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A Summary of the High Temperature Alkali Metal Corrosion Program at Brookhaven National Laboratory

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INTRODUCTION

Alkali metals have been proposed as coolants and working fluids in high temperature, compact space power plants utilizing the Rankine cycle. Studies are presently being carried out at Brookhaven National Laboratory to evaluate materials to contain liquid and boiling Na in the temperature range 1000 to 1315°C (1832-2400°F). In this temperature range only refractory metals and their alloys could be considered as suitable container materials for the Na.

The major objectives of the alkali metals corrosion program at BNL are as follows:

1. To study the behavior of refractory metals and their alloys in boiling-condensing Na up to 1315°C.
2. To study corrosion and mass transfer in all liquid Na systems up to 1210°C.
3. To evaluate the relative aggressiveness of Li,

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Na, K, Cs and Rb in boiling-condensing systems up to 1210°C.

4. To investigate the effect of high velocity Na vapor impingement on refractory metal alloys.

The objectives are being carried out in capsules, natural convection loops and a pumped loop.

Results of earlier work[1] showed that unalloyed Cb (containing 600 ppm O) was attacked intergranularly by purified Na* but that under the same conditions, Cb-1Zr was not corroded in capsules containing Na reflux boiling at 1210°C (2200°F) for 5000 hours. In addition, localized corrosion of Cb-1Zr was observed in capsules where up to 150 ppm oxygen was added to the Na. No corrosion was detected after 5000 hours at 1095°C (2000°F) when purified Na was circulated at a flow rate of about 5 gr/min (0.7#/hr) in a natural convection boiling loop made of Cb-1Zr.

(1) NASA-AEC Liquid Metals Corrosion Meeting, Oct. 2-3, 1963, NASA SP-41.

* Henceforth, purified Na will refer to Na prepared by cold trapping at ~150°C for 24 hours and then hot trapping with Zr at 600°C for about 250 hours.

Evaluation of Cb-1Zr in Capsules and Loops

Capsule Test #3

Twelve Cb-base alloy capsules (9 of which were Cb-1Zr) containing Na refluxing at a rate of about 1 gr/min (0.15#/hr) were operated at 1266°C (2300°F) in a vacuum chamber at a pressure of $<5 \times 10^{-8}$ torr. Three of the capsules were removed after 5000 hours and examined both metallographically and chemically. The remaining nine capsules were then operated at the same conditions for an additional 3000 hours. The results of the examination of the three Cb base high strength alloys will be discussed later. The operating conditions and results of examination for the 12 capsules are given in Table I.

The inner surfaces of these capsules were highly polished prior to test and consequently the limit of detection of corrosion was about 0.005 mm (2×10^{-4} in.). The addition of 600 ppm O (as Na_2O_2) to the Na resulted in localized corrosion of the Cb-1Zr at the liquid-vapor interface of capsule 31 as shown in Fig. 1; the maximum depth of penetration was 0.025 mm (0.001"). The oxygen in the Na apparently concentrates at the liquid-vapor interface where it reacts with the Cb-1Zr at a rapid rate resulting in localized oxidation and spalling of the surface. Sodium attack was

not observed in any of the other Cb-1Zr capsules. Although the addition of carbon to the Na did not cause corrosion of Cb-1Zr, it did penetrate the grain boundaries to a depth of about 0.015 mm (~1/2 mil) (capsule 33). Of the oxygen getters added to the Na, only Y had any detectable effect; it was found in a deposit in the vapor region where it apparently reacted intergranularly with the Cb-1Zr alloy to a depth of 0.100 mm (0.004") as shown in Fig. 2.

Capsule Test #4

Six capsules containing refluxing Na were operated at 1094°C (2000°F) for 10,000 hours to study the effect of weld contamination and post-weld heat treatment on corrosion of Cb-1Zr by purified Na. The test was carried out in a chamber at a pressure of 2×10^{-6} torr. The capsules were prepared in the following manner. Duplicate capsules were welded at three levels of dry box atmosphere contamination (O_2, N_2 and H_2O vapor added to Ar). One capsule from each set of duplicates was then post-weld heat treated at 1210°C (2200°F) for 1 hour while the other three were not. After purified Na was added to each capsule, operation at temperature was started.

Examination of these capsules is underway. Slight

intergranular corrosion (0.100 mm, 0.004") was observed at the liquid-vapor interface of the capsules which were welded in the most contaminated atmosphere. A photomicrograph of the liquid-vapor interface of capsule 42 is shown in Fig. 3. At the liquid-vapor interface of the other four capsules, a slight transgranular roughening of the surface was observed (0.025 mm, 0.001"). Metallographic examination will be completed and chemical analyses will be performed.

Loop #204

A small natural convection boiling loop (made from Cb-1Zr) containing purified Na and having a flow rate of about 10 gr/min (1.5 #/hr) was operated at 1095°C (2000°F) boiling for 8007 hours. No corrosion was detectable by metallographic examination even on polished surfaces where the limit of detection was 0.005 mm (2×10^{-4} in.).

