COMPATIBILITY OF SEVERAL IRON-, COBALT-, AND NICKEL-BASE ALLOYS WITH REFLUXING POTASSIUM AT 1800° F

by John H. Sinclair

Lewis Research Center
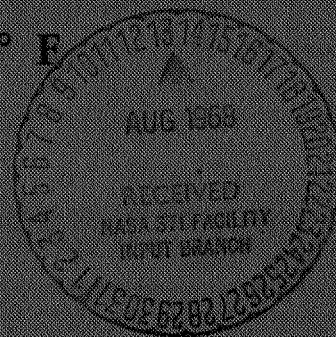Cleveland, Ohio

COMPATIBILITY OF SEVERAL IRON-, COBALT-, AND NICKEL-BASE ALLOYS WITH REFLUXING POTASSIUM AT 1800° F

By John H. Sinclair

Lewis Research Center
Cleveland, Ohio

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

ABSTRACT

Capsules of HS-25, Rene 41, Hastelloys N, C, and X, and AISI 318 were corrosion tested with refluxing potassium at 1800° F (982° C) for times up to 2000 hours. The objective was to determine the corrosion resistance of these alloys for possible use in facilities for ground testing of design concepts for space-power systems. Only AISI 318 appeared to be unsuitable from the standpoint of resistance to corrosion by potassium. The materials could arbitrarily be ranked into three groups in descending order of resistance to corrosion: Rene 41 and HS-25; then, Hastelloys N, C, and X (in that order); and finally, AISI 318.

COMPATIBILITY OF SEVERAL IRON-, COBALT-, AND NICKEL-BASE

ALLOYS WITH REFLUXING POTASSIUM AT 1800° F

by John H. Sinclair

Lewis Research Center

SUMMARY

The corrosion resistance of the cobalt-base alloy HS-25, the nickel-base alloys Rene 41 and Hastelloys N, C, and X, and the stainless-steel AISI 318 to refluxing potassium at 1800° F (982° C) was evaluated for times up to 2000 hours. The objective was to determine if these materials had adequate corrosion resistance for use in hardware for ground testing of design concepts for future Rankine-cycle space-power systems. Such usage would eliminate the expense and complication of testing in vacuum, which is required if refractory metals are used for containment of the alkali metal.

The corrosion tests were made in reflux capsules machined from rod stock. These capsules had the following approximate dimensions: a 0.5-inch (1.27-cm) outside diameter, a 1.75-inch (4.45-cm) length, and a 0.040-inch (1.02×10^{-1}-cm) wall thickness. The capsule wall, machined to a surface of 16 microinches rms, served as the test specimen. The initial oxygen content of the potassium was a maximum of 20 ppm as determined by mercury amalgamation and vacuum distillation techniques. The materials were tested in beds of 10 individually heated capsules in a static air atmosphere.

Although all of the materials showed some evidence of corrosion, it was concluded that all except AISI 318 had adequate resistance to potassium at 1800° F (982° C) to warrant consideration for the intended use. The capsules could be arbitrarily ranked into three groups in descending order of corrosion resistance to boiling potassium under these conditions: Rene 41 and HS-25; then, Hastelloys N, C, and X (in that order); and finally, AISI 318.

INTRODUCTION

Advanced Rankine-cycle space-power systems will be required to operate at temperatures as high as 2400° F (1316° C) for times in excess of 10 000 hours. Such sys-

tems are expected to be constructed of refractory alloys of columbium or tantalum and are likely to use potassium as the working fluid or heat-transfer medium.

Although refractory alloys have outstanding corrosion resistance to alkali metals, they are inherently costly and are expensive to fabricate. Also, because of their poor oxidation resistance and their enhanced susceptibility to corrosion if contaminated with oxygen, high vacuum equipment is necessary for testing them.

Preliminary testing of design concepts for components of space-power systems can often be made for shorter times and at temperatures lower than those ultimately used in the actual system. If more conventional and oxidation resistant iron-, cobalt-, or nickel-base alloys could be used for such ground test facilities, considerable cost savings would result.

Prior work had indicated that the cobalt-base alloy HS-25 has good corrosion resistance at 1850° F (1010° C) to boiling potassium (ref. 1). Furthermore, it had been shown that the austenitic stainless-steel AISI 316 was as resistant to boiling potassium as HS-25 at 1600° F (871° C) (ref. 2). Some work had been done with the nickel-base alloy Hastelloy X which indicated that this alloy would be unsuitable for use with potassium at 1800° F (982° C) (ref. 3), but data were not presented to indicate the role of oxygen impurity in the corrosion observed in the tests. Oxygen impurity of liquid metals is known to be an important factor in determining the corrosion rates of containment metals (refs. 4 and 5).

Therefore, a corrosion capsule test was initiated to determine the compatibility of several alloys with boiling potassium. HS-25, known to be resistant to boiling potassium, was used as a standard against which the other materials were compared. Several promising nickel-base alloys (Hastelloys C, N, and X and Rene 41) were selected for evaluation. A stainless steel (AISI 318) was included in the tests as representative of the best iron-base materials for this application even though it does not have good oxidation resistance at the test temperature. This alloy, one of the 18-8 molybdenum bearing stainless steels, is similar to AISI 316 with an addition of columbium which, due to its great affinity for carbon, prevents the precipitation of chromium carbides and thereby reduces the susceptibility of the steel to intergranular aqueous corrosion (ref. 6).

Small capsules containing refluxing potassium were tested in air at a temperature of 1800° F (982° C) for times up to 2000 hours. This temperature is near the maximum useful temperature for these alloys from strength and oxidation considerations. The time at temperature was selected arbitrarily, but should be long enough for testing design concepts. It should also be long enough to reveal significant differences in the resistances of the six alloys to boiling potassium.

Test results were evaluated by metallographic examination, chemical analyses, and electron beam microprobe analyses.

MATERIALS, APPARATUS, AND PROCEDURE

The six alloys were tested in the form of reflux capsules (fig. 1) machined from as-received rod stock. The capsule wall served as the test specimen. In this type of test, liquid potassium vaporizes from a pool at the capsule bottom and condenses near the capsule top. Condensate flows down the capsule wall to rejoin the liquid pool.
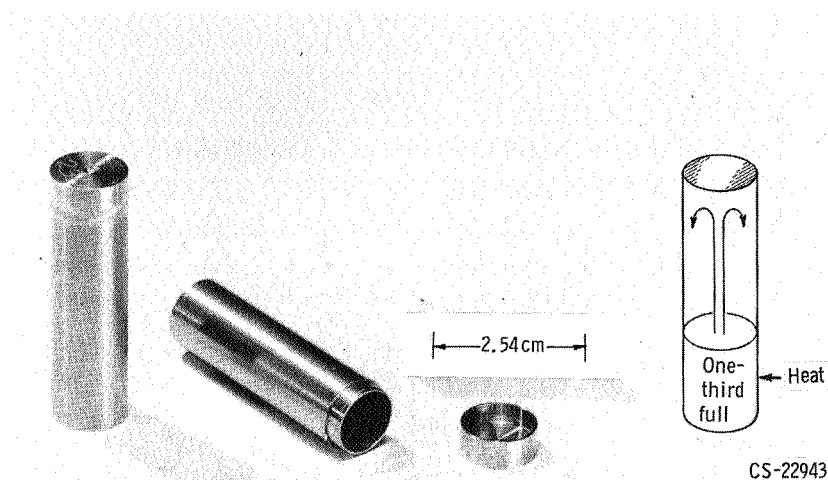

Figure 1. - Capsule used in the refluxing potassium corrosion study.

