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AEC RESEARCH AND DEVELOPMENT REPORT

SAVANNAH RIVER LABORATORY ISOTOPIC POWER AND HEAT SOURCES

QUARTERLY PROGRESS REPORT

OCTOBER - DECEMBER 1967

PART I - COBALT-60

DU PONT
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H. S. Hilborn, Compiler

January 1968

E. I. DU PONT DE NEMOURS & COMPANY
SAVANNAH RIVER LABORATORY
AIKEN, S. C. 29801

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PREFACE

This report is one in a series on the applied aspects of isotopes that are under study at the Savannah River Laboratory (SRL), and that are of interest as isotopic heat source materials. Principal emphasis is on isotopes that are produced by neutron addition, since these are the materials for which the production capabilities of the Savannah River Plant (SRP) reactors and other facilities can be used effectively. Data for other materials will be included if pertinent -- such as the isotopic or chemical composition of fission products that can be recovered from Savannah River process wastes.

These reports are intended to present data that are useful to system designers and also to potential or active user agencies. The reports thus deal with the following subject areas of SRL programs:

1. Properties and reactions of isotopes useful or potentially useful as heat sources.

2. Information on the irradiation and postirradiation processing of these materials, when the information is relevant to their use as heat sources and is not in a sensitive area of production technology.

3. Development of design data directed toward manufacturing capability for isotopic heat sources.

The report is issued in two parts: Part I includes only information on cobalt; Part II includes information on the other isotopic heat source materials. Both parts contain principally data from work performed during the report period. Previous reports are listed on the last page.

SUMMARY

Operation of capsules at 1000°C for one year will not be limited by diffusion of ^{60}Co in "Hastelloy" X, "Hastelloy" C, or "Haynes" 25, but may be limited by diffusion in "Inconel" 600 and TD Nickel. (p 1)

Several encapsulating alloys showed acceptable oxidation resistance at 1000°C in air for 9400 hr. (p 4)

"Inconel" 600 and "Hastelloy" X capsules that were heated in air at 1000°C for 5000 hr had no measurable dimension changes or leaks and predictably small oxidation and reaction layers. The capsules had 0.050-inch-thick walls and contained inactive cobalt wafers. (p 10)

A 0.050-inch-wall "Inconel" 600 capsule containing 15,000 curies of ^{60}Co as 150-curie/gram wafers had no measurable dimension changes or leaks after 5000 hr in air at ~850°C. Destructive examination is in progress. (p 11)

CONTENTS

PROGRAM

The purpose of the Savannah River Laboratory (SRL) program on ^{60}Co is to provide data that will be required for designing, fabricating, and operating ^{60}Co heat sources. The initial objective is to establish allowable operating limits for capsules of radioactive cobalt metal contained in oxidation resistant alloys. Development of specific heat source concepts is not at present included in the scope of the SRL program.

MATERIALS TECHNOLOGY AND DEVELOPMENT

Evaluation of Encapsulating Materials for Radioactive Cobalt Metal

The materials evaluation program is designed to select the most promising alloys for encapsulating ^{60}Co, to define the limiting operating conditions of these alloys, and to demonstrate capsule integrity at conditions typical of heat source operation. The kinetics of compatibility reactions,[1,2] diffusion of ^{60}Co,[1,4] oxidation,[1,3] and creep are being measured using short-term (<500 hr) laboratory tests. Selection of the most promising alloys is based on extrapolation of these results to the expected service life (1 to 5 yr). Limiting operating conditions are defined by the time and temperature dependency of each of the reactions. The predicted behavior of the materials is being verified by 1000-, 5000-, and 10,000-hr heating tests of experimental capsules, Table I.[1,4] Tests of companion capsules of unirradiated and irradiated cobalt will measure any effects of the radiation field and the increased nickel content (from radioactive decay of the cobalt) on the performance of the capsule materials.

Diffusion of ^{60}Co

The diffusion of ^{60}Co through prospective encapsulating materials is being measured to determine whether it will be a limiting factor in the design of heat sources. Earlier tests showed that diffusion would not be a limiting factor in several materials during one year of operation at 800°C, because the permissible concentration of about 1 ppm ^{60}Co occurs only 0.010 to 0.020 inch from the capsule-cobalt interface.[1,4]

Recent results showed that operation at 1000°C for one year will not be limited by diffusion in "Hastelloy"* X, "Haynes"* 25, or "Hastelloy"* C. It will be limiting for "Inconel"** 600 and TD Nickel*** in applications where the capsule wall is exposed

* Trademark of Union Carbide Corporation
** Trademark of International Nickel Co.
*** Product of E. I. du Pont de Nemours and Co.