Originally it was intended to operate this loop at 1204°C (2200°F) but boiling at this temperature was extremely unstable (40 bumps/hr); the loop did not have an artificial means of inducing stable boiling i.e. bubble nucleation device. Since more stable boiling (1 bump/hr) could be achieved at 1095°C (2000°F), the loop was operated

at that temperature for the next 8000 hours.

Natural Circulation Sodium Loop #1

A large (8 foot tall) natural convection boiling loop (made of Cb-1Zr) containing purified Na was operated at boiling temperatures between 1094°C (2000°F) and 1150°C (2100°F) for 1330 hours. The flow rate in this loop was about 75 gr/min. (10#/hr). The primary purpose of this loop was to develop the techniques and experience required in refractory metal loop technology which would be applied to the construction and operation of a forced circulation boiling loop. No corrosion was detected by metallographic examination of this loop.

Evaluation of Other Alloys in Capsules

Cb Base Alloys

Three Cb base-high strength alloys were evaluated in Capsule Test #3; these were Cb-10W-10Ta (S-291), Cb-10W-1Zr-0.1C (D-43), and Cb-5W-3Zr-0.1C (modified form of D-43). The non-gettered (by Zr) alloy S-291, was severely attacked intergranularly throughout the condensing region (0.30 mm, 0.012" maximum depth) as shown in Fig. 4. Slight intergranular and some transgranular corrosion was found in the boiler region of the capsule. (0.075 mm, 0.003" maximum

depth). The two alloys containing Zr were not attacked even after 8000 hours at 1260°C (2300°F). The inner surfaces of all three capsules had been polished prior to operation. The results of the examination are shown in Table I.

Ta Base Alloys

Two Ta-10W capsules containing refluxing Na were operated at 1266°C (2300°F) for 168 hours. Each capsule contained an insert tab of Ta-10W having a longitudinal heli-arc weld extending the length of the capsule. The capsules were filled with Na under vacuum and sealed in an electron beam welder. Prior to sealing, air inadvertently entered one of the capsules (#61) at room temperature but was removed within 30 minutes by evacuation in the E.B. welder. Thus the Na in this capsule was contaminated. The filled and sealed capsules were then sealed in individual Cb-1Zr containers.

After 168 hours, radiographs showed Na had leaked out of both of the Ta-10W capsules. Metallographic examination revealed extensive intergranular corrosion of the capsule and tab containing the contaminated Na (#61) with the deepest penetration (up to 0.750 mm, 0.030")

occurring at the capsule welds as shown in Figs. 5 and 6. The second capsule (#62) exhibited localized intergranular attack of the capsule weld in the vapor region as shown in Fig. 7. The operating conditions and results of examination are given in Table II.

Tests in Progress

Capsule Tests

Three capsule tests are currently underway; the operating conditions and variables for these tests are given in Table III.

Capsule Test #5 is designed to evaluate the relative agressiveness of the alkali metals Li, Na, K, Rb and Cs in Cb-1Zr container material at 1150°C (2100°F).

Capsule Test #9 is designed to evaluate several high strength alloys. These are being tested as tab inserts in D-43 capsules containing Na refluxing at 1315°C (2400°F).

In Capsule Test #11, four different cermets are being evaluated in D-43 capsules containing K refluxing at 1205°C (2200°F).

Natural Convection Loops

Four natural convection loops are in operation; two loops are made from Cb-1Zr while the other two are of

D-43. Two loops, one Cb-1Zr and one D-43, are being run to study the resistance of these alloys to corrosion and mass transfer by liquid Na at high temperatures. The other two loops contain boiling Na in which stable boiling has been achieved (in both loops) by means of a "bubble nucleation device" inserted below the boiler liquid level. The operating conditions and test times for these four loops are given in Table IV.

Proposed Tests

Capsule Tests

The following tests are proposed to be started in the near future.

1. Evaluation of high strength alloys as capsules with Na.
2. Evaluation of D-43 as container material for Li, Na, K, Rb and Cs.
3. Evaluation of cold-worked (2T 180° bends) high strength alloy specimens in Na.

Natural Convection Loops

The following loops are proposed to be started in the near future.

1. A Ta-8W-2Hf loop containing boiling Na

2. A Mo-1/2Ti-0.08Zr loop containing boiling Na

3. A Cb-28Ta-10W-1Zr loop containing boiling Na

4. An all liquid Na loop containing inserts of several high strength alloys.

Forced Circulation Loop

A forced circulation boiling loop (shown in Fig. 8) made of Cb-1Zr will be operated to obtain corrosion and erosion data on high velocity nozzles and impingement specimens. Twenty pounds per hour (150 gr/min) of purified Na will be pumped to the boiler which will operate at 1093°C (2000°F). The vapor will be slightly superheated before passing through a three stage turbine simulator consisting of Cb-1Zr nozzles and B-66 (Cb-5V-5Mo-1Zr) impingement specimens. All loop components are Cb-1Zr including a helical induction electromagnetic pump.

All of the loop components have been welded and the loop assembled into four sections. Due to the size of the loop, it will be necessary to heat treat the four sections before final assembly. The final welds will be heat treated in operation. Fabrication of the loop is about 25% complete.

