Proposed Paper ARS
AIAA Journal
Final Editorial Version

N65-88781

~~X63-15515~~

(NASA TMX 50554)

CODE-2A

19 p. caps.

Preliminary Report on

TITLE: an Experimental Investigation of Container Materials for the Snap-8 Secondary Mercury Loop

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Submitted for Publication

E-2109

ABSTRACT

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An experimental study of the compatibility of materials with mercury for possible use in the Snap-8 30 kw nuclear turbogenerator space power system is presented. Twenty-four materials were selected for reflux capsule materials screening from the following catagories: austenitic stainless steels, semi-austenitic stainless steels, martensitic chromium steels, cobalt-base alloys, refractory metals and alloys, and nickel-base alloys. Preliminary results of the program are described and their significance is discussed.

SUMMARY

A reflux capsule materials screening program was initiated to provide corrosion data helpful in selecting a containment material or materials to be used in the Snap-8 secondary mercury loop. Alloys were selected for testing from the materials catagories of austenitic stainless steels, semiaustenitic stainless steels, martensitic chromium steels, cobalt-base alloys, refractory metals and alloys, and nickel-base alloys. The refractory metals, as a class, showed the best corrosion resistance in tests run up to 2000 hours (the limit of tests in this category to date). The next best corrosion resistance for test times up to 5000 hours was demonstrated by the martensitic chromium

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steels. All other materials were considerably less corrosion resistant.

INTRODUCTION

Development of the Snap-8 30-kilowatt nuclear turbogenerator space power system (fig. 1) was started in 1960. Among the areas where the requisite technology for system development was lacking was that of materials for mercury containment. At that time, data from large-scale mercury boiler operation, run as long as 10,000 hours and at various temperatures as high as 1200° F, were available for a few ferrous materials. These results were presented as a review of unpublished data (ref. 1), and their significance could not be evaluated satisfactorily. Before 1960, other ferrous materials as well as molybdenum, tungsten, and Stellite had been tested in all-liquid dynamic harps (loops) for short periods of time (up to 1000 hours) and temperatures up to 1200° F (ref. 1). Two-phase (boiling-condensing) mercury compatibility data were available for some refractory metals as well as nickel-, cobalt-, and iron-base alloys at temperatures of 700° and 900° F for times up to 60 days; also, two-phase corrosion tests were run on HS-25, PH 15-7Mo, 347 stainless steel, and columbium at 1100° F for 12 days (ref. 2). When the aforementioned test data conditions were compared to the Snap-8 system requirements (upper mercury temperature of 1300° F and an operational lifetime of 10,000 hours), a technological gap was apparent.

In an attempt to provide the corrosion data needed to guide a Snap-8 secondary mercury loop materials selection, a reflux capsule materials screening program was initiated at the Lewis Research Center. Twenty-four materials were chosen for this program from the following categories: (1) austenitic stainless steels, (2) semiaustenitic stainless steels, (3) martensitic chromium steels, including 400-series stainless steels,

(4) cobalt-base alloys, (5) refractory metals and alloys, and (6) nickel-base alloys. Although prone to mercury attack, the nickel-base alloys were included for purposes of comparison.

The purpose of this paper is to describe some of the preliminary results of the Snap-8 materials screening program and to discuss their significance.

EXPERIMENTAL PROCEDURE

The compatibility of the various test materials (listed in table I) with mercury was determined by means of reflux capsules, 1/2-inch O.D. by 1 3/4-inch long by 0.040-inch wall (fig. 2). The capsule wall served as the test specimen.

The capsules were filled to approximately 1/3 with triple-distilled mercury and sealed by electron-beam welding in a vacuum of about 10^{-5} Torr. Resistance-type heaters were placed around the lower 2/3 of the capsule to provide the heat needed to boil the mercury. Test conditions are listed in table II.

At the conclusion of the tests, vertical sections of the capsules were examined metallographically, and maximum penetration for each capsule measured with a filar eyepiece. Specimens of particular interest were analyzed by an independent laboratory using electron-beam microprobe analysis techniques. This method utilizes an electron beam to produce primary X-ray emission from the elements present in a small volume of a specimen. The X-ray wavelengths and their intensities provide a measure of the quantity of each element present.

RESULTS

Penetration Data

Typically, visual examination of materials that were attacked by the mercury showed crystalline deposits along the capsule walls in the boiling section, predominantly at the boiling interface. Metallographic examination showed penetration attack in the condensing sections of the capsules. An example of the type of attack normally found in the condensing sections is illustrated in figure 3.

Of the 174 capsules tested under the conditions listed in table II, 63 were run as singles, 74 as duplicates, 24 as triplicates, 8 as quadruplicates, and 5 as quintuplicates. When multiple capsules of one material were tested at one test condition, the average of the observed maximum penetrations was determined, and the average deviation from this figure was calculated. The average deviations for all materials were found to vary linearly with the averages of the maximum penetrations; a penetration of 7 mils had an average deviation of 1 mil. The averages of the maximum penetrations were plotted as functions of temperature, the average deviation being used to delineate the upper and lower limits of the scatter band.

