Solute Materials

The special $\frac{1}{4}$ per cent zirconium alloys of molybdenum, tungsten, tantalum, and niobium have been ordered from Westinghouse Astronuclear Division, and are scheduled for shipment by August 22, 1966. To date, no suitable source has been located for the procurement of the $\frac{1}{4}$ per cent zirconium alloy of rhenium. However, an unalloyed rhenium crucible has been procured from the Chase Brass and Copper Co., Inc.. The supplier's typical analysis of the rhenium sheet stock from which the crucible was made is given in Table II. Our present tentative plans are to use this crucible in the testing program if an alloyed one cannot be procured.

TABLE II

Lot Analysis of Rhenium

Crucible Stock Material* (Lot #RS-58)

Metal	Analysis	Metal	Analysis
Al	< 1 ppm	Mg	< 1 ppm
Ca	< 1 ppm	Mo	30
Cr	< 1	Na	< 1
Cu	≤ 1	Ni	≤ 1
Fe	29	Si	< 1

* Provided by the supplier, Chase, Brass, and Copper Co., Inc., Rhenium Div.

The pure elements zirconium and hafnium have been ordered from Materials Research Corporation as triple-pass zone-refined rods, and have been delivered.

The alloys T-111 and Cb-1Zr made from arc-melted ingot stock are on hand and have been made into crucibles for use in the first series of tests.

The supplier's typical analysis of the T-111 material is given in Table III, and the analysis of the Cb-1Zr alloy is given in Table IV.

The alloy ASTAR-811C [Ta-8W-1Re-1Hf-0.025C] is to be supplied by the program sponsors, and is scheduled for shipment in September, 1966.

TABLE III

Lot Analysis of T-111 Rod*

Chemical Analysis:			
Element	Analysis	Element	Analysis
C	< 10 ppm	Fe	< 20 ppm
O	25 ppm	Ni	< 10 ppm
N	20 ppm	V	< 10 ppm
H	< 5 ppm	Co	< 10 ppm
W	7.70%	Hf	2.33%
Cb	110 ppm	Ta	Balance
Mo	100 ppm		
Physical Properties:			
Yield Strength	72,700 psi		
Tensile Strength	89,100 psi		
Elongation (1")	43%		

* Provided by the supplier, J. T. Ryerson and Son, Inc.

TABLE IV

Typical Analysis of Cb-1Zr Rod*

(Haynes Alloy CB 751)

Chemical Analysis:

Element	Analysis	Element	Analysis
Fe	<100 ppm	Ta	<100 ppm
C	~50 ppm** avg	O	50 ppm
Si	300 ppm	H	3.5 ppm
Ti	<100 ppm	N	~ 50*** avg

Physical Properties:

Microhardness,	Edge	98, 92, 92 DPH
	Center	92.8, 96.2 DPH
Tensile Strength		54,200 psi, 56,200 psi
0.2% Yield Strength		34,300 psi, 34,000 psi
Elongation		40.0% 42.0%
Stress Rupture (2000°F)		10,000 psi, 19.6 hours, 63% elongation
		10,000 psi, 96.1 hours, 14% elongation

* Material obtained from General Electric Co., Space Power and properties Section, Cincinnati, Ohio. Analysis from original supplier, Union Carbide Corp., Stellite Division.

** A difference was noted along the length of the rod: 10 ppm, minimum to 80 ppm, maximum.

*** A difference was noted along the length of the rod: 39 ppm, minimum to 100 ppm, maximum.

Test Component Parts

The T-222 capsules and caps which were ordered from Wah Chang have been delivered and are being stored for use in the high temperature tests to be made in the new furnace.

The Cb-1Zr and Mo-$\frac{1}{2}$Ti collector materials have been received and parts have been machined to the proper shapes for the new design collectors.

Test welds of T-111 to Cb-1Zr and of Cb-1Zr to Mo-$\frac{1}{2}$Ti were very readily made, so that there was no delay in our being able to prepare the crucible-collector welds with these materials combinations.