TABLE I

SUMMARY OF COBALT CAPSULE HEATING TESTS

Capsule Material	Heating Time, hr	Heating Temp, °C	Wall, mils	No. of Capsules	Activity Spec. Ci/g	Activity Total, Ci	Approx. Starting Date	Approx. Completion Date	Remarks
A. Inactive Capsules									
"Inconel" 600	1,000	850	50	1	-	-	12-66	2-67	Capsule intact
	5,000	850	50	1	-	-	12-66	7-67	Capsule intact
	10,000	850	50	1	-	-	12-66	1-68	
	10,000	850	95	2	-	-	7-67	9-68	
	1,000	1,000	50	4	-	-	8-66	10-66	3 capsules intact; 1 capsule oxidized(b)
	5,000	1,000	50	1	-	-	4-67	11-67	Capsule intact
	1,000(a)	1,000	95	2	-	-	7-67	9-67	No severe oxidation of Co
	5,000	1,000	95	1	-	-	8-67	2-68	
	10,000	1,000	95	1	-	-	8-67	10-68	
	10,000	1,000	95	1	-	-	10-67	12-68	
"Hastelloy" C	1,000	1,000	50	4	-	-	8-66	10-66	3 capsules intact; 1 capsule oxidized(b)
	5,000	1,000	95	1	-	-	10-67	5-68	
	10,000	1,000	95	1	-	-	10-67	12-68	
	10,000	1,000	95	1	-	-	10-67	12-68	
TD Nickel	1,000	850(c)	95	1	-	-	10-67	12-67	Examination in progress
	5,000	850	95	1	-	-	10-67	5-68	
	10,000	850	95	1	-	-	10-67	12-68	
	10,000	850	95	1	-	-	10-67	12-68	
	1,000	1,000	50		-	-	12-66	2-67	Capsule intact
	1,000(a)	1,000	95	2	-	-	10-67	12-67	Examination in progress
TD Nickel Chromium	1,000(a)	1,000	95	2	-	-	10-67	12-67	Examination in progress
	1,000	1,000	95	1	-	-	10-67	12-67	Examination in progress
	5,000	1,000	95	1	-	-	10-67	5-68	
	10,000	1,000	95	1	-	-	10-67	12-68	
	10,000	1,000	95	1	-	-	10-67	12-68	
"Haynes" 25	1,000	1,000	95	1	-	-	10-67	12-67	Examination in progress
	5,000	1,000	95	1	-	-	10-67	5-68	
	10,000	1,000	95	1	-	-	10-67	12-68	
	10,000	1,000	95	1	-	-	10-67	12-68	
"Incoloy" 825	1,000	1,000	50	2	-	-	6-66	8-66	1 capsule intact; 1 capsule oxidized(b)
"Hastelloy" X	1,000	1,000	50	1	-	-	4-67	6-67	Capsule intact
	5,000	1,000	50	1	-	-	4-67	11-67	Capsule intact
B. ^{60}Co Capsules									
"Inconel" 600	130	850(d)	50	1	120	16,000	2-67	2-67	Swelled due to overheating
	1,000	850	50	1	100	5,000	4-67	6-67	Capsule intact
	5,000	850	50	1	150(e)	15,000(e)	4-67	10-67	Examination in progress
	10,000	850	50	1	150(e)	15,000(e)	4-67	6-68	
	10,000	850	50	1	150(e)	9,000(e)	5-67	7-68	
"Hastelloy" C	100	850	50	1	120	9,000	1-67	1-67	Capsule intact

(a) Two capsules, one not welded and one with drilled hole in wall, to test effects of capsule defects.
(b) Capsules reacted with fire-brick. See DP-1094, "SRL Isotopic Power and Heat Sources - Quarterly Progress Report," October-December 1966.
(c) Tests of TD Nickel at 850°C in flowing argon.
(d) Excursion to >1100°C for 3-6 hr. See DPST-67-102-2.
(e) Activity as of 2-67.