Figure 4 shows the maximum penetration observed in 300 hours for the alloys (listed in table I) grouped as to their material category. The least corrosion resistant materials were the austenitic stainless steels, the nickel-base alloys, and the cobalt-base alloys. Exhibiting noticeably less corrosion than these were the martensitic chromium steels and the austenitic stainless steel, AM-350, while the refractory metals were completely unaffected by the mercury.

A surprising result was the negative temperature coefficient of penetration found over most of the temperature range for the austenitic stainless steels, 304 and AF-71. This same effect was found at test times up to and including the 5000 hours for type-304 stainless steel. (Type AF-71 was not run for longer times.) Further work will be needed to explain this apparently anomalous result.

Because of limitations in experimental test space and time, only a few selected materials were tested for periods longer than 300 hours. Figure 5 gives the penetration observed in 1000 hours for selected materials from five material categories. In relation to the other materials, both the austenitic stainless steel, type 304, and the cobalt-base alloys, HS-25, H-8187, ML-1700, and HS-23, exhibited the greatest penetration. The martensitic chromium steels, Sicromo 9M, H-46, and 410, and the semiaustenitic stainless steel, AM-355, showed considerably less attack. No measurable penetration was observed in the case of the refractory materials, Cb-1Zr and Ta.

The results of the 5000-hour tests completed to date are given in figure 6. The AM-350 and 304 stainless steels and the HS-25 showed relatively great penetrations. Copious deposits were found at the boiling interface in the test capsules, all but plugging the capsules at that point. The negative temperature coefficient of penetration was again evidenced for 304 stainless steel, and in addition AM-350 showed a slight negative coefficient. Sicromo 9M falls into a lower penetration range than AM-350 and HS-25, with 1/4 to 1/5 the penetration. Nevertheless, heavy deposits (not quite as heavy as in the case of HS-25) were found at the capsule boiling interface. The 5000-hour tests with Cb-1Zr and Ta are presently in progress; still, it should be noted that these materials showed no observable penetration in the 2000-hour tests already completed.

Electron-Beam Probe Data

Results of numerous electron-beam microprobe analyses showed an almost complete depletion, or leaching, of Mn, Cr, and Ni from the capsule inner surface layers when they were initially present in a test alloy. Cobalt, when present, was partially depleted. In HS-25, for example, the cobalt leaching was incomplete, possibly due to the formation of an insoluble intermetallic compound with tungsten. Figure 7 is a plot of the ratio of the amount of each major alloying element to the amount of tungsten present as a function of distance, determined by an electron-beam microprobe analysis of an HS-25 capsule tested for 1000 hours at 1200° F. This plot illustrates the cobalt partial depletion effect. An X-ray diffraction analysis of the depleted area revealed the presence of Co_3W. Iron was relatively little affected by mercury as shown by analyses of 304, AM-350, Sicromo 9M and UMCo 50 + Ti. The refractory metals, Mo and W, were unaffected as shown by similar analyses of AM-350, Sicromo 9M, HS-25, and H-8187.

DISCUSSION

Materials compatibility screening tests cannot uniquely be used to select a material for a system application since other factors, such as strength, fabricability, and availability, must also be considered. Even from compatibility considerations alone, a screening test, such as the reflux capsule test, cannot provide all of the information needed to evaluate corrosion resistance since it cannot simulate either the nature or magnitude of the corrosion attack that takes place in all parts of an actual system or the effect of corrosion products on system components. This simulation can only be realized in a pumped loop experiment*. Nevertheless, a reflux capsule study is of value in examining a large number of materials conveniently and inexpensively and in distinguishing in a relative manner between good and poor corrosion resistant materials.

Within the limits of significance of this capsule test program as discussed previously, two major results may be pointed out. First, the preferential leaching of specific elements shown by the electron-beam microprobe analyses illuminated an important point concerning the nature of mercury corrosion in the temperature range under investigation: namely, the corrosive attack is approximately related to the solubility of the elements in mercury and to the total amount of soluble elements present in the alloy. From the limited solubility data available, (refs. 3 to 6) the solubility of the elements of interest in mercury at test temperatures may be conjectured to be as follows: Mn > Ni > Cr > Co > Fe > W with one or two orders of magnitude difference in solubility between Ni and Fe. This is essentially the same as the order of leaching attack indicated in the electron-beam probe analyses. By comparing alloys on the basis of penetration and the total percentage of mercury soluble elements present in them, it can be confirmed that there is a general trend toward greater

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*Natural convection boiling loops (NCBL) are inherently incapable of simulating a pumped loop because of two important limitations. First, there is no appreciable temperature or pressure difference imposed between the boiling and the condensing section (with concomitant small area flow passages). Second, if a NCBL is to operate stably, it can do so only at low flow rates (about the same as stable reflux capsule boiling rates). An attempt to increase flow rate by increasing the heat flux at the boiler merely promotes unstable flow, the so-called slugging. Therefore, the flow rate in a stably operated NCBL will be three to four orders of magnitude lower than in a Snap-8 system, for example.

penetration as the soluble element concentration in an alloy increases. When accurate and consistent mercury solubility data does become available, hopefully, it will be possible to make a quantitative correlation between corrosion attack and solubility.