Figures 1 and 2 show two views of the Cb-1Zr crucible-to-Mo-$\frac{1}{2}$Ti collector tube weld. The weld was very readily made and is helium leak-tight. Figure 3 shows the weld made between the T-111 crucible and the Cb-1Zr collector tube. Again, the weld was readily made, and the joint is helium leak-tight. Note in Figure 3 that this "weld" is really a joint made by the melting of the Cb-1Zr (m.p.$\sim$2500°C) and its adherence (probably with some tantalum solution) to the higher melting T-111 (m.p.$\sim$ 3000°C). One cannot actually melt the T-111 in making such a joint because the Cb-1Zr would then be well above its melting point all around the joint, and the weight of the collector tube would cause it to slump and/or sag to form a heavily thickened and, probably, a crooked joint.

Experimental System

The experimental system used in this program was designed and built for an earlier program, and is described in detail in the final report (3). Briefly, the system consists of five sequently-connected stainless steel vacuum chambers, each with its own pumping system, and separated by vacuum gate valves. The first chamber is nominally 24 inches in diameter and 22 inches high. It is fitted with a sample and test capsule outgassing furnace, storage racks for outgassed parts, and the sample delivery outlet of the potassium purification system. The second chamber is nominally 24 inches in diameter and 18 inches high. It is fitted with the test capsule welding gun, a chuck for rotating the test capsule during welding, and the capsule-opening assembly. The third, fourth, and fifth chambers are all 24 inches in diameter and 22 inches high. They house test heaters and the associated timing and sample quenching equipment. Figure 4 shows an external view of the system.

Since the system was idle for several months, it has been checked over carefully and put into operating condition. Chambers #1, #2, and #3 are all capable of achieving an ultimate vacuum level of $<1\times10^{-7}$ torr or lower, and a normal working level of $\sim1\times10^{-6}$ torr. Chanber #4 has been removed and sent to Centorr Associates for the installation of the new furnace.

At the conclusion of a molybdenum capsule weld closure, the electron-beam welding gun filament burned out and, apparently, a high voltage short developed at the end of the power cable to the gun. The arc which occurred damaged the connectors, and the cable has been sent to the manufacturers for repair. This is not expected to cause any delay in operation, because the cable will be returned during the first week in June. However, it will be necessary to establish the cause of the arc before we can put the welder back into full operation.

IV. NEXT REPORT PERIOD ACTIVITIES

During the next quarter, the final approval of the 1600°C furnace will be obtained; and, if materials can be procured it time, the furnace will be shipped.

Solubility tests will be initiated on those solutes which are to be tested at temperatures in the range 900°-1200°C.

Analytical chemical techniques will be verified in terms of the needs of the program, and the pertinent routine tests will be made.

V. REFERENCES

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2. W. S. Ginell and R. J. Teitel, "Determination of the Solubility of Transition Metals in Molten Potassium", SM-48883 (1965).

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VI. APPENDIX

REPORTS AND PAPERS ISSUED ON PRECEEDING CONTRACT NAS3-4163

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G. R. Argue, H. L. Recht, and W. A. McCollum, "Double Layer Capacitance Measurements on Iron Crucibles to Determine Surface Area," AI-TDR-64-229, December (1964).