to a flowing coolant because concentrations greater than 1 ppm ^{60}Co are expected at the outer surface, Figure 1. The new data are shown in Table II with previous data for 800°C for comparison. Similarly, operation at 1200°C for one year will be limited by diffusion in all materials (^{60}Co concentrations in excess of 10,000 ppm are expected at the surface). These predictions were based on radiotracer measurements of the coefficients of volume and grain-boundary diffusion during 40-hour tests at 1000°C and during 4-hour tests at 1200°C. Diffusion was assumed to occur in a semi-infinite slab of each alloy rather than in a 0.100-inch-thick capsule wall. This assumption leads to results that are only slightly lower than the real values, and that are satisfactory for ranking the candidate alloys.

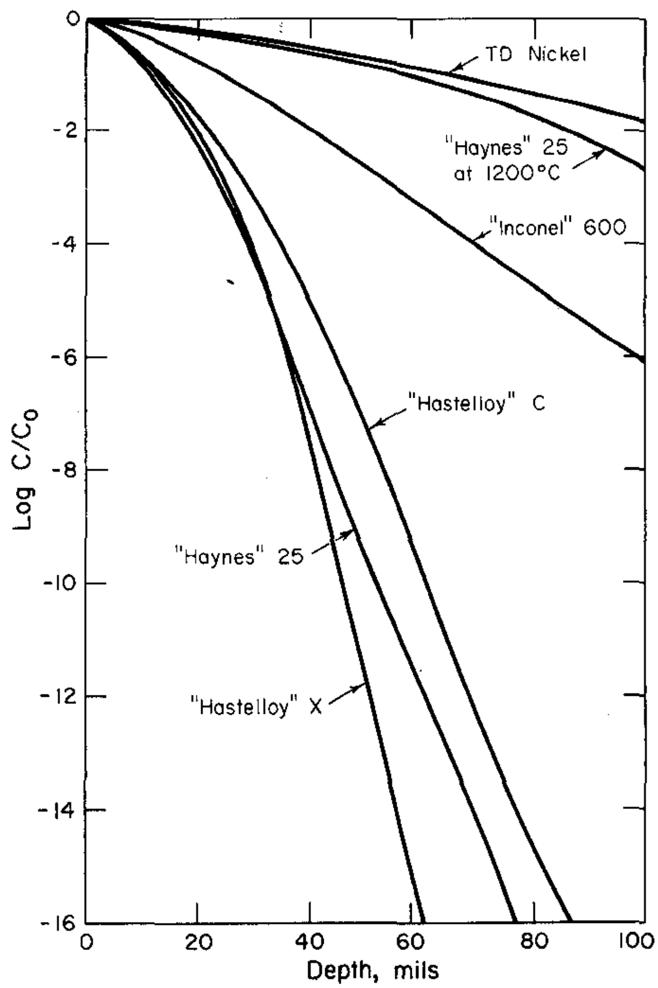

FIG. 1 ^{60}Co CONCENTRATIONS EXPECTED AFTER OPERATION AT 1000°C FOR ONE YEAR. Concentration profile for "Haynes" 25 at 1200°C is shown for comparison; other alloys at 1200°C have similar profiles.

TABLE II

CALCULATED DIFFUSION OF ^{60}CO IN CAPSULE MATERIALS DURING ONE YEAR

Material	Depth at which ^{60}Co Concentration is 1 ppm, mils	
	800°C	1000°C
"Hastelloy" X	8	35
"Haynes" 25	11	37
"Hastelloy" C	13	45
"Inconel" 600	20	~100
TD Nickel	60	>100

Future work includes calculation of the expected penetration during five years at 800 and 1000°C and measurement of the concentration profile in samples of "Inconel" 600 and "Hastelloy" X heated for 5000 hr at 1000°C.

Oxidation Resistance

Time Dependency

The oxidation characteristics of two groups of encapsulating alloys are being defined at 1000°C for periods up to 10,000 hr.[1,3] Tests of the first group, terminated after 9400 hr, show that TD Nickel-Chromium*** is the most resistant to oxidation. The nickel-based alloys such as "Hastelloy" X have intermediate resistance and are superior to the iron-based alloys, such as "Incoloy"** 825 (Table III). No change was observed in the mechanism of oxidation as the exposure time increased to 9400 hr, but the alloys oxidized somewhat more rapidly than expected.