The second result of the capsule test program was that a marked difference in corrosion resistance was shown among the materials tested. The refractory metals appeared to be completely resistant to penetration attack in the tests run up to 2000 hours (the limit of the tests to date), while all other materials exhibited penetration attack varying from moderate to extreme.

A comparison with the results of other investigators would be helpful for confirmation of the test results reported here; however, it should be recognized that such a comparison is difficult to make. Data from among different investigators are usually generated under different experimental conditions, i.e., mercury boiling rate, capsule surface treatment, and test temperature control. Also, since test temperatures and times do not often coincide among investigators, extrapolation is required to permit comparison of data.

Nevertheless, it is found that there is fair agreement in many cases. For example, the Thompson Ramo Wooldridge (TRW) 1000-hour penetration results (refs. 2 and 7) for 410 stainless steel, Sicromo, 300-series stainless steels, and HS-25, (all compared at 1000° F by extrapolation of the TRW 700° and 900° F data) agree within a factor of three with the results presented in this paper. Poor agreement, however, is found for AM-355 where extrapolation of the data of this investigation to 900° F showed an order of magnitude difference when compared with the AM-350 data of TRW at 900° F. This large discrepancy in penetration would not be expected from the slight difference in composition of these steels.

A comparison of capsule tests of the refractory metals and alloys shows good agreement. The quartz capsule test results of Brookhaven National Laboratory (ref. 8) for Ta and Cb-1Zr at 1100° F up to 3000 hours showed virtually no change in weight, and metallographic examination showed no detectable corrosive attack. In this case good agreement of results is obtained because, with an extremely corrosion resistant material, variations in test conditions should produce immeasurably small differences in penetration.

CONCLUSIONS

The conclusions that can be derived from the preliminary results of the reflux capsule screening program for a Snap-8 mercury containment material are as follows:

1. Of all the materials tested, tantalum and columbium-1 percent zirconium alloy are the most corrosion resistant. They showed no measurable penetration in 2000 hours, the limit of tests to date.

2. The martensitic and low alloy steels were next best in corrosion resistance for test times up to 5000 hours, but exhibited measurable penetration.

3. All other materials tested showed considerably less corrosion resistance for test times up to 5000 hours.

4. The corrosive attack of a material by mercury is directly related to the total percentage of mercury-soluble elements present in these materials.

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TABLE 1. - MATERIALS CHOSEN FOR THE MERCURY REFLUX CAPSULE SCREENING PROGRAM

Test Material	Type	Composition							
		Ni	Co	Fe	Cr	Mn	Mo	W	Other
Austenitic stainless steel	304	10	----	Bal.	19	2	-----	----	----------------
Austenitic stainless steel	AF-71	----	----		12.6	18.4	3	----	0.20 B, 0.8 V
Semiaustenitic stainless steel	AM-350	4.3	----		16.5	.8	2.75	----	.20 (N + C)
Semiaustenitic stainless steel	AM-355	4.3	----		15.5	.95	2.75	----	.23 (N + C)
Martensitic chromium steel	410	.5	----		12	1	-----	----	----------------
	422	.8	----			.75	1	1	.25 V
	Lapelloy C	.5	----			1	3	----	2.25 Cu, 0.10 N
	Sicromo 9M	----	----		10	.5	1.1	----	----------------
	Dynaflex	----	----		5	.3	1.3	----	.5 V
	H-46	.6	----		14.0	.80	.8	----	.6 (Cb + Ta), 0.4V
Cobalt-base alloy	HS-23	----	Bal.	1	24.5	1	-----	5	----------------
	HS-25	10		3	20	1.5	-----	15	----------------
	H-8187	----		2	20	1	12.5	----	.02 B
	Haynes 6B	3		3	30	2	1.5	4.5	1.10 C
	Co-25W-1Ti	----		----	----	-----	-----	25	1.0 Ti
	UMCo 50 + Ti	----		20	30	-----	-----	----	.2 Ti
	ML-1700 (Mod.)	----		----	25	-----	-----	15	.4 B
	Co-15Mo-15Cr	----		----	15	-----	15	----	----------------
Refractory metal or alloy	Molybdenum	----		----	----	-----	100	----	----------------
	Columbium	----		----	----	-----	-----	----	100 Cb
	Cb-1Zr	----		----	----	-----	-----	----	99 Cb, 1 Zr
	Tantalum	----		----	----	-----	-----	----	100 Ta
Nickel-base alloy	Inconel	Bal.		7	14.5	-----	-----	----	----------------
	Hastelloy B	Bal.		6	----	-----	-----	----	----------------