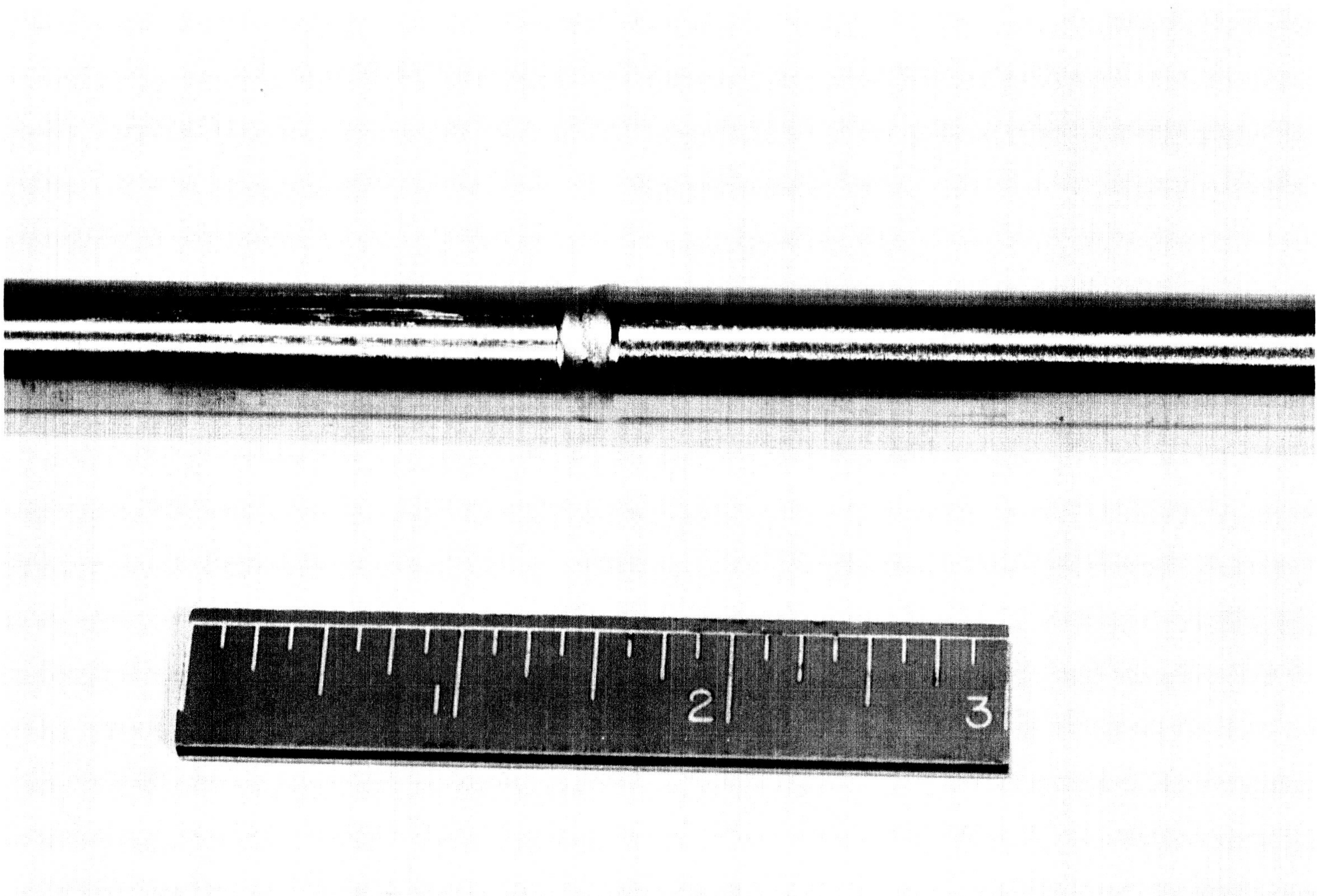

FIGURE 1. Weld Between Cb-1Zr Crucible and Mo-$\frac{1}{2}$Ti Collector Tube (View Normal to Axis).