Table I

Capsule Test #3 - Operating Conditions[a] and Results of Examination

Capsule No.	Test Time Hours	Material	Additives[b] ppm	Corrosion, Max. Depth and Type	Micro-hardness[c] DPH	O_2 in Na[d] ppm	Net Increase O_2[e] in Capsule ppm	Net Increase N_2[e] in Capsule ppm
25	8000	Cb-1Zr	None	None	-	11		
26	8000	Cb-1Zr	500 Ca	None	-	12		
27	8000	Cb-1Zr	500 Mg	None	-	9		
28	5000	Cb-1Zr	500 Ba	None	96	<20	190	12
29	8000	Cb-1Zr	Y	Deposit of Y in vapor region no corrosion	97	9		
30	8000	Cb-1Zr	150 O	None	-	11		
31	5000	Cb-1Zr	600 O	0.025 mm trans. & inter. at liquid interface	96	<25	244	18
32	8000	Cb-1Zr	150 C	None	-	<20		
33	8000	Cb-1Zr	600 C	None	99	18		
34	5000	Cb-10W-10Ta	None	0.30 mm inter. in vapor region 0.80 mm inter. in seal weld region	148	<140	142	6
35	8000	Cb-10W-1Zr-0.1C	None	None	154	5		
36	8000	Cb-5W-3Zr-0.1C	None	None	145	8		

See next page for notes.

Table I continued

[a]Test temperature: 1266°C; chamber pressure $<5 \times 10^{-8}$ torr.

[b]All capsules were filled with Na which was cold trapped and hot trapped. Additions were made in a dry box. Oxygen added as Na_2O_2; C added as spectrographic carbon; Y not soluble and added as metal turning; Ca, Mg, Ba added as pure metals. Capsules 34, 35, 36 machined from bar stock.

[c]Pre-test DPH values were: Cb-1Zr = 152; Cb-10Ta-10W = 183; Cb-10W-1Zr-0.1C = 210; Cb-5W-1Zr-0.1C = 181.

[d]Analyses performed by inert gas Hg amalgamation method. Average of 2-3 samples (except for #34, only 1 sample) with blank deducted. High blanks reported on samples shown by <.

[e]Average of all samples for each capsule with initial O_2 or N_2 content deducted (90 ppm O_2 and 70 ppm N_2 for Cb-1Zr; 100 ppm O_2 and 12 ppm N_2 for Cb-10W-10Ta).

Table II

Capsule Test #10
Operating Conditions and Results
of Examination

Number of Capsules: 2 each 1.27 cm (½") I.D. by 10 cm (4") high

Test Material: Ta-10W (NRC Tubing)

Type Capsule: Reflux Boiling

Inserts: Ta-10W Tabs with longitudinal Heli-arc welds in each capsule

Temperature: 1266°C in Na for 168 hours.

Environment: Ta-10W - Purified argon sealed in Cb-1Zr container
Cb-1Zr - 2×10^{-7} torr.

Capsule No.	Type	Filled w/Na	Cleaned in Methanol	Corrosion, Severity and Location	Type Attack	Microhardness[d] DPH/200
61	Contam-[a] inated	Twice[c]	Once	Deep penetration in all welds and heat affected zones. Slight attack of base material in vapor and liquid regions.	Inter.	232 in welds and base material
62	Standard[b]	Once	None	Deep penetration of weld in vapor region only. Slight attack of fill tube area (vapor region).	Inter.	232 in welds and base material

[a]Capsule 61 was filled with purified Na. Air entered the capsule at room temperature and was removed by evacuating after 30 minutes.

[b]Filled with purified Na under standard operating procedures and seal weld in E.B. welder.

[c]Capsule 61 was overfilled on initial attempt and was cleaned by dissolving Na in Methyl alcohol.

[d]DPH/200 readings for pre-test tubing and welds were approximately 230.

Table III

Review of Capsule Tests in Operation

Test No.	No. of Capsules	Capsule Material	Temp. °C (°F)	Variables	Test Time Hours
5	12	Cb-1Zr	1150 (2100)	Li, Na, K, Rb, Cs	2525
9	5	D-43	1315 (2400)	Inserts of D-43 TZM, FS-85, Ta-10W, T-111	1190
11	2	D-43	1205 (2200)	Inserts of cermets with varying binder compositions	170

Table IV

Review of Loops in Operation

Loop No.	Type Loop	Material	Temperatures °C (°F)	Estimated Flow Rate	Test Time Hours
206	Boiling	Cb-1Zr	1204 (2200) Boil - 1260 (2250) Vapor	1-2 #/Hr	6990
208	All Liquid	Cb-1Zr	1095 (2000) Hot - 895 (1650) Cold	-	1535
209	All Liquid	D-43	1204 (2200) Hot - 1000 (1835) Cold	-	1535
210	Boiling	D-43	1260 (2300) Boil - 1350 (2460) Vapor	1-2 #/Hr	150

