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AEC RESEARCH AND DEVELOPMENT REPORT

SAVANNAH RIVER LABORATORY
ISOTOPIC POWER AND HEAT SOURCES

QUARTERLY PROGRESS REPORT

OCTOBER-DECEMBER 1968

PART I - COBALT-60

Savannah River Laboratory

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H. S. Hilborn, Compiler

February 1969

E. I. DU PONT DE NEMOURS & COMPANY
SAVANNAH RIVER LABORATORY
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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

Preliminary (theoretical) analyses indicate that CoO and CoO-MgO solid solutions are promising high temperature fuel forms of ^{60}Co. (p 1)

Extrapolation of stress-rupture data from the literature indicates that superalloy capsules will perform satisfactorily for 5 years at 1000°C or higher. "Haynes" 25 has the highest long-term strength of the materials tested. (p 10)

Satisfactory performance of an inactive "Inconel" 600 capsule at 1000°C for 10,000 hr (1.14 yr) was confirmed by destructive examination. (p 12)

More internal reaction than expected was revealed by destructive examination of two active capsules after 10,000 hr at 900°C. (p 13)

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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. A complete list of Savannah River Laboratory ^{60}Co publications is included at the end of this report.

MATERIALS TECHNOLOGY AND DEVELOPMENT

HIGH-TEMPERATURE FUEL CANDIDATES

Alloys and compounds of cobalt that have higher melting temperatures than cobalt metal are being explored for use in ^{60}Co heat sources, to provide increased safety and possible fuel forms for thermionic converters. An earlier examination of literature data indicated that cobalt oxide-magnesium oxide (CoO-MgO) solid solutions and cobalt-rhenium (Co-Re) alloys would have sufficiently high melting temperatures and power densities.(1) The mixed oxide could be fabricated before irradiation. The Co-Re alloys would have to be fabricated after irradiation because of the high cross-section of rhenium and its conversion to osmium, which forms a lower-melting alloy with cobalt.

High-Temperature ^{60}Co Oxide Fuel Forms

Preliminary evaluations of high-temperature ^{60}Co oxide fuel forms for increased safety in all applications and for possible thermionic applications indicate solid solutions of cobalt oxide in magnesium oxide (CoO-MgO) are promising. The CoO-MgO compositions as well as CoO may be compatible with rhenium or noble metal containers, though they will react with tantalum, tungsten, or molybdenum containers at high temperatures. Potentially deleterious oxidation to Co_3O_4 should not occur above about 600°C in air environments, and atmospheres of greater than 10^{-8} to 10^{-7} atm oxygen will prevent reduction to Co metal at 1500°C. The relatively high vapor pressures of CoO at high temperatures may result in significant redistribution in capsule temperature gradients.

Cobalt forms generally less stable oxides than more electropositive metals such as magnesium, aluminum, zirconium, or the rare earths. Combination of the cobalt oxides with a refractory oxide to produce a high melting point compound is therefore desirable. Properties of candidate oxide forms are listed in Table I, with the power density that 300 Ci/g ^{60}Co would provide.

TABLE I

CANDIDATE OXIDIZED COMPOUNDS OF ^{60}Co

Compound	Melting Temp, °C	Theoretical Density, g/cc	Power Density (300 Ci/g ^{60}Co) w/cc
CoO	1800	6.407	23.5
50% CoO-MgO (solid soln)	2250	5.024	12.0
$CoO \cdot Al_2O_3$	1960	4.41	6.9
$3CoO \cdot Y_2O_3$(a)	~2200	4.38	8.0
$CoO \cdot La_2O_3$(a)	>2050	~4	~6
$CoO \cdot Cr_2O_3$(a)	>1700	5.08	>6
$CoO \cdot ZrO_2$(a)	~2100	~5	~7.5

(a) Postulated existence and melting point by analogy to nickel and iron.

Besides CoO, only the solid solutions of CoO in MgO provide the required power density of about 10 w/cc needed for thermionic applications; the lower power density compounds may be suitable for other applications. Power densities of the CoO-MgO solid solutions for various specific activities of ^{60}Co are shown in Figure 1.

Because both oxides have a face-centered-cubic (fcc) lattice with nearly the same parameter, CoO and MgO are mutually and ideally soluble in all proportions. Melting points are shown as a function of composition in the phase diagram of Figure 2; for a composition of 50 mol % CoO-MgO a melting point (solidus) of 2250°C is obtained, significantly improved over that of the simple CoO (1800°C), as well as that of cobalt metal (1495°C).