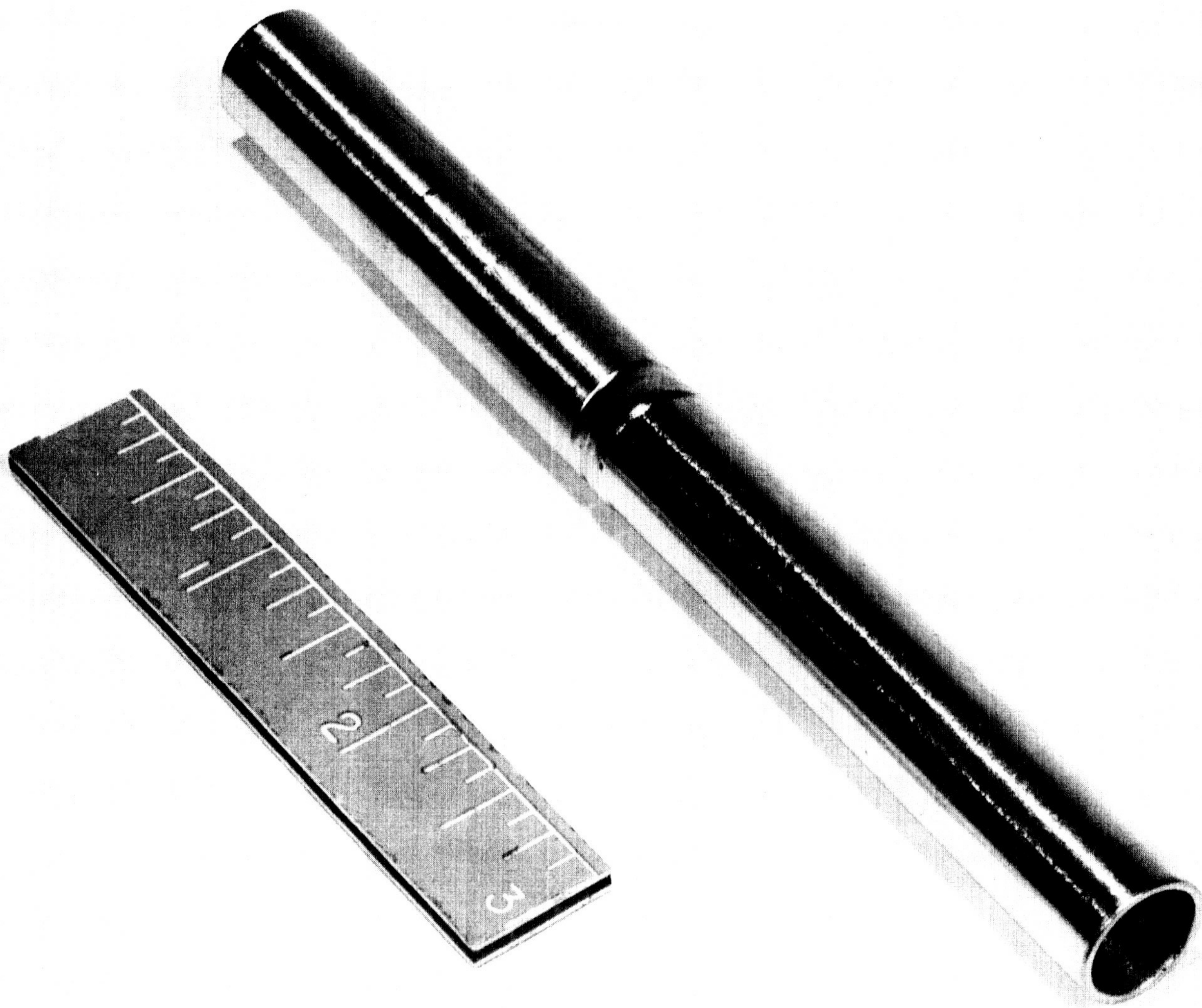

FIGURE 2. Weld Between Cb-1Zr Crucible and Mo-$\frac{1}{2}$Ti Collector Tube (View Showing Open End of Collector).