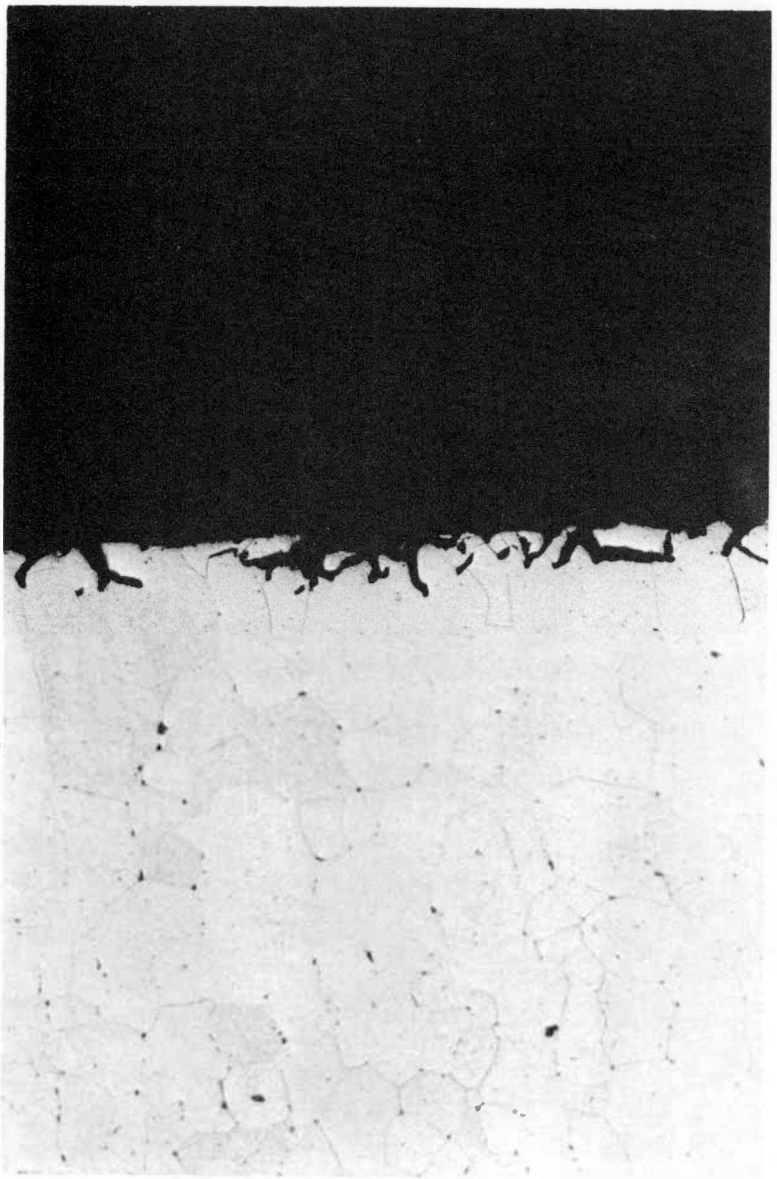

Fig. 1
Capsule 31 - Localized Corrosion of the Cb-1Zr at the Liquid-Vapor Interface - 250X