Materials

The alloys tested and their compositions are shown in table I. They were purchased as rod stock in standard mill-annealed condition. Photomicrographs of these materials are presented in figure 2.

Capsule Preparation

Rod stock was turned down by lathe and then precision drilled to form a capsule. The nominal dimensions of the finished capsules were the following: a 0.5-inch (1.27-cm) outside diameter, a 1.75-inch (4.45-cm) length, and a 0.040-inch (1.02×10^{-1}-cm) wall thickness. Interior capsule finish was 16 microinches rms for side walls and 32 microinches rms for bottoms and caps.

After machining, the capsules were vapor degreased, ultrasonically cleaned in a detergent, rinsed several times with distilled water, and oven dried in warm air. From this point on, the capsules were handled with white gloves under conditions selected to avoid possible contamination until they were filled with potassium and sealed.

3

TABLE I. - CHEMICAL ANALYSES OF AS-RECEIVED ROD STOCK

| Ele-ment	Alloy					
	AISI 318	HS-25	Hastelloy C	Hastelloy N	Hastelloy X	Rene 41
	Heat					
		L3-1495	C2-3259	N1-5083	X2-4406	T2-8219
	Weight percent					
Cr	17.67	19.91	15.86	7.58	21.75	18.95
W	-------	14.90	3.68	.06	.66	------
Fe	Balance	1.73	5.47	3.36	18.35	2.89
C	0.046	.09	.08	.05	.12	.07
Si	.53	.56	.59	.55	.68	.21
Co	-------	Balance	1.30	.11	1.50	10.98
Ni	13.97	9.41	Balance	Balance	Balance	Balance
Mn	1.85	1.46	0.57	0.58	0.54	0.03
V	-------	-------	.27	.30	-------	-------
Mo	2.74	-------	16.31	16.92	8.92	9.76
P	-------	0.017	.009	.001	.014	-------
S	-------	.012	.010	.007	.006	0.011
Al	-------	-------	-------	.01	-------	1.51
Ti	-------	-------	-------	.01	-------	3.14
B	-------	-------	-------	.007	-------	.007
Cu	-------	-------	-------	.01	-------	-------
Cb	0.67	-------	-------	-------	-------	-------
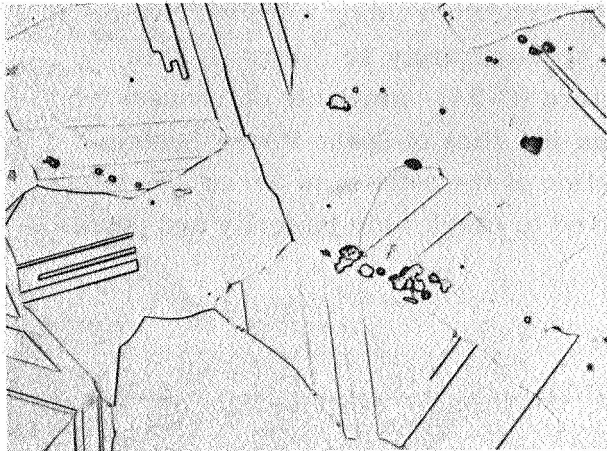
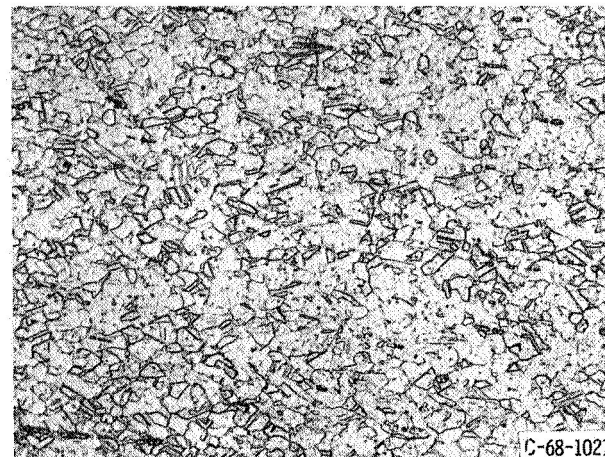(a) HS-25.
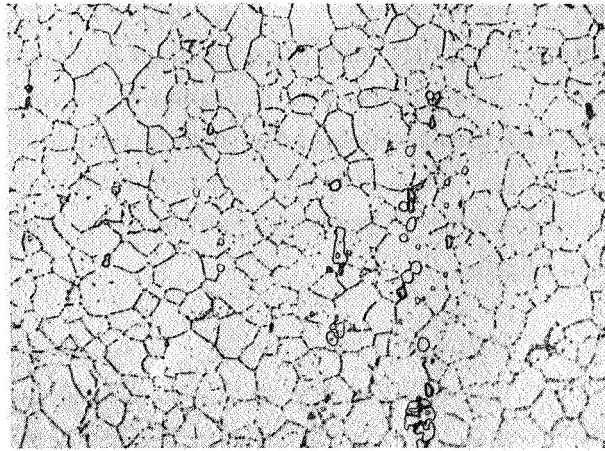
(b) Rene 41.
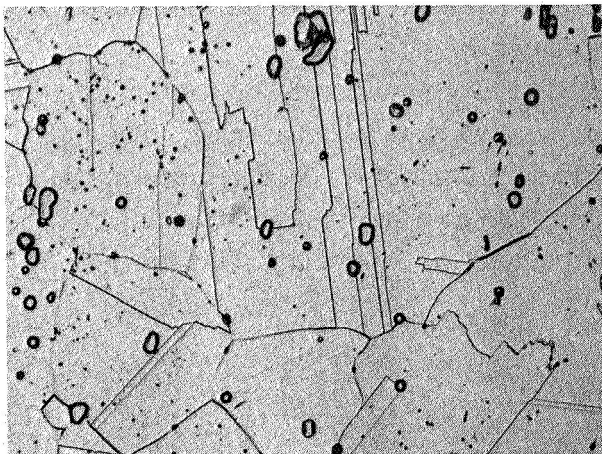
(c) Hastelloy N.
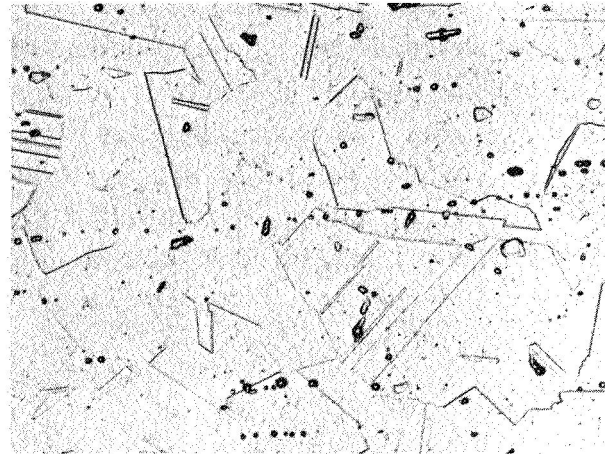
(d) Hastelloy C.
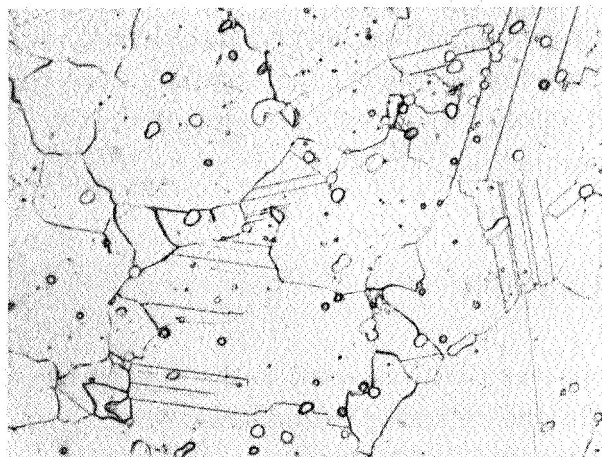
(e) Hastelloy X.