Extrapolation of the 1000°C data from 9400 to 50,000 hr indicates that all the useful alloys will oxidize in air to a depth of 0.020 to 0.040 inch during a ^{60}Co half-life of 5.24 years (46,000 hr); TD Nickel and "Incoloy" 825 will oxidize to a depth of over 0.060 inch, Figure 2. The similarity in slope of the oxidation-time relationship for each alloy before and after 5000 hr, and periodic metallographic examinations of test coupons during the 9400-hr exposure, indicate no change in mechanism of oxidation that would invalidate this extrapolation. Data for "Inconel" 600 at 850°C from oxidation tests for 500 hr and from inactive capsules heated for 1000 and 5000 hr are also shown in Figure 2 for comparison.

TABLE III

OXIDATION OF CANDIDATE ENCAPSULATING ALLOYS
(Still air at 1000°C for 9400 hr)

Material	Zone Thickness, mils Total Affected	Surface Scale	Intergranular Oxidation	Zone Affected by Oxidation(a)
TD Nickel-Chromium	2.4	2.4	None	None
"Hastelloy" X	9.0	2.0	7.0	7.0
"Hastelloy" C	11.2	3.3	3.2	7.9
"Inconel" 600	11.2	2.1	9.1	9.1
"Inconel" 625	>12.5	(b)	6.7	12.5
"Incoloy" 800	16.0	3.1	8.8	13.0
"Incoloy" 825	17.0	4.0	13.0	13.0
TD Nickel	34.0	34.0	None	None
"Nickel 270"	>36.0	36.0	(c)	(c)

(a) Zone in which either new phases were formed or pre-existing phases disappeared.
(b) All oxide scale spalled off.
(c) Extended throughout the 60-mil thickness of the coupon (both surfaces exposed).

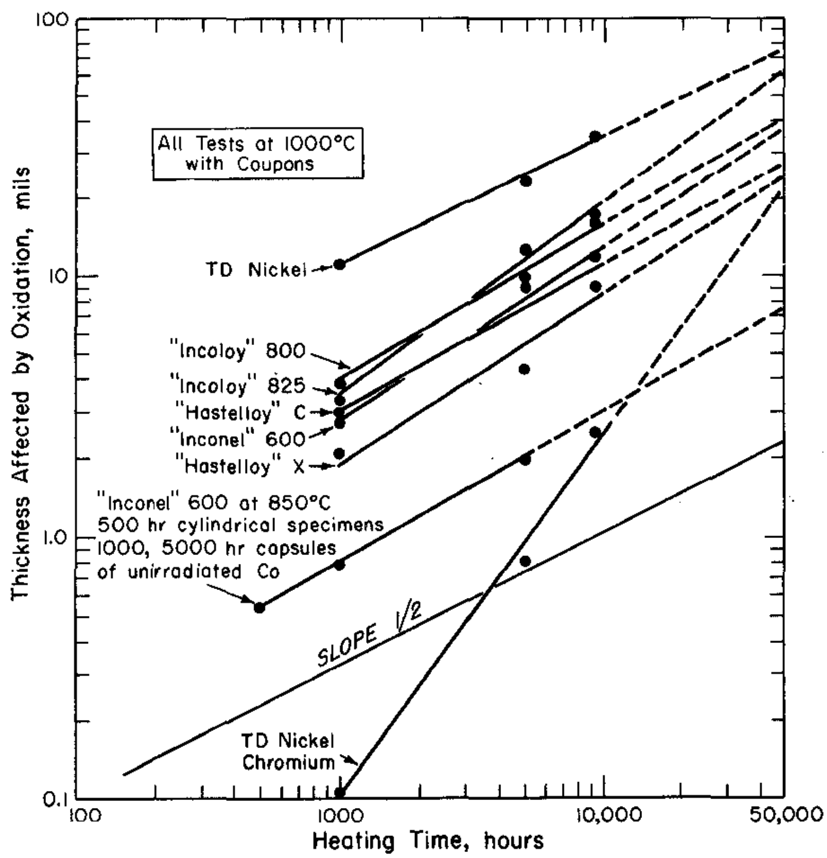

FIG. 2 OXIDATION OF CAPSULE MATERIALS IN STILL AIR AT 1000°C

Published data on metal oxidation indicate that penetration has a parabolic relationship with time (slope of ½ in Figure 2) when the oxidation is controlled by diffusion and the surface scale is protective. For all the useful alloys the exponent of time is higher than ½, which indicates that the protective ability of the surface scale is limited by cracking and spalling.