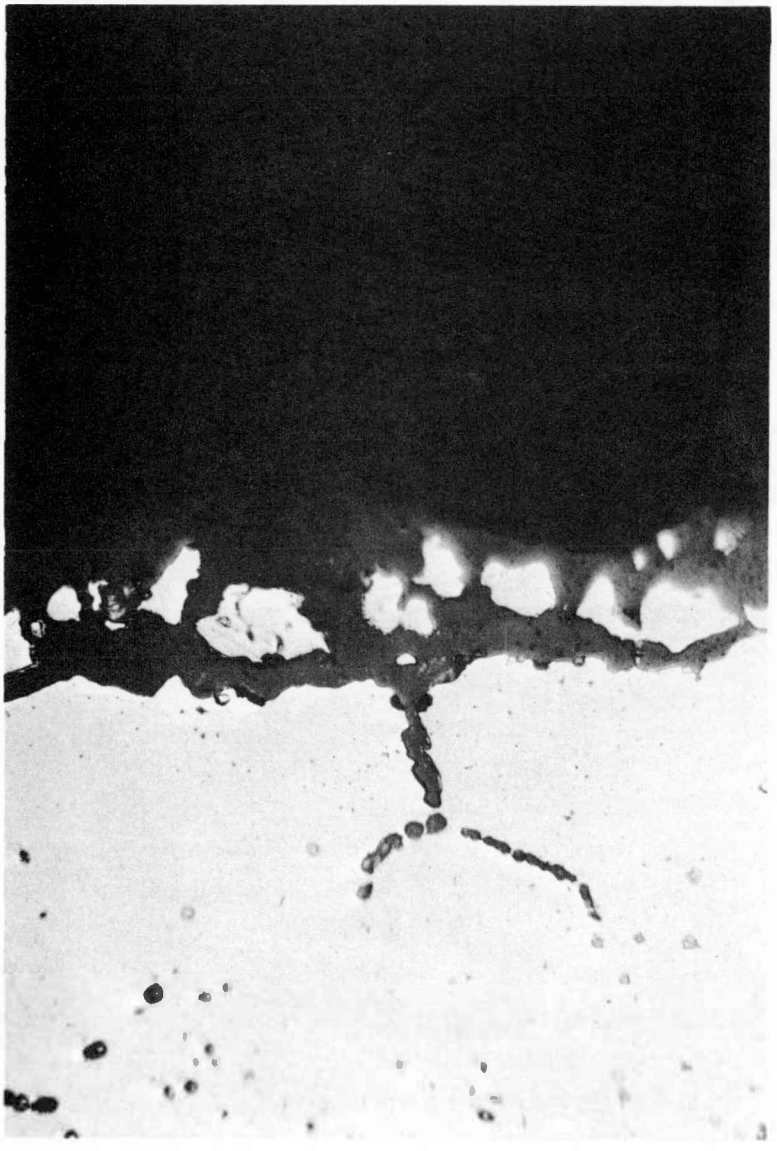

Fig. 2
Capsule 29 - Intergranular Penetration of Cb-1Zr by Y in the Vapor Region - 500X

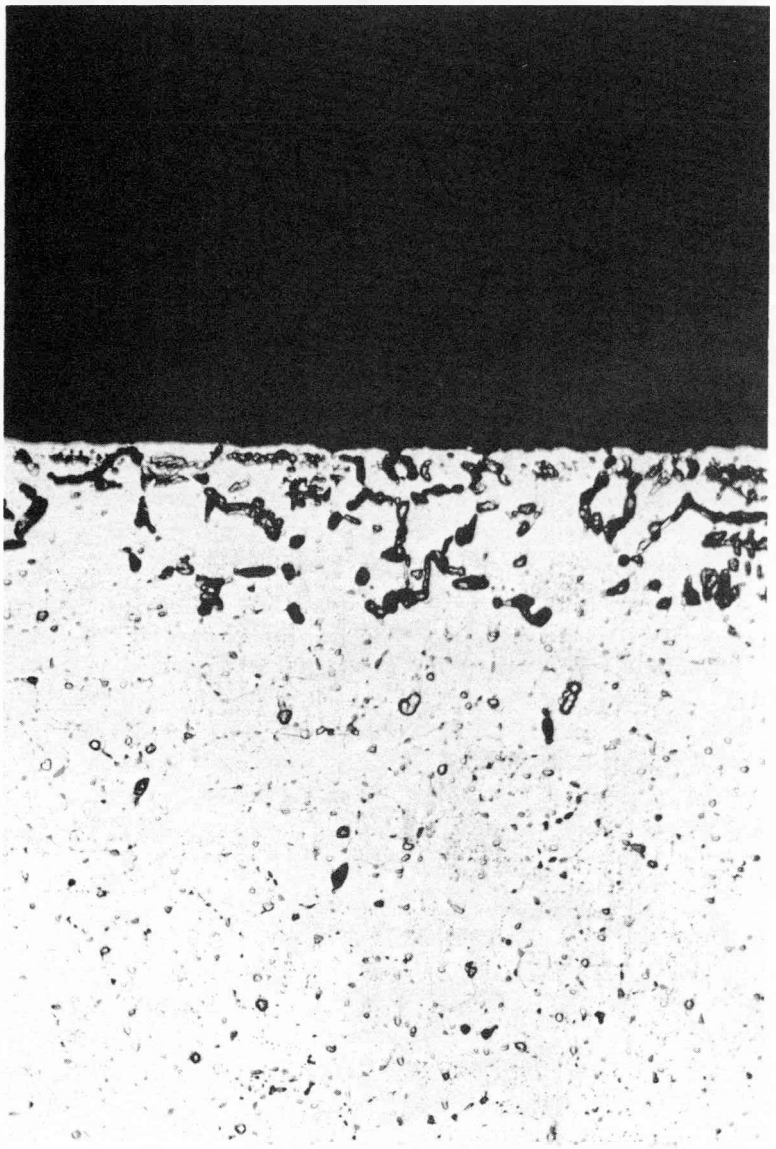

Fig. 3
Capsule 42 - Intergranular Corrosion of Cb-1Zr at Liquid-Vapor Interface - 250X