(f) AISI-318.

C-68-1021

Figure 2. - Microstructures of as-received rod stock.

The capsules were filled with approximately $1\frac{1}{4}$ cubic centimeters of potassium. The operations of filling, capping, and sealing by electron beam welding were carried out in a vacuum facility which maintained a pressure of approximately 10^{-5} torr (1.3×10^{-3} N/m^2). This procedure is shown in a motion picture (C-241, available on request from the NASA Lewis Research Center) entitled Vacuum Handling of Space Power System Materials. This procedure minimized contamination of the potassium during the welding of the capsules. Sealed capsules were then X-rayed to check weld integrity and potassium content.

Capsule Testing

Capsules were tested in static air in cylindrical chambers 18 inches (46 cm) in diameter by 52 inches (130 cm) long. Platinum - platinum-13-percent-rhodium thermocouples were spot welded to the tops and bottoms of the capsules.

A capsule test bed consisted of 10 capsules individually surrounded by heaters of coiled 80-nickel - 20-chromium alloy wire insulated with a ceramic material. The heaters were manually controlled with metered variable transformers. Test temperatures were recorded on multipoint strip-chart recorders. The nominal test conditions were 1800° F (982° C) (measured at the bottom of the capsules) for a period of 2000 hours.

Post-Test Processing

After removal from the test bed, capsules on which chemical analyses for oxygen in the potassium were to be made were opened under vacuum in a specially designed product separation apparatus (ref. 7); the others were pierced by drilling under butyl alcohol. When the reaction between the alcohol and potassium was complete, the capsules were rinsed with distilled water and dried with acetone. They were then sliced longitudinally, photographed, and mounted for metallographic examination.

RESULTS AND DISCUSSION

The alloys evaluated may be ranked in order of merit with respect to the overall extent to which the capsule walls have been affected by the refluxing potassium. Microstructural features resulting from reaction with potassium, which can be separated from aging effects, consist of such phenomena as intergranular penetration, voids, depletion zones and second-phase regions resulting from compositional changes brought about by

6

preferential leaching of alloying elements, and diffusion between deposits and original base metal.

When the overall extent of these features is used as criteria for arbitrary ranking, the alloys appear to fall into three groups: HS-25 and Rene 41 are least affected by refluxing potassium; Hastelloys N, C, and X show moderate effects (in increasing order of severity); and AISI 318 is the alloy most severely affected. An attempt was made to rank the alloys on a quantitative basis by measuring wall penetration caused by reaction with the refluxing potassium. This was not satisfactory because in some cases there was gross solution or wall recession in addition to grain boundary penetration. Also, oxidation of the exterior capsule surfaces resulted in thinning of the capsule walls and made it difficult to determine what portion of the reduction in wall thickness was due to the solution effect of the refluxing potassium.

Test conditions for the individual capsules are summarized in table II; the alloys tested are discussed individually in the subsequent sections. In this discussion, microstructural changes believed due to corrosion by potassium are described. Additional microstructural changes believed due solely to aging for long times at high temperatures were observed but are not a subject of this report.

HS-25 .

HS-25, the only cobalt-base alloy evaluated, showed very good corrosion resistance to boiling potassium at 1800° F (982° C). This result is in agreement with those reported in reference 1. Due to premature heater burnout, the longest test time was 1606 hours (table II). There was some darkening of the capsule interiors near the liquid-vapor interface (fig. 3). Metallographic examination of these regions revealed both slight solution attack and deposition in close proximity (fig. 3, area C). There appeared to be a zone of compositional change near the surface beneath the deposit. Material was leached out before deposition occurred. This may indicate an unstable liquid level.

Electron beam microprobe analysis profiles across the material near the liquid-vapor interface showed depletion of nickel as the inner wall surface was approached. There appeared to be a slight enrichment of cobalt while chromium remained nearly constant.

Rene 41

Three of the four Rene 41 capsules ran the full 2000 hours; the fourth ran only 1854 hours due to heater burnout. There was considerable darkening of the capsule walls at

TABLE II. - CAPSULE REFLUX TIMES AND TEMPERATURES

Alloy	Reflux time, hr	Mean temperature at -							
		Capsule bottom				Capsule top			
		^{o}F		^{o}C		^{o}F		^{o}C	
		Measured	Standard deviation	Measured	Standard deviation	Measured	Standard deviation	Measured	Standard deviation
HS-25	1606	1797	12	981	7	1643	9	895	5
	1461	1796	14	980	8	1640	9	893	5
	1132	1796	11	980	6	1644	10	896	6
Rene 41	2000	1795	8	979	5	1598	18	870	10
	2000	1797	8	981	4	1616	10	880	6
	2000	1793	5	978	3	1618	17	881	10
	1854	1798	7	981	4	1624	12	884	7
Hastelloy N	2000	1798	6	981	3	1683	9	917	5
	2000	1793	5	978	3	1630	7	888	4
	2000	1798	8	981	4	1599	16	871	9
Hastelloy C	2000	1798	6	981	3	1680	11	916	6
	2000	1794	5	979	3	1663	11	906	6
	1988	1798	6	981	3	1634	12	890	7
Hastelloy X	2000	1798	9	981	5	1660	8	904	4
	2000	1801	9	983	5	1665	7	907	4
	1837	1799	15	982	8	1684	14	918	8
AISI 318	974	1797	12	981	7	[a]1638	63	892	35
	[b]952	1766	14	963	8	[a]1658	13	903	7
	638	1788	15	976	9	1654	14	901	8
	[b]346	1789	15	976	8	[a]1640	20	893	11

[a]Thermocouple separated from capsule top during test run.
[b]Capsule leaked.