TABLE II. - REFLUX CAPSULE TESTING TIMES AND TEMPERATURES

Material	Type	Test temperature, °F	Test time, hr
Austenitic stainless steel	304	1000, 1100, 1200, 1300	300 to 5000
Austenitic stainless steel	AF-71	1100, 1200, 1300	300
Semiaustenitic stainless steel	AM-350	1100, 1150, 1200, 1250, 1300	300 to 5000
Semiaustenitic stainless steel	AM-355	1100, 1200, 1300	1000
Martensitic chromium steel	410	1000, 1100, 1150	300 to 1000
	422	1100, 1200	300
	Lapelloy C	1100, 1200	300
	Sicromo 9M	1000, 1100, 1150, 1200, 1250	300 to 5000
	Dynaflex	1000, 1100, 1200	300
	H-46	1100, 1200	300 to 1000
Cobalt-base Alloy	HS-23	1100, 1200, 1300	300 to 1000
	HS-25	1000, 1100, 1200, 1300	300 to 5000
	H-8187	1100, 1200, 1300	300 to 1000
	Haynes 6B	1200, 1300	300
	Co-25W-1Ti	1200, 1300	300
	UMCo 50 + Ti	1100, 1200, 1300	300
	ML-1700 (Mod.)	1100, 1200, 1250, 1300	300 to 1000
	Co-15Mo-15Cr	1100, 1200, 1300	300
Refractory metal or alloy	Molybdenum	1300	300
	Columbium	1100	300
	Cb-1Zr	1100, 1200, 1300	300 to 1000
	Tantalum	1100, 1200, 1300	1000 to 2000
Nickel-base alloy	Inconel	1100, 1200	300
Nickel-base alloy	Hastelloy B	1100, 1200	300