Results of 5000-hr tests on the second group of alloys, Table IV, showed that none of these alloys was as resistant to oxidation as TD Nickel-Chromium, as also observed after 1000 hr.[3] Five alloys, GE 2541,† "Haynes" 25, 50Ni-50Cr, "Tophet"‡ C, and RA 333†† had adequate resistance and were comparable to "Hastelloy" X and "Inconel" 600 (<0.010 inch total depth affected).

TABLE IV

OXIDATION OF CANDIDATE CAPSULE MATERIALS[a]
(5000 hr in still air at 1000°C)

Material	Zone Thickness, mils: Total Affected	Surface Scale	Intergranular Oxidation	Zone Affected by Oxidation
Group I				
TD Nickel-Chromium	0.8	0.8		
"Hastelloy" X	4.3	1.3		3.0
"Hastelloy" C	8.0	1.8	3.2	6.2
"Incoloy" 800	9.2	0.8	6.1	8.4
"Inconel" 600	9.4	1.8	7.6	
"Incoloy" 825	12.0	3.0	9.0	9.0
"Inconel" 625	13.3	4.0	6.0	9.3
TD Nickel	23.0	23.0		
Nickel 270	26.7	26.7		
Group II				
GE 2541	3.2	0.4	2.8	
"Haynes" 25	6.0	2.0	4.0	4.0
50Ni-50Cr	6.4	1.4		5.0
"Tophet" C	6.6	2.0	4.6	(b)
RA 333	7.0	1.0	2.0	4.0(b)
"Haynes" 8188	12.0	3.0	3.0	9.0
"N-155"	13.0	2.4	5.6	10.6
"Tophet" A	14.0	1.0	4.0	13.0
"Tophet" 30	15.0	2.0	4.6	13.0
"Hastelloy" G	15.8	4.4	11.4	

(a) Composition and source of candidate materials listed in Table I, p 5, of Reference 3.
(b) Metallographically observed zone on surface of metal that was depleted in alloy due to preferential oxidation.

† Product of General Electric Company
‡ Trademark of Wilbur B. Driver Company
†† Product of Rolled Alloys, Incorporated

However, changes in the microstructures indicated that "Tophet" C and RA 333 may have become severely embrittled and may not be suitable for encapsulating cobalt. Exposure of companion samples of these alloys to 10,000 hr is continuing.

Temperature Dependency

The temperature dependency of the oxidation rate was measured by heating samples of selected alloys for 500 hr at 850, 950, and 1150°C. These data fit the expected Arrhenius relationship with temperature, Figure 3. None of the alloys could be used for long times in an oxidizing atmosphere at temperatures much above 1000°C. Oxidation-affected zones greater than 0.100-inch thick would be predicted by extrapolating the oxidation observed at 1150°C in 500 hr to 50,000 hr using the relationships shown in Figure 2.