8
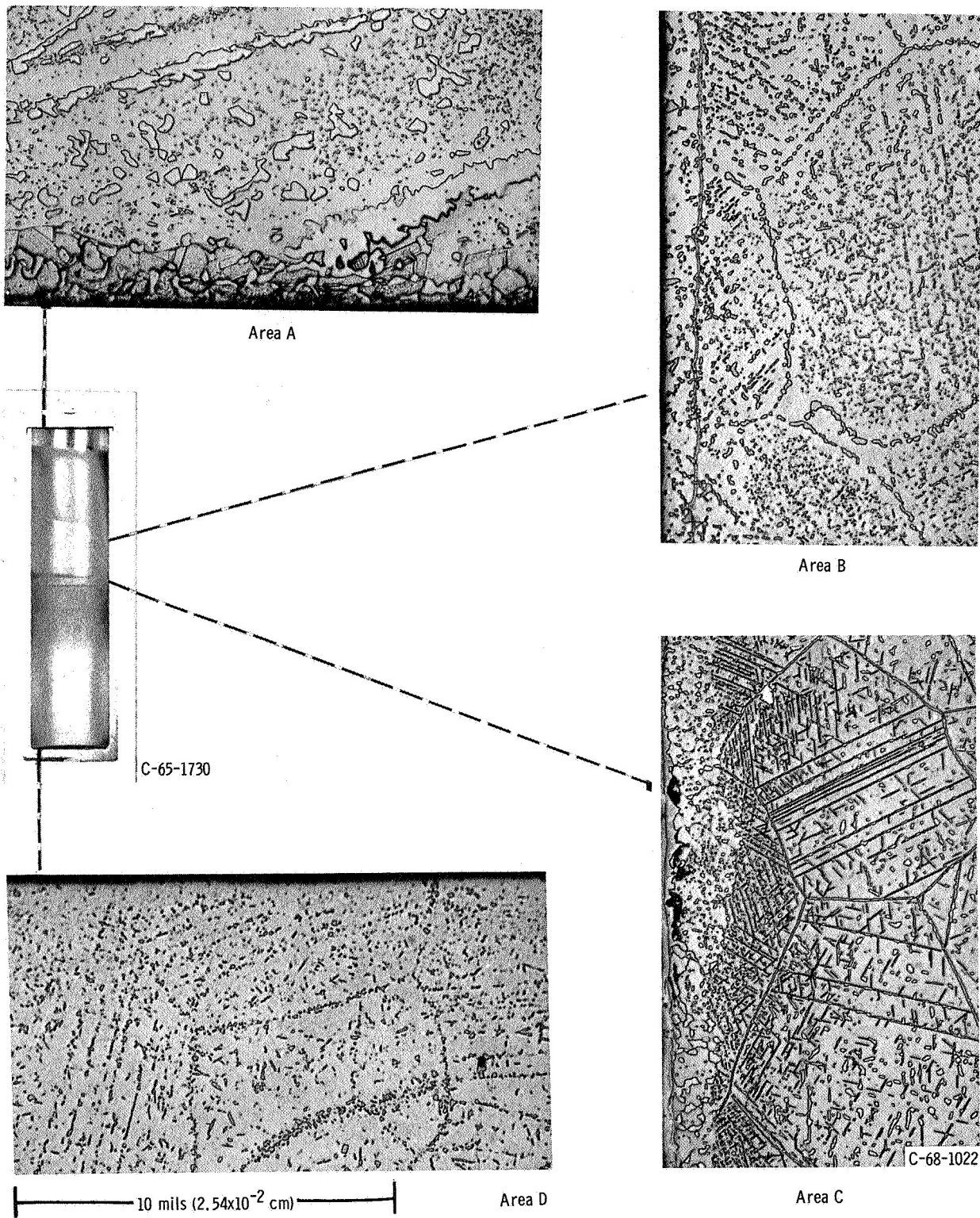
Area A

Area B

Area D

Area C

C-65-1730

C-68-1022

10 mils (2.54x10^{-2} cm)

Figure 3. – Microstructure of HS-25 capsule tested at 1800° F (982° C) for 1606 hours with refluxing potassium.