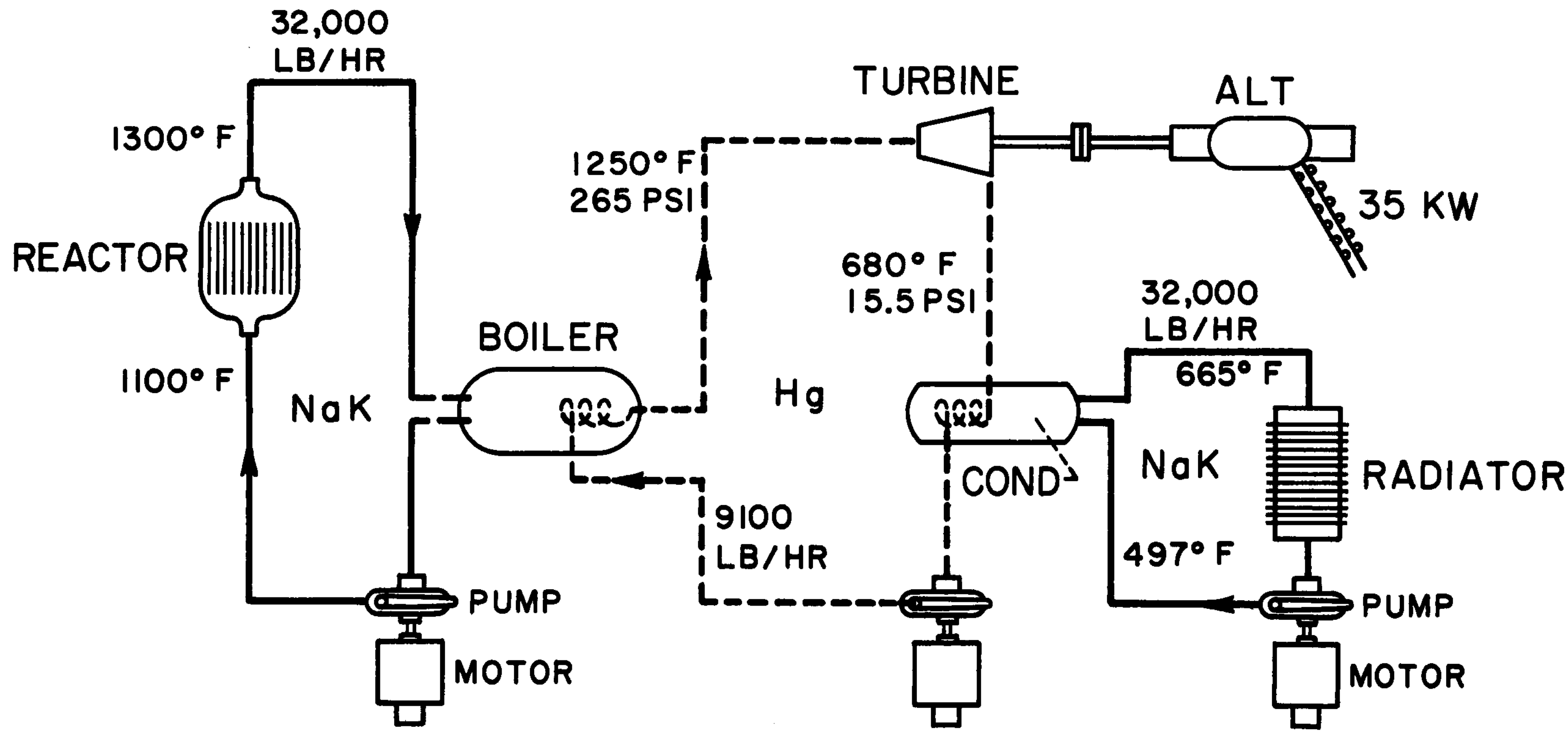

Figure 1. - Schematic of the Snap-8 system.

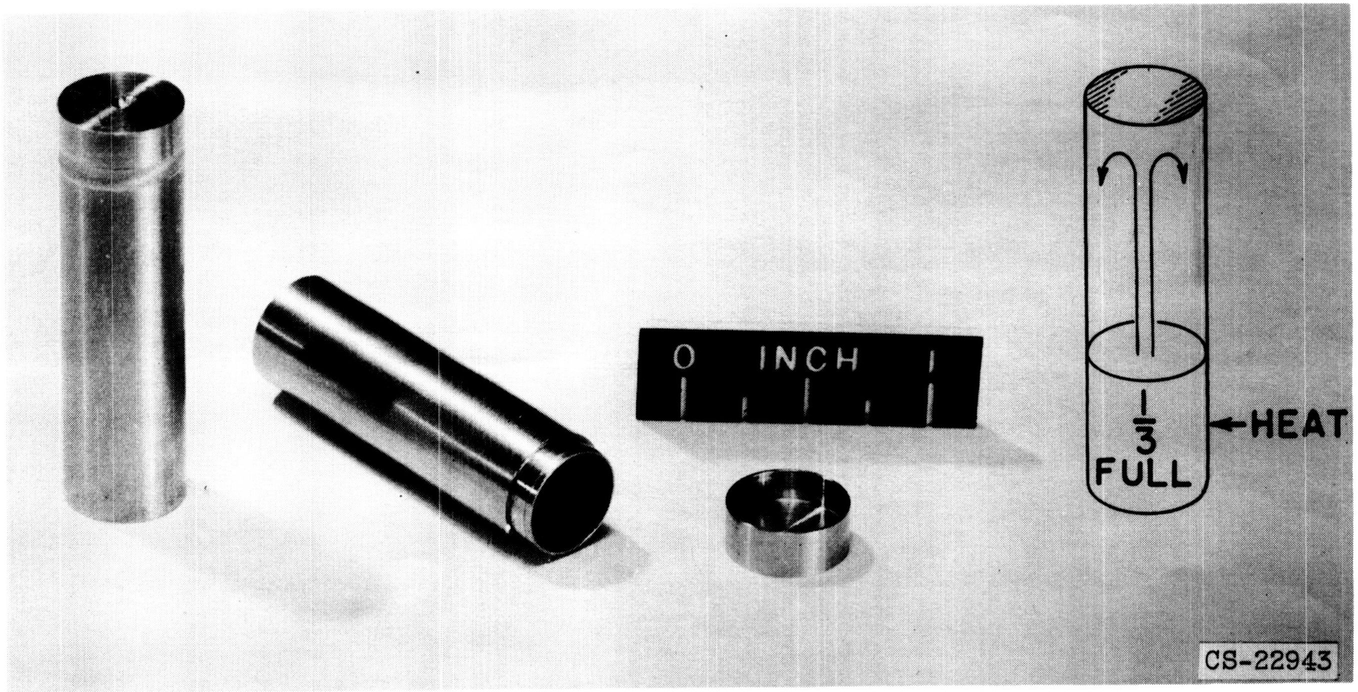

Figure 2. - Reflux capsules used in liquid metal corrosion studies.

Figure 3. - Typical appearance of depleted zone in mercury reflux capsules.