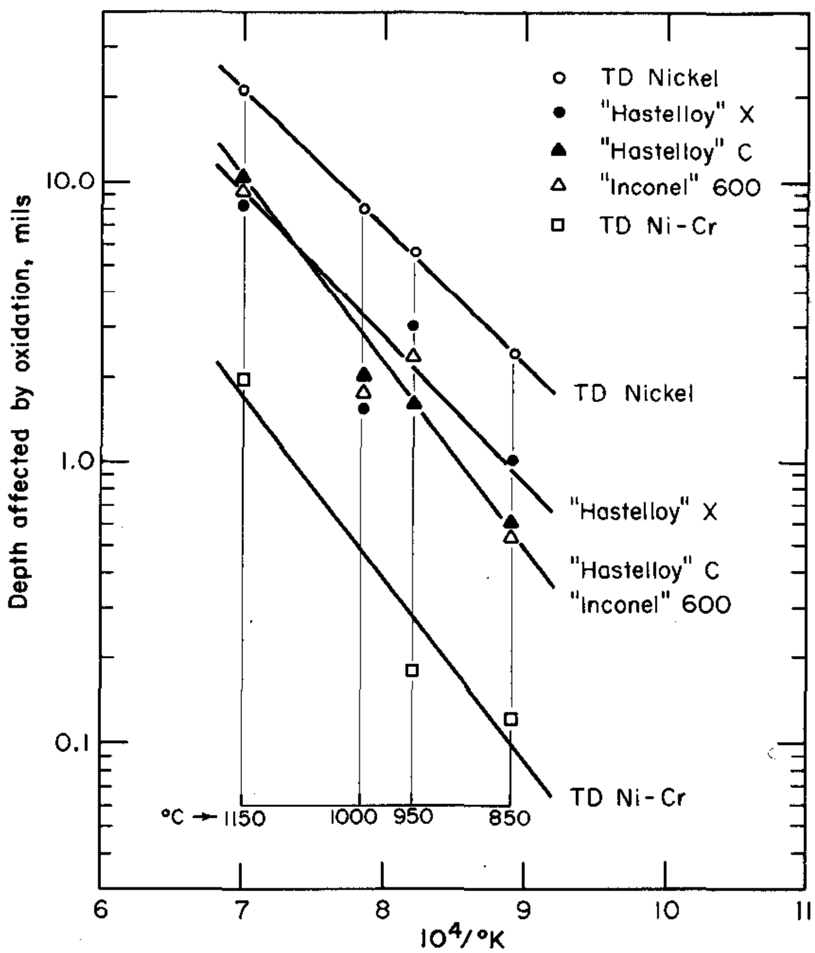

FIG. 3 EFFECT OF TEMPERATURE ON THE OXIDATION OF CANDIDATE CAPSULE MATERIALS (500-hr Tests)

Capsule Fabrication and Testing

Welding of Capsules

Tungsten inert gas (TIG) techniques are used for welding test capsules of prospective materials. The wall thickness of these capsules, Figure 4, has been increased from the 0.050 inch used previously to 0.095 inch to make the capsules more representative of those in actual heat sources. Sound, leak-tight welds in "Inconel" 600 and "Hastelloy" C were made with the wall thickness at the ends of the capsule reduced from 0.095 to 0.060 inch.

Additional tests indicate that TIG welds of TD Nickel and TD Nickel-Chromium are acceptable for capsule heating tests although the welds have irregular surfaces and contain random voids and agglomerates of thoria. Welds of "Haynes" 25 alloy have cracked in the heat-affected zone, Figure 5. Helium leak tests of capsules of these three materials show surface outgassing, but no leakage. This was verified by testing facsimile "capsules" fabricated from solid bar stock and pressurized externally with helium.