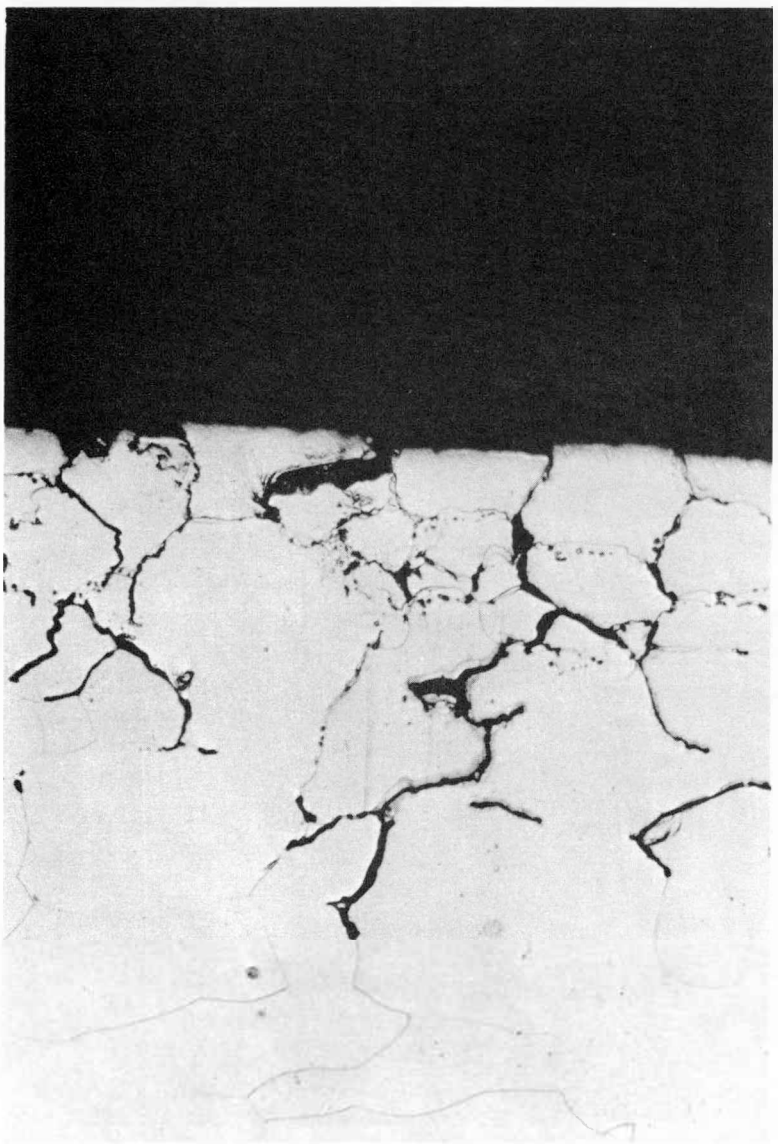

Fig. 4
Capsule 34 - Intergranular Corrosion of Cb-10W-10Ta
in Vapor Region - 250X

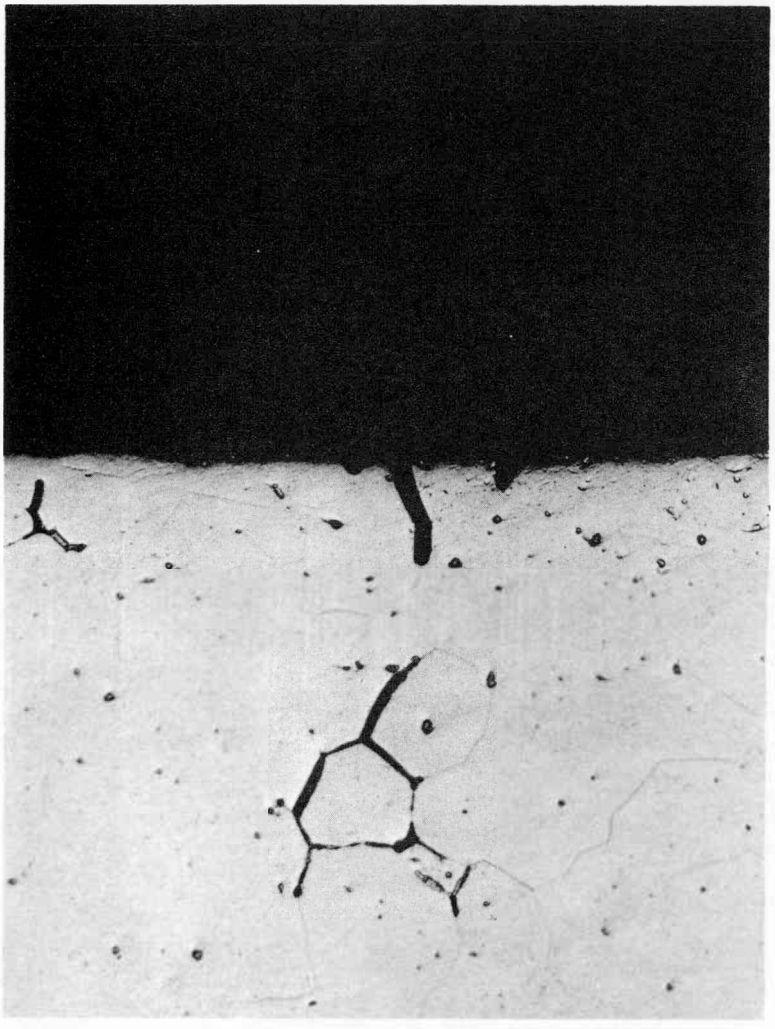

Fig. 5
Capsule 61 - Intergranular Corrosion of Ta-10W in Vapor Region - 250X (Transverse Section)