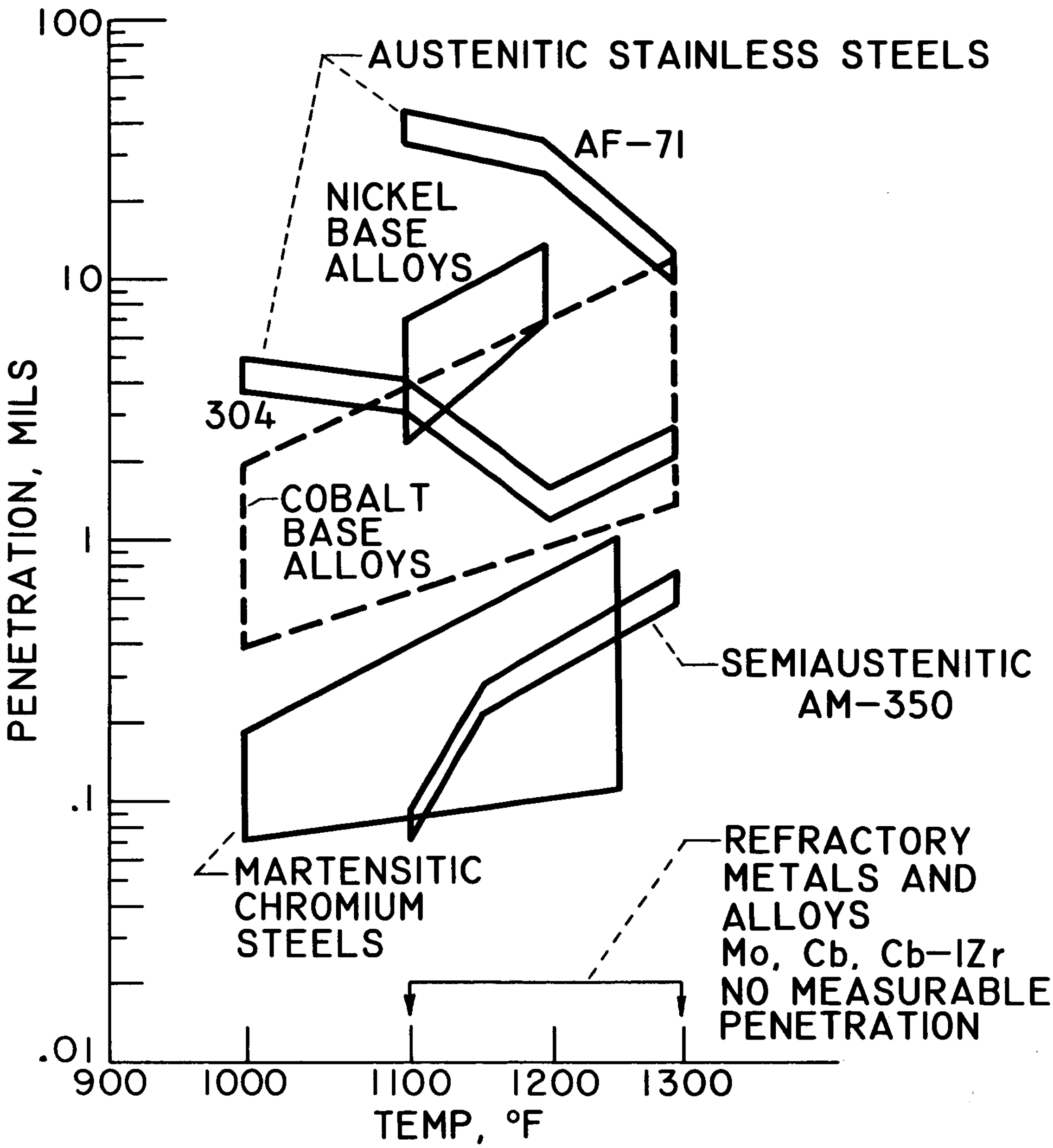

Figure 4. - Mercury corrosion penetration of materials tested for 300 hours.