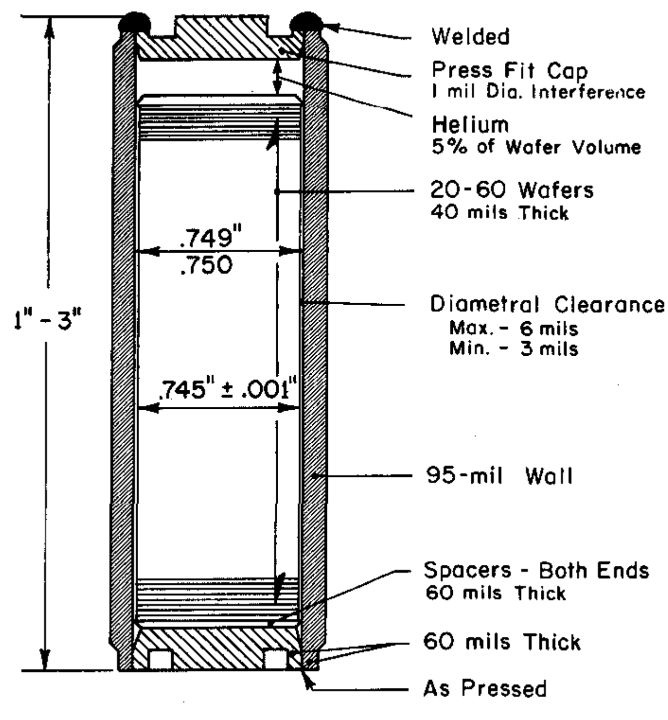

FIG. 4 THICK-WALLED COBALT CAPSULE

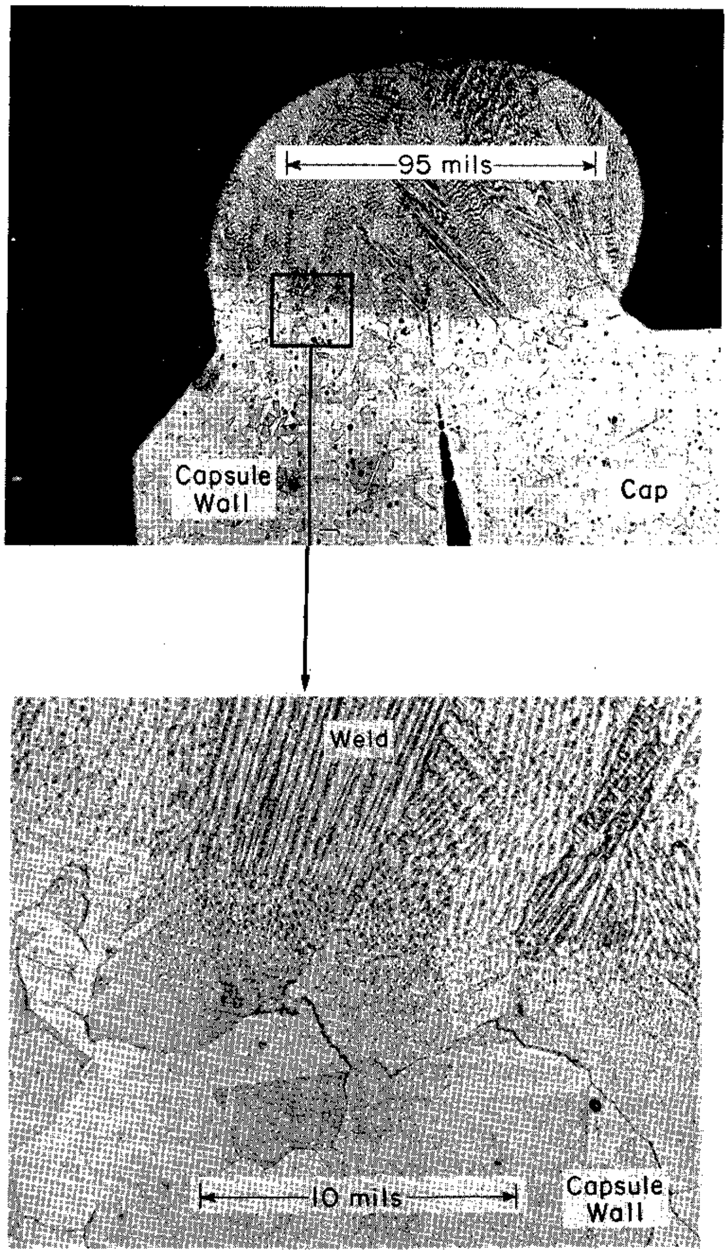

FIG 5 INTERGRANULAR CRACKS IN HEAT-AFFECTED ZONE OF "HAYNES" 25 WELD

Test capsules of "Haynes" 25 are being welded under various conditions to reduce the tendency to hot-short cracking in the heat-affected zone. The test conditions include press fit with minimum interference, comparison of argon with helium as the weld gas, and precautions to minimize chilling of the capsule.

A 3-inch-long "Inconel" 600 capsule containing about 40,000 curies (620 watts) of 280-curie/gram ^{60}Co was fabricated for a 10,000-hr test at ~850°C to begin next quarter.

Heating Tests of Capsules Containing Unirradiated Cobalt

In previous tests, several capsules remained sound and demonstrated acceptable oxidation resistance and compatibility during heating for either 1000 or 5000 hr at 850°C or for 1000 hr at 1000°C.[1,3]

Early in this quarter twenty additional capsules were placed in test, Table I. Capsules of TD Nickel are being heated in flowing argon at 850°C; capsules of "Inconel" 600, TD Nickel-Chromium, and "Haynes" 25 are being heated in still air at 1000°C. The 1000-hr tests have been completed and metallographic examinations are in progress.