Area A

Area B

C-66-3611

C-68-1023

Area D
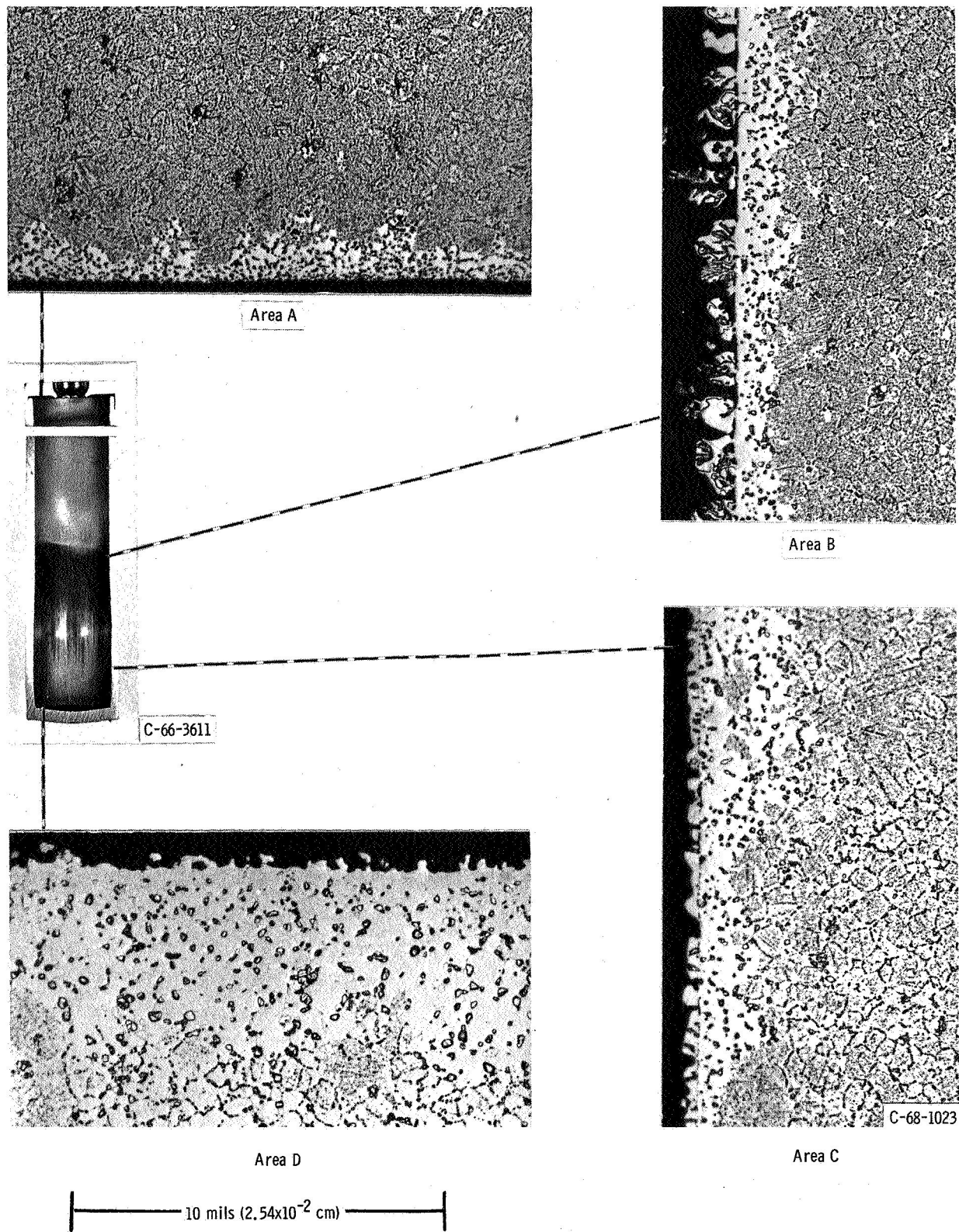
Area C

|← 10 mils (2.54x10^{-2} cm) →|

Figure 4. - Microstructure of Rene 41 capsule tested at 1800° F (982° C) for 2000 hours refluxing potassium.

10

and below the liquid-vapor interface (fig. 4). Near the liquid-vapor interface, deposits were found which are up to 1.5 mils (3.8×10^{-3} cm) thick (fig. 4, area B). These deposits consist of material which was probably leached from the inner capsule surface near the top of the capsule (fig. 4, area A). Electron beam microprobe analysis profiles show the deposits to be high in molybdenum, nickel, and chromium.

The white zone beneath the deposits was higher in nickel and chromium than the matrix material indicating diffusion from the deposits into the capsule wall during the test (fig. 4, area B). During the course of this test, the capsule bulged noticeably as a result of creep (fig. 4).

Hastelloy N

The three Hastelloy N capsules ran the full 2000 hours. Capsule interiors were bright in the liquid-vapor interface region with a duller, matte appearance occurring at the tops and bottoms (fig. 5).

There is considerable intergranular and solution attack at the tops and bottoms of the capsules (fig. 5, areas A and D). Deposits of the leached out materials occurred near the liquid-vapor interfaces (fig. 5, area C). These are lower in molybdenum and iron, and higher in nickel than the matrix, as indicated by electron beam microprobe analysis profiles.

Hastelloy C

Two Hastelloy C capsules ran the full 2000 hours; the third was stopped at 1988 hours due to heater burnout. There was darkening of the capsule walls near the liquid-vapor interface and at the top and bottom of the capsules (fig. 6). Relatively thick deposits were visible near the boiling interfaces (fig. 6, area C). The large amount of material deposited from solution indicates extensive solution attack. This attack is evident at the top of the capsule shown in figure 6 (area A). A second phase, or what appears to be a second phase, is left behind as a result of the solution attack. Further down, the capsule walls show depletion zones and what appear to be internal voids (fig. 6, area B).

Electron beam microprobe analysis profiles showed that the deposits contained more nickel than the matrix contained. However, in one capsule which had enough deposit to allow a semiquantitative spectrographic analysis, all elements analyzed showed up as strongly in the deposit material as in the control material taken from the capsule itself.
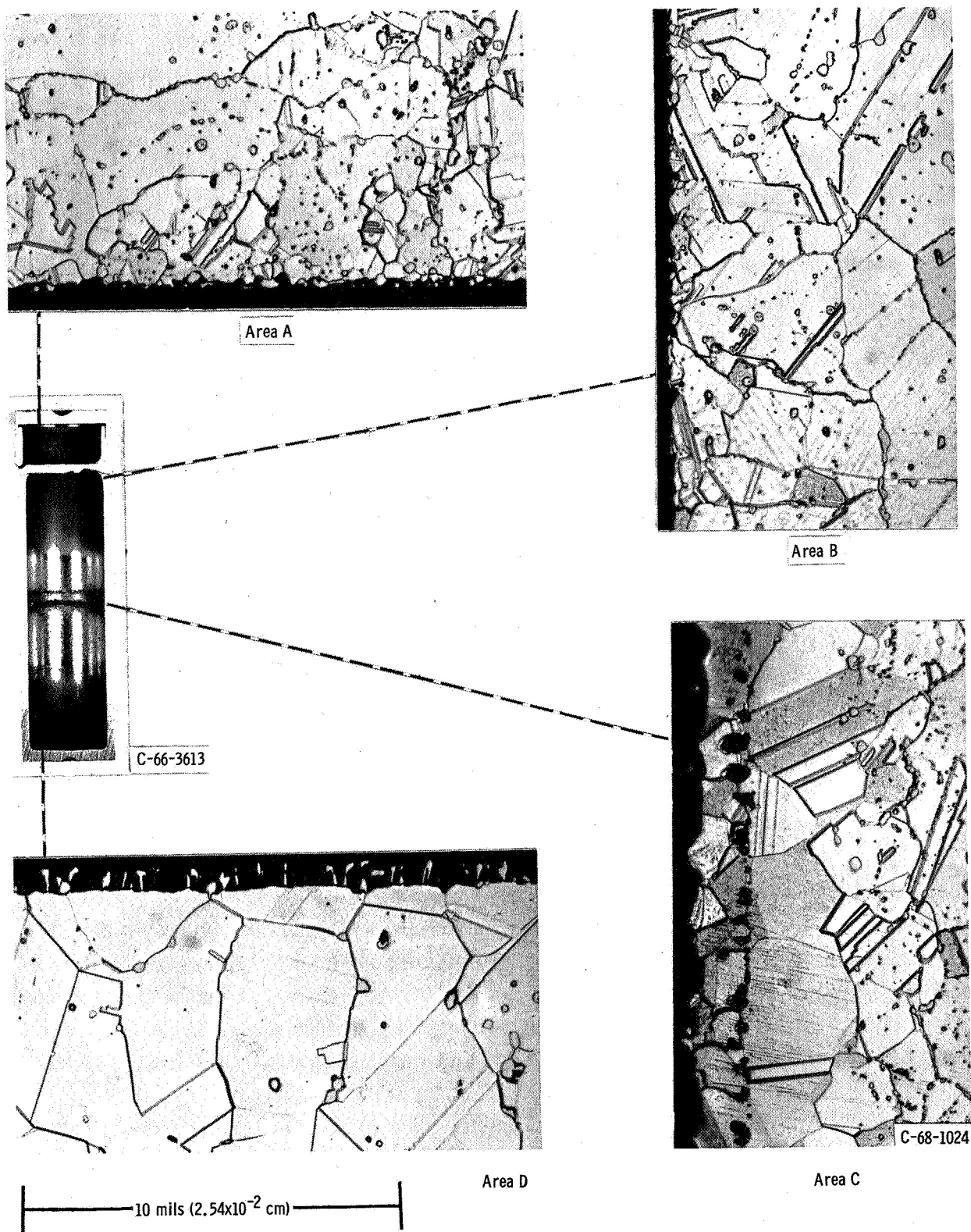
Area A