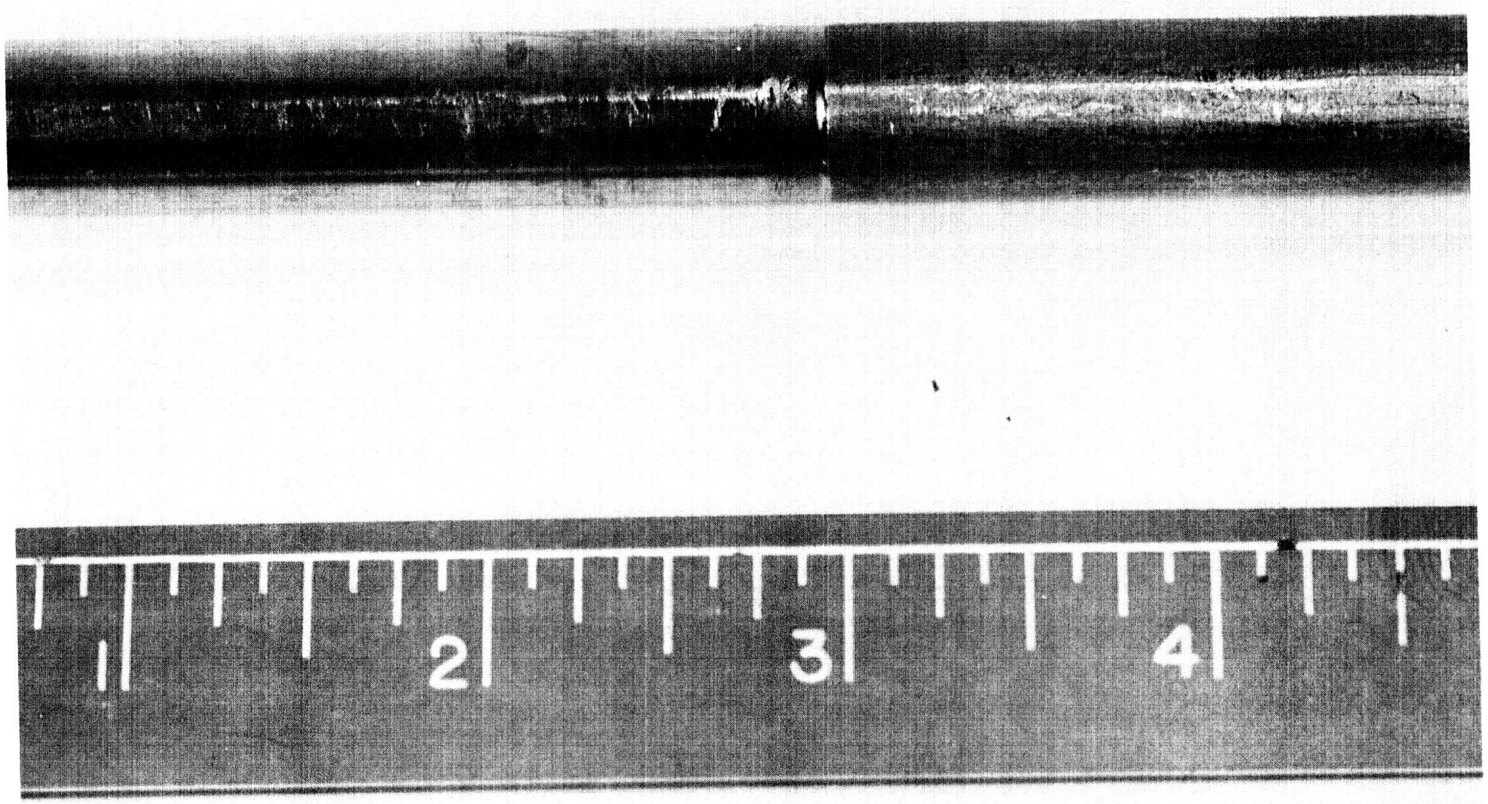

FIGURE 3. Weld Between T-111 Crucible and Cb-1Zr Collector Tube (View Normal to Axis).