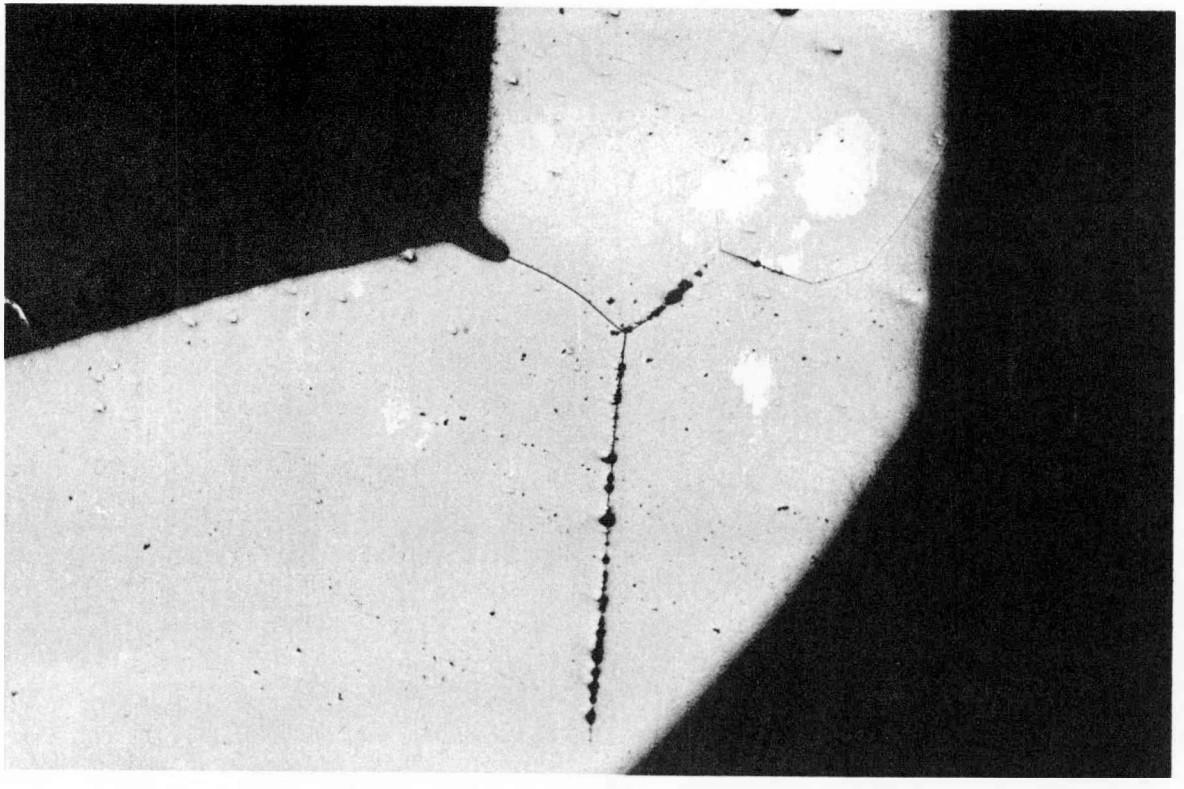

Fig. 6
Capsule 61 - Intergranular Corrosion of Ta-10W
Weld in Liquid Region - 100X