Area B

C-66-3613

Area D

Area C

C-68-1024

|—— 10 mils (2.54x10^{-2} cm) ——|

Figure 5. – Microstructure of Hastelloy N capsule tested at 1800° F (982° C) for 2000 hours with refluxing potassium.

12

Area A

Area B

C-66-3612

Area D

Area C

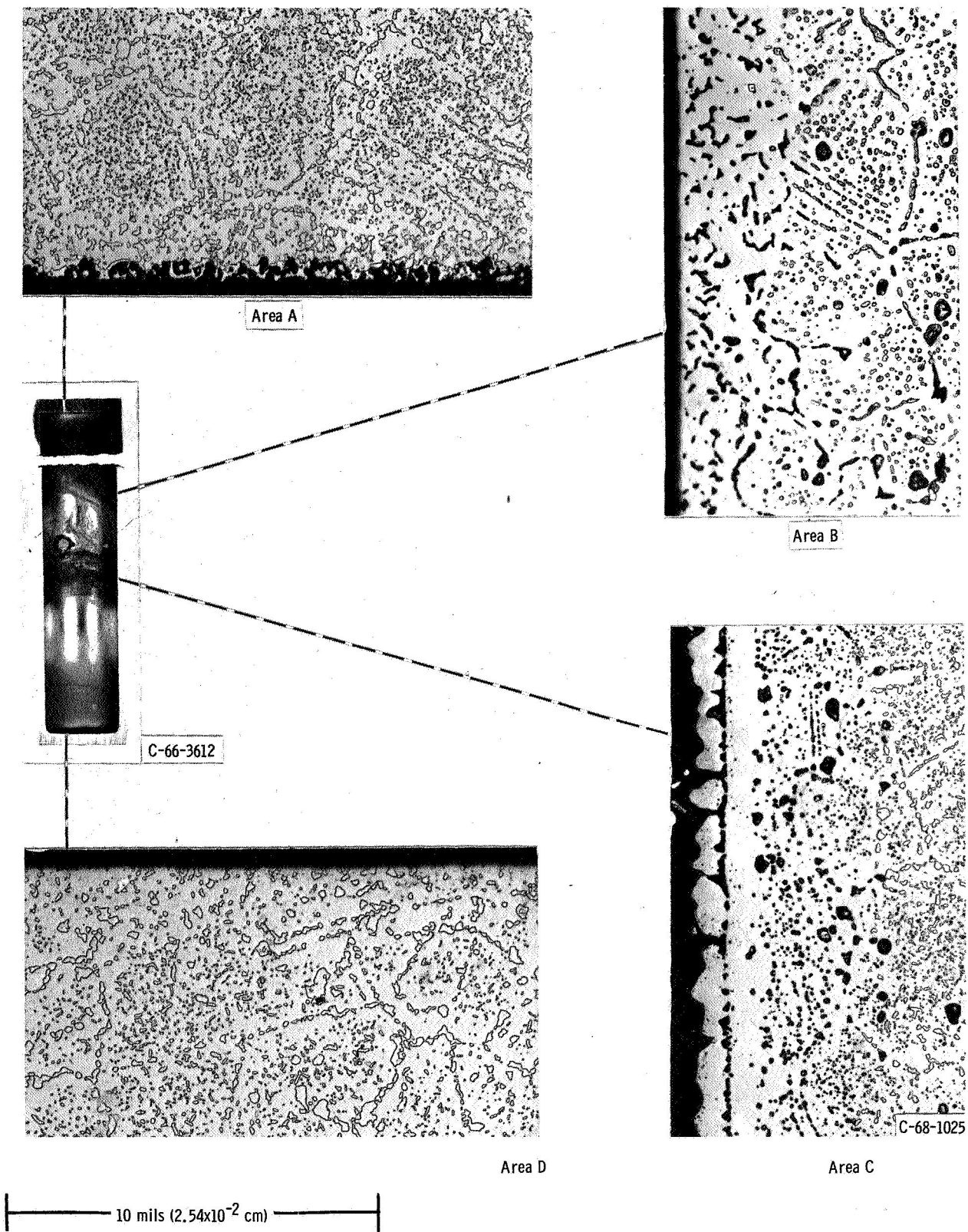C-68-1025

10 mils (2.54x10^{-2} cm)

Figure 6. – Microstructure of Hastelloy C capsule tested at 1800° F (982° C) for 2000 hours with refluxing potassium.

13

Hastelloy X

Two of the three Hastelloy X capsules ran the full 2000 hours; the third ran only 1837 hours due to heater burnout. There was some darkening of the capsule interiors near the liquid-vapor interfaces (fig. 7). Metallographic examination of these areas revealed a layer of deposit approximately 1/2 mil (1.3×10^{-3} cm) thick (fig. 7, area B).

Generally, the zone of noticeable change due to attack was limited to a depth of about 1 mil (2.5×10^{-3} cm). However, one capsule showed severe intergranular attack at the liquid-vapor interface where the attack zone plus depletion zone was 6 mils (1.5×10^{-2} cm) deep (fig. 7, area B).

Electron beam microprobe analysis profiles through a depletion zone and deposit (or phase change) region near the liquid-vapor interface of a capsule showed mainly an increase in nickel in the "deposit" region (fig. 7, area B).

AISI 318

The outside surfaces of the AISI 318 capsules tested were severely oxidized by reaction with the static air atmosphere in which all of the capsule reflux tests were conducted. Wall thicknesses near the bottoms of some of the capsules were reduced to less than 50 percent of the original, and two capsules leaked; one after about 350 hours and the other after about 950 hours at temperature. Mean heater life for these capsules was only 728 hours, because the heavy scale buildup on the capsules resulted in greater than normal power requirements to maintain the capsules at the desired reflux temperature.