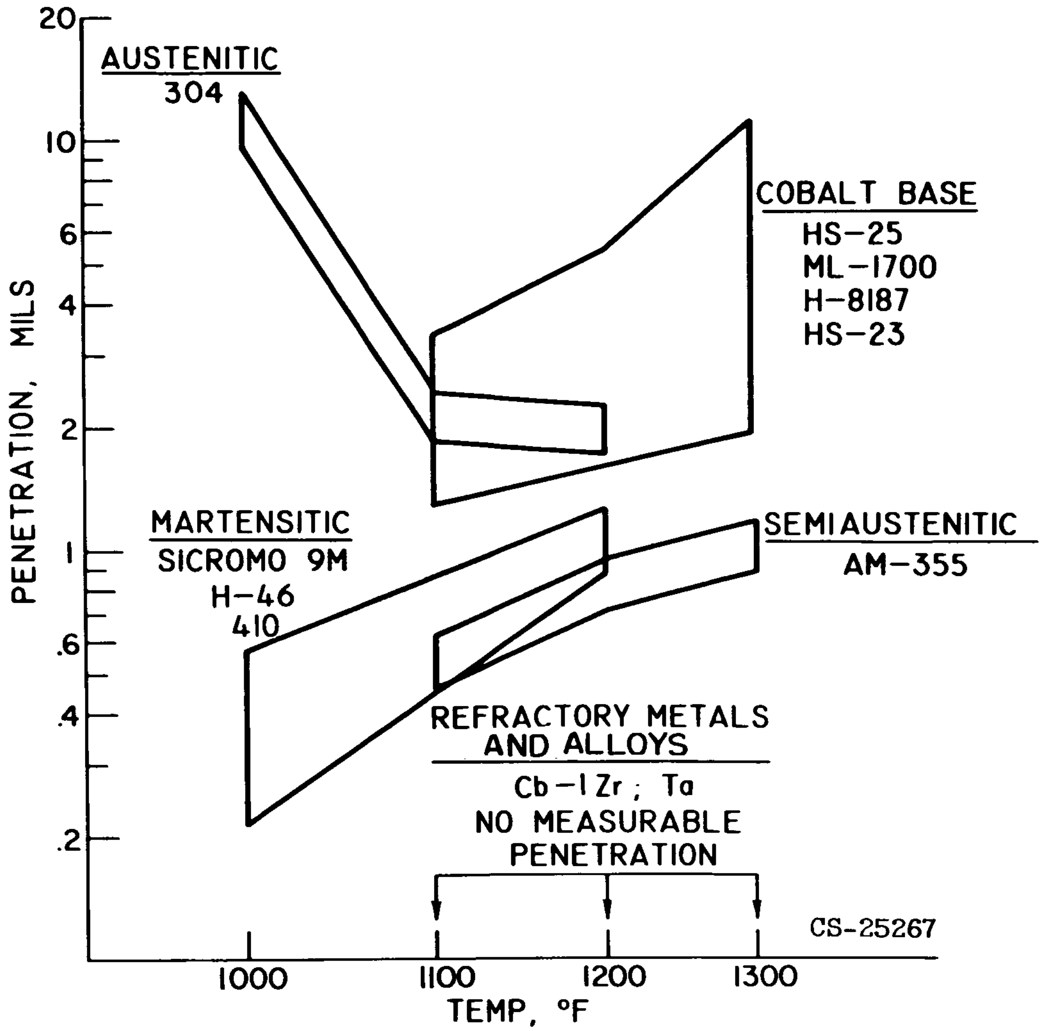

Figure 5. - Mercury corrosion penetration of materials tested for 1000 hours.

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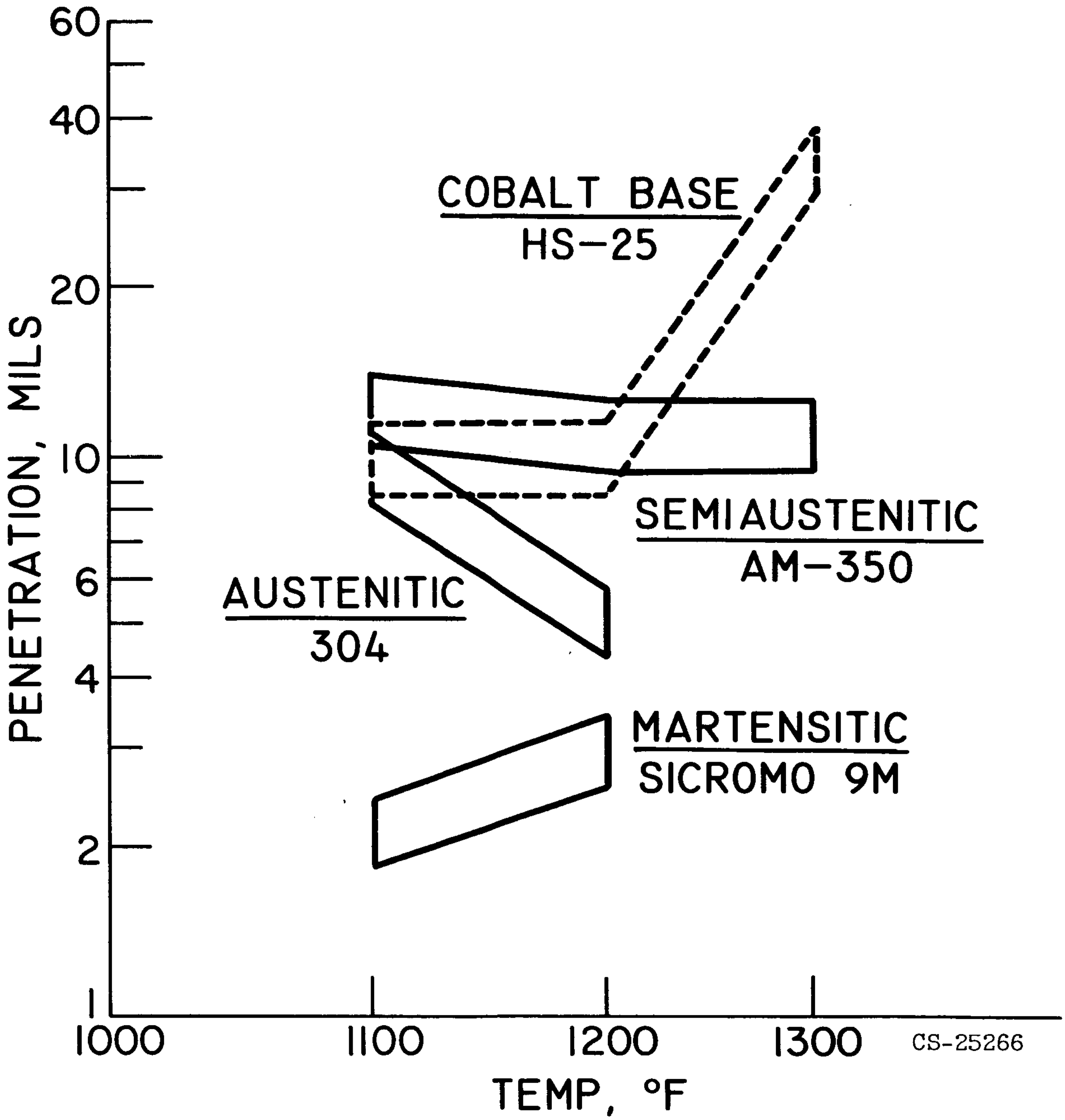