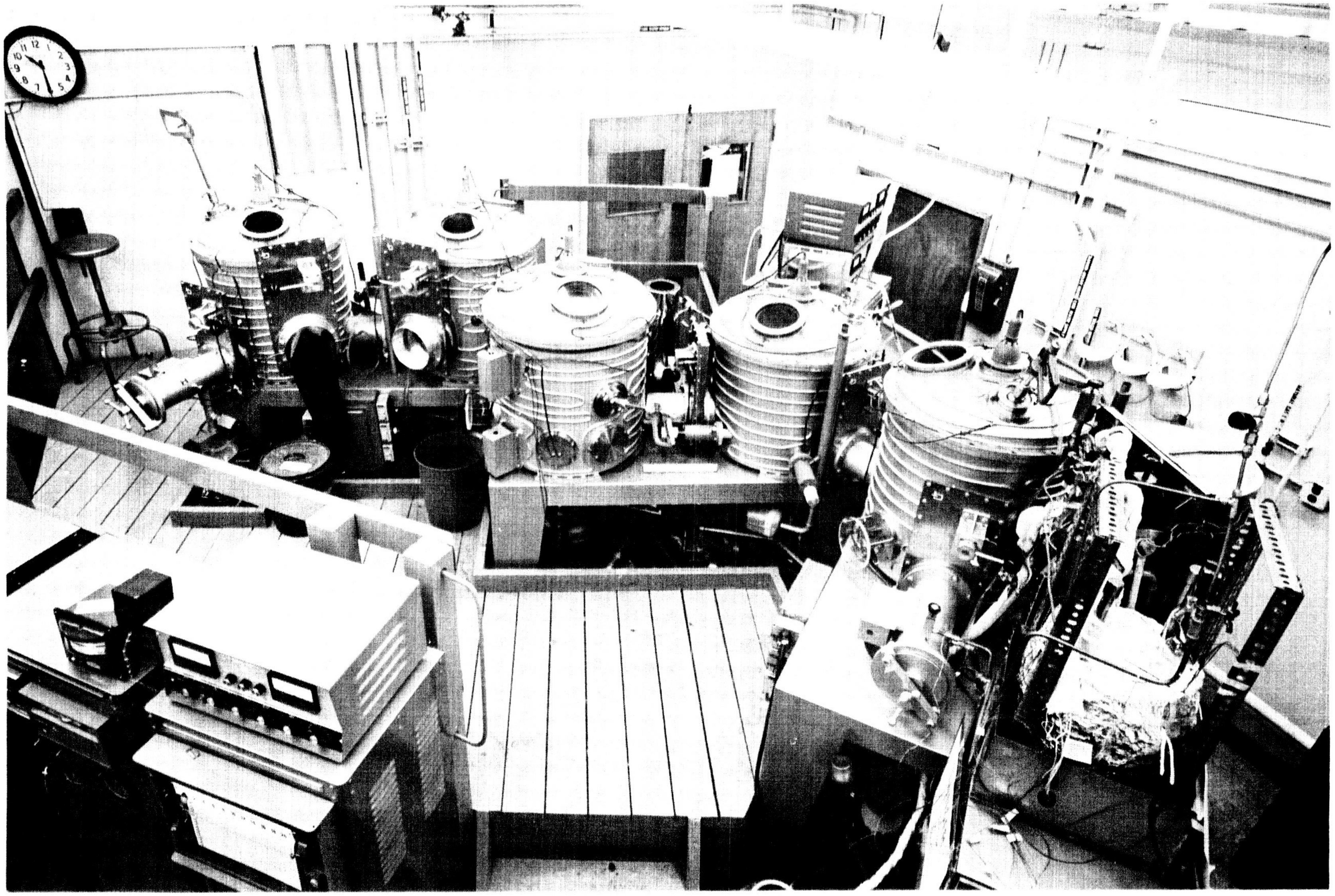

FIGURE 4. Environmental Test System