Intergranular attack at and above the liquid-vapor interface occurred to depths of at least 3 mils (7.6×10^{-3} cm) (fig. 8, areas B and E). There appears to be a formation of a second phase at grain boundaries near the interface (fig. 8, area E). This structure occurs to a depth of 17 mils (4.3×10^{-2} cm) from the inner capsule wall. Electron beam microprobe analysis was unsuccessful in identifying this second phase material; its composition appeared to be essentially the same as that of the matrix alloy.

A small amount of material was deposited near the liquid-vapor interface as shown in figure 8, area E. Electron beam microprobe analysis profiles of this material for nickel, chromium, and iron revealed that the deposit material had essentially the same composition as the matrix, within the limits of the probe.

The fact that AISI 318, the only iron-base alloy evaluated, showed poorer resistance to refluxing potassium than the cobalt- and nickel-base alloys tested is in agreement with other results found in this laboratory (ref. 8) where J. H. Swisher reported iron to be more soluble in potassium than nickel, and nickel to be more soluble than cobalt.
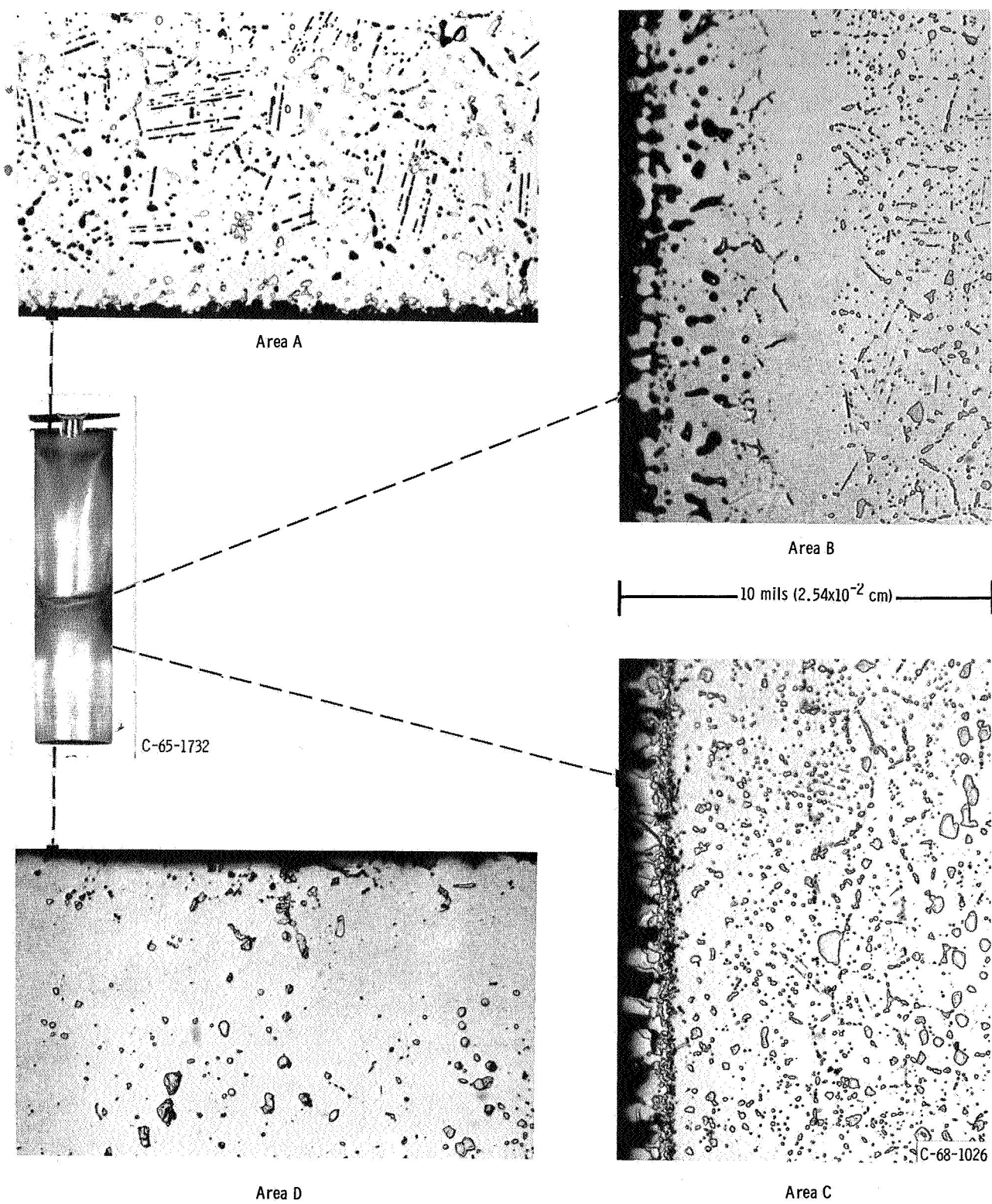
Area A

Area B

10 mils (2.54x10^{-2} cm)

C-65-1732

Area D

Area C

C-68-1026

Figure 7. – Microstructure of Hastelloy X capsule tested at 1800° F (982° C) for 1837 hours with refluxing potassium.