Figure 6. - Mercury corrosion penetration of materials tested for 5000 hours.

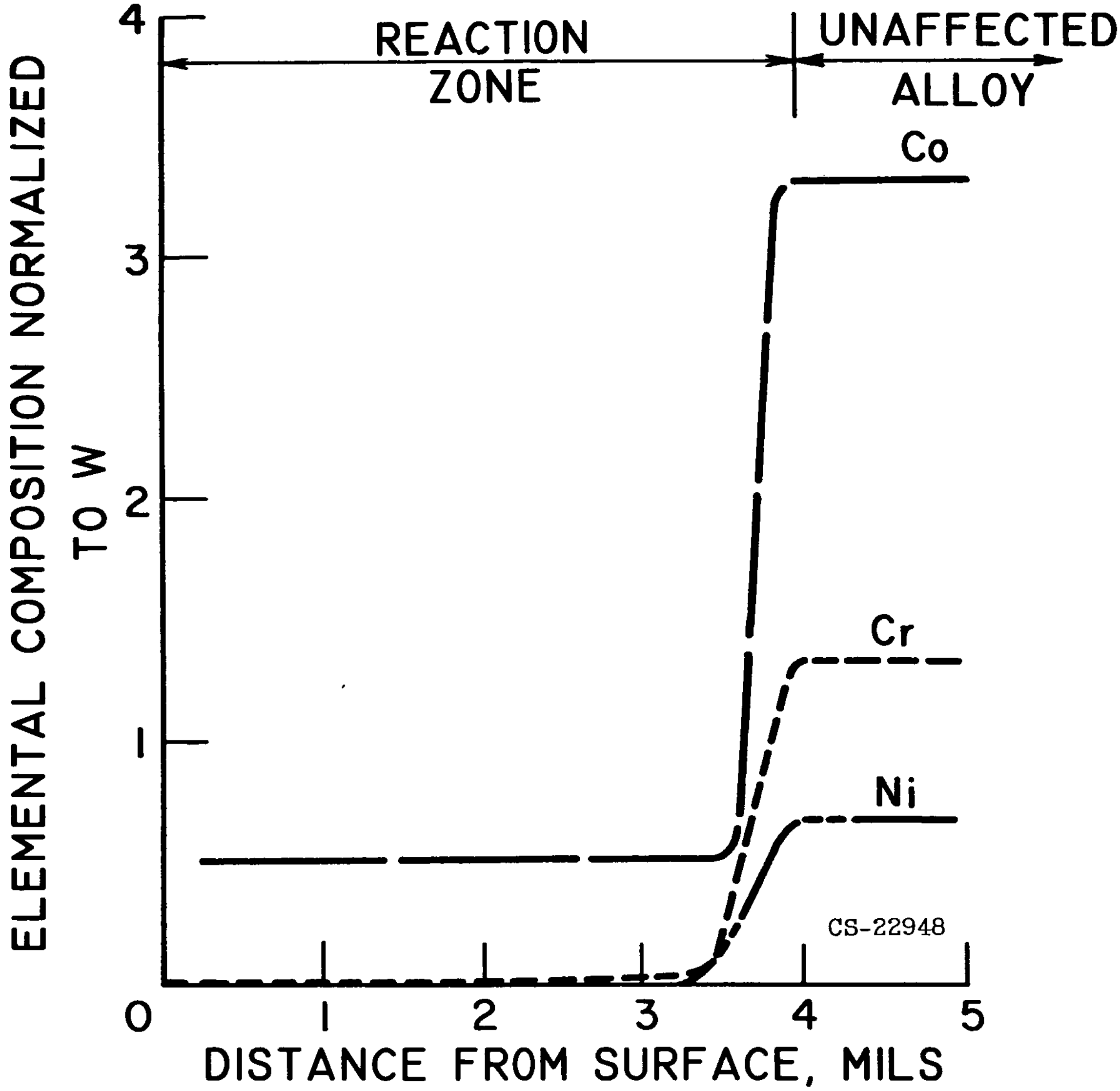

Figure 7. - Electron-beam microprobe analysis of HS-25 reflux capsule tested for 1000 hours at 1200° F.