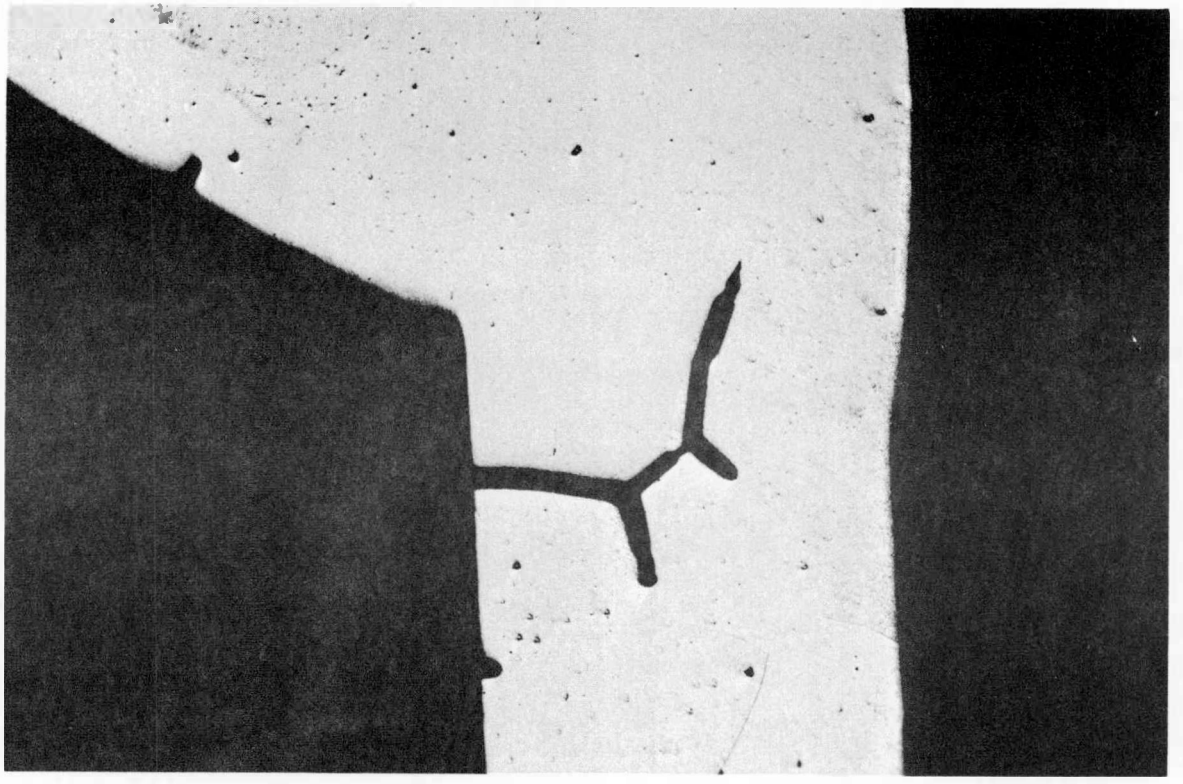

Fig. 7
Capsule 62 - Intergranular Corrosion of Ta-10W
Weld in Vapor Region - 100X

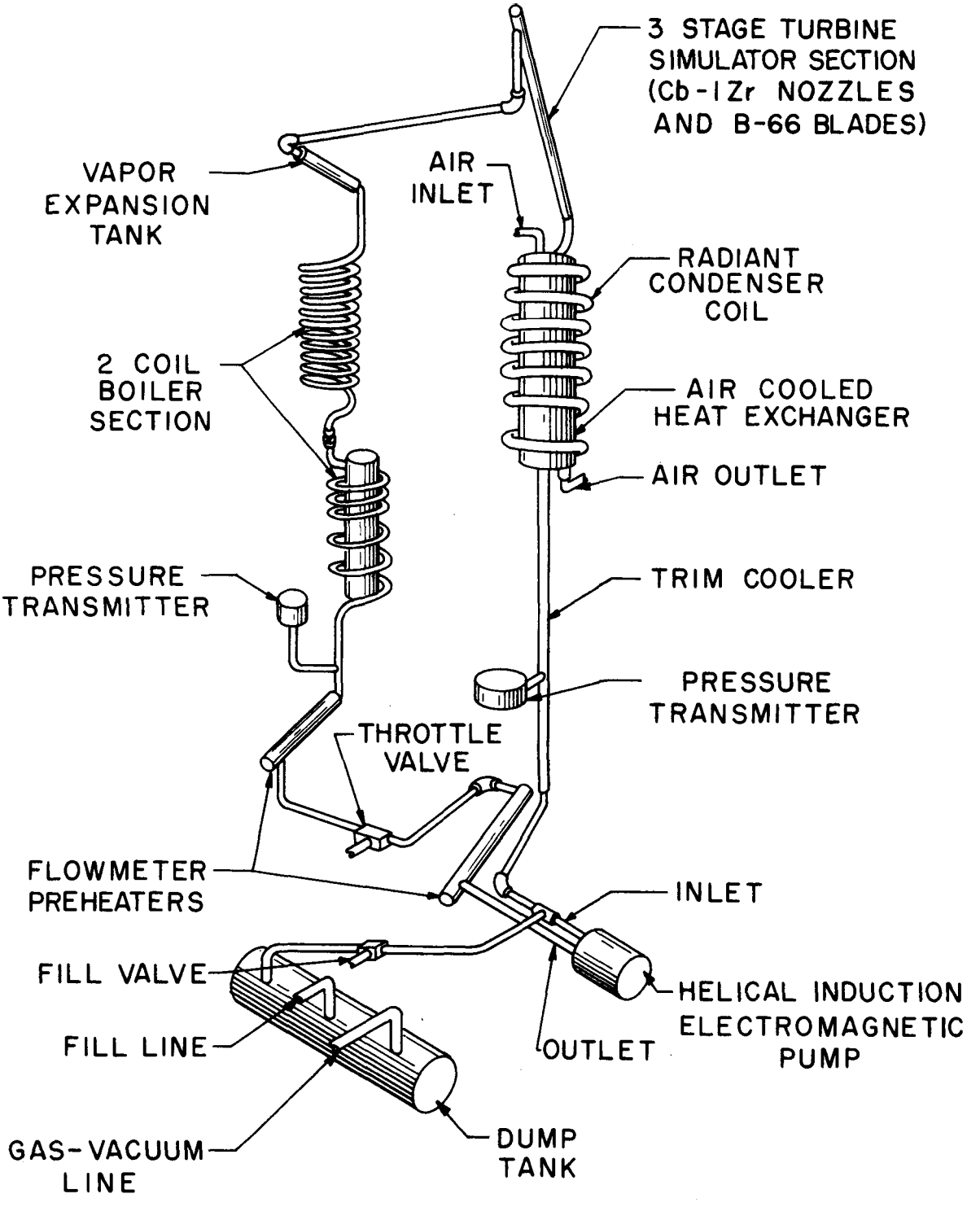

FIG. 8
PUMPED BOILING SODIUM LOOP SCHEMATIC