15

Area A

Area B

Area E

Deposit

C-65-1731

Area C

C-68-1027
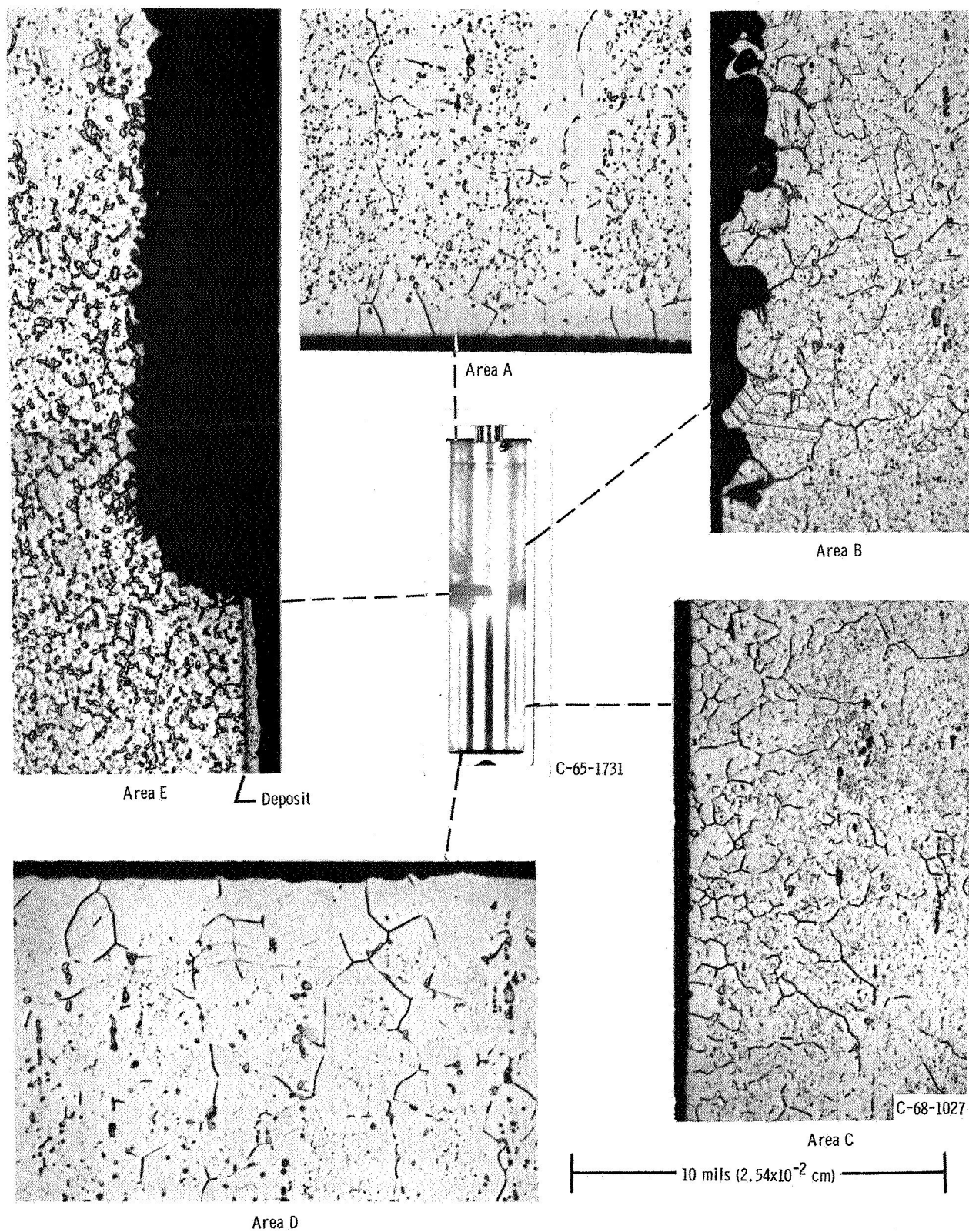
Area D

10 mils (2.54x10^{-2} cm)

Figure 8. – Microstructure of AISI 318 capsule tested at 1800° F (982° C) for 638 hours with refluxing potassium.

16

Determination of Oxygen Content in Potassium from Refluxed Capsules

The oxygen content of the potassium taken from two refluxed capsules each for three of the alloys after 2000 hours of testing was determined as a spot check. The initial oxygen content of the potassium used in these tests was 20 ppm or less by weight. Results are shown in table III. Due to these relatively high values for the oxygen content of

TABLE III. - OXYGEN CONTENT IN

POTASSIUM AFTER TEST

Capsule material	Oxygen content, ppm	
	Capsule 1	Capsule 2
Hastelloy C	500	350
Hastelloy N	250	240
Rene 41	75	60

potassium from tested capsules, an analysis for oxygen was made on the potassium from a filled and sealed Hastelloy C capsule that had not been tested. The result of this analysis was 87 ppm oxygen. All three Hastelloy C capsules were filled from the same tube, which contained potassium with approximately 20 ppm of oxygen. Thus it appears that part of the oxygen pickup resulted from the filling and sealing process. However, this does not account for the bulk of the pickup observed in the Hastelloys after long time tests as indicated previously. One might suspect that there were variations in the oxygen content of the three alloys at the start of the test and that this oxygen was gettered by the potassium, or that diffusion rates of oxygen through the walls of the three alloys differed greatly because of compositional variations.

Although the source of the oxygen is unknown, there appears to be a correlation between the oxygen content of the potassium after test and the amount of corrosion found in the capsules; Rene 41 had less corrosion than Hastelloy N, and Hastelloy N appeared to have less than Hastelloy C. This is in agreement with the hypothesis for the role of complex oxides in corrosion processes as reported earlier (refs. 4 and 5).

SUMMARY OF RESULTS

Corrosion capsules of six alloys (AISI 318, HS-25, Hastelloys C, N, and X, and Rene 41) containing refluxing potassium were evaluated in an air atmosphere at 1800° F

17

(982° C) for times up to 2000 hours. The investigation yielded the following results:

1. On the basis of this testing, the five cobalt- and nickel-base alloys tested (HS-25, Hastelloys C, N, and X, and Rene 41) appear to have sufficient corrosion resistance to boiling potassium at temperatures up to 1800° F (982° C) to warrant consideration for use as hardware for the ground testing in air of design concepts for components of space-power systems. The five alloys may arbitrarily be ranked into two groups based on the amount of corrosion resulting from these tests:

      (a) HS-25 and Rene 41 - very little corrosion

      (b) Hastelloy N, Hastelloy C, and Hastelloy X - intermediate amounts of corrosion (listed in increasing tendency to corrode)

2. The stainless steel (AISI 318) should not be used for this purpose because of its poor corrosion resistance. This confirms previous indications that stainless steels might be unsuitable for use under the given conditions.

Lewis Research Center,

    National Aeronautics and Space Administration,

        Cleveland, Ohio, March 11, 1968,

        129-03-03-01-22.

REFERENCES

1. Semmel, J. W., Jr.; Young, W. R.; and Kearns, W. H.: Alkali Metals Boiling and Condensing Investigations. Vol. II. Materials Support. Rep. No. GE63FPD66, General Electric Co., Jan. 14, 1963, p. 3.

2. Gurinsky, D. H.; Weeks, J. R.; Klamut, C. J.; Rosenblum, L.; and DeVan, J. H.: Corrosion in Liquid Metal Systems. Reactor Materials. Vol. 9 of Proceedings of the Third International Conference on the Peaceful Uses of Atomic Energy, United Nations (New York), 1965, pp. 550-558.

3. Kovacevich, E. A.: Potassium Corrosion Studies. NASA-AEC Liquid Metals Corrosion Meeting, Brookhaven National Laboratory, Dec. 14-15, 1961. AEC Rep. No. TID-7626, Pt. 1, Apr. 1962, pp. 63-68.

4. Epstein, Leo F.: Static and Dynamic Corrosion and Mass Transfer in Liquid Metal Systems. Chem. Eng. Prog. Symp. Ser., vol. 53, no. 20, 1957, pp. 67-81.

5. Horsley, G. W.: Mass-Transport and Corrosion of Iron-Based Alloys in Liquid Metals. Reactor Tech., vol. 1, Aug. 1959, pp. 84-91.

6. Anon.: Stainless Steel Handbook. Allegheny Ludlum Steel Corporation, 1959, p. 21.

7. Gahn, Randall F.: Technique for Recovery of Alkali-Metal Reaction Products. NASA TN D-4310, 1968.

8. Swisher, James H.: Solubility of Iron, Nickel, and Cobalt in Liquid Potassium and Effect of Oxygen Gettering Agents on Iron Solubility. NASA TN D-2734, 1965.