Examinations of one capsule each of "Inconel" 600 and "Hastelloy" X, heated for 5000 hr at 1000°C, showed no measurable dimensional changes and no severe oxidation of the capsule or reaction of the capsule with the cobalt. The total depth affected by oxidation was 0.006 inch for the "Hastelloy" X capsule and 0.009 inch for the "Inconel" 600 capsule; these values are in general agreement with other 5000-hr data (see Table IV). The width of the reaction zone between cobalt and capsule wall ranged from 0.008 to 0.014 inch in both capsules.

Comparison of the widths of these reaction zones with earlier data from 1000-hr capsule tests and 168-hr diffusion-couple tests indicates that the parabolic growth law provides a conservative estimate for the extent of reaction expected at the end of capsule life (50,000 hr), Figure 6. The data for "Inconel" 600 follow this relationship very well. The data for "Hastelloy" X indicate a slightly slower reaction. In each of the tests the observed zones were slightly thinner than predicted from the results of the previous, shorter-term tests.

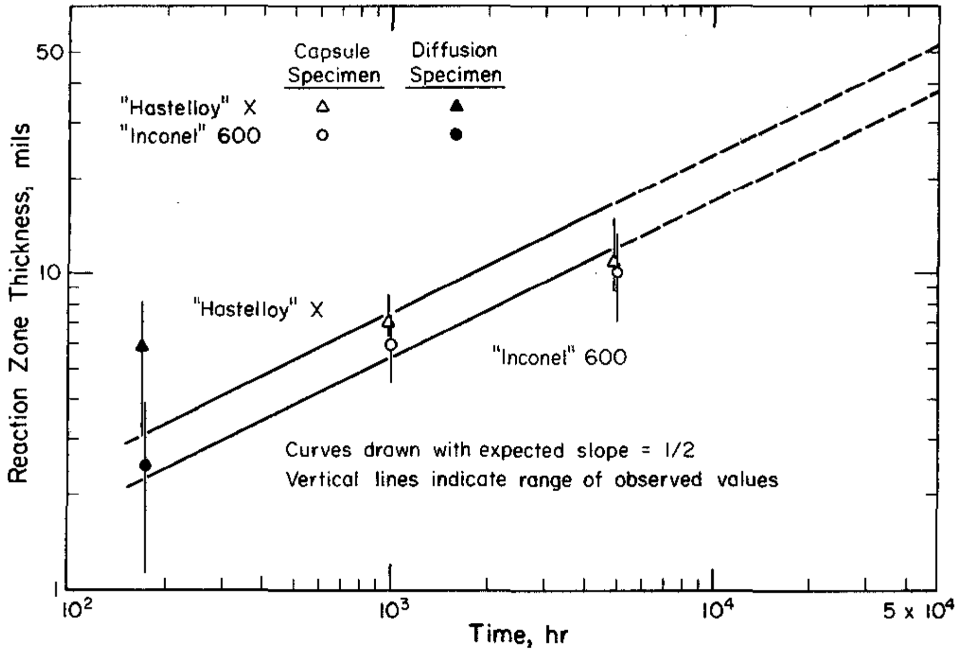

FIG. 6 GROWTH OF REACTION ZONES BETWEEN COBALT AND CAPSULE MATERIAL (1000°C)

Heating Tests of Capsules Containing Irradiated Cobalt

In previous tests, capsules of irradiated cobalt in "Hastelloy" C and "Inconel" 600 were sound after 100 hr at 850°C and showed no apparent effect of the ^{60}Co radiation.[3] Another "Inconel" 600 capsule remained stable during heating at ~850°C for 1000 hr, although slightly more oxidation and cobalt-capsule interaction were observed in this active capsule than in a companion inactive capsule.[4]

Recently, a 5000-hr test at ~850°C was completed on an "Inconel" 600 capsule containing 15,000 Ci of ^{60}Co (150 Ci/g). The surface appearance of the heated capsule was satisfactory, and no changes in dimensions were measurable (<0.001 inch); helium leak tests indicated no loss of integrity. Metallographic examinations are in progress.

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Previous Quarterly Progress Reports Issued Include:

DP-1088
DP-1094
DP-1105-I and -1105-II
DP-1120-I and -1120-II
DP-1129-I and -1129-II