Thermodynamic analysis of the potential for deleterious reaction of CoO and CoO-MgO solid solutions with candidate high-temperature capsule metals indicates that only rhenium and the noble metals (typically platinum, iridium, and rhodium) may be compatible with ^{60}Co oxide fuels. Other refractory capsule metals - tantalum, tungsten, and molybdenum - are expected to reduce the oxides to cobalt metal and ternary compounds. Calculated free energies of formation of CoO and of 50 mol % CoO in

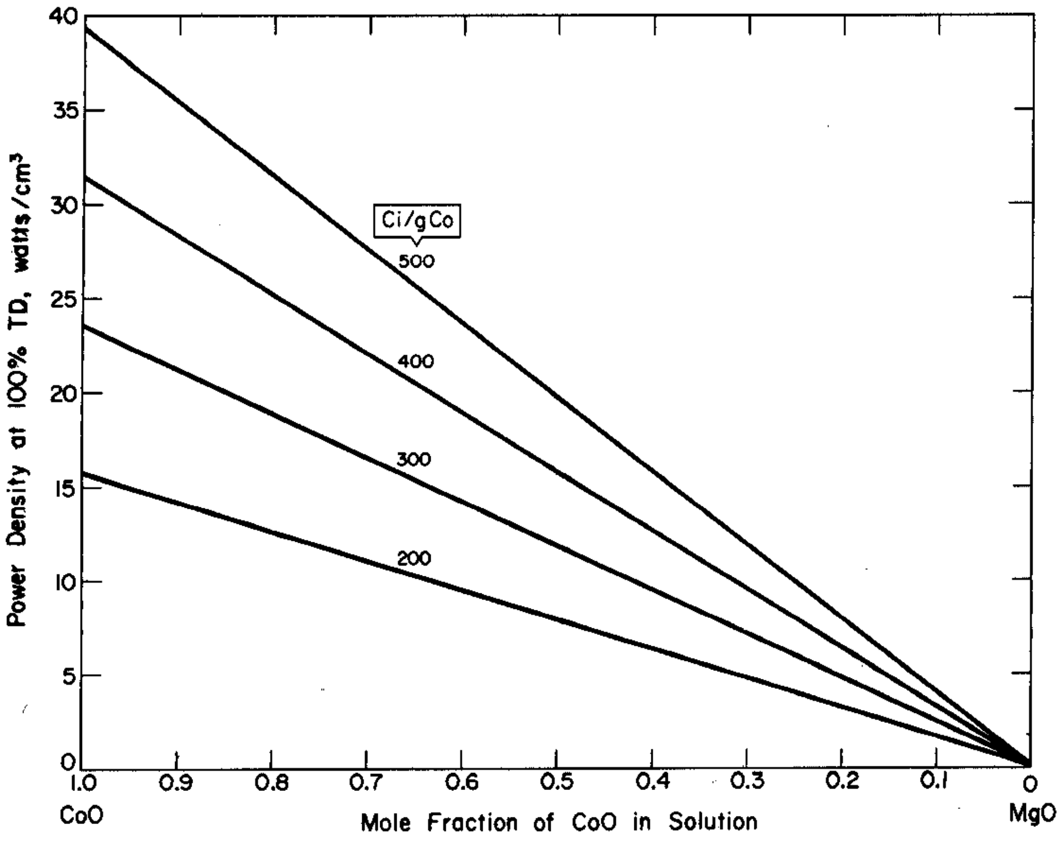
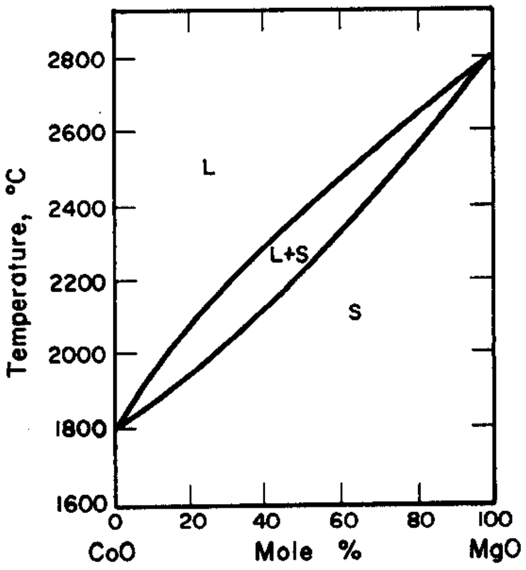


FIG. 1 POWER DENSITY OF CoO-MgO SOLID SOLUTIONS

FIG. 2
CoO-MgO PHASE DIAGRAM



MgO are compared with those for container metal oxides Ta_2O_5, WO_2, MoO_2 in Figure 3; reduction of CoO will occur in the corresponding metals, whose oxides have free energies of formation lower than CoO. The free energies of formation of the refractory metal oxides were taken from Schick(2) and for CoO from Aukrust and Muan.(3) Partial molar free energies of formation of CoO in MgO ($\Delta\bar{G}_f^o(ss)$) were calculated from

$$\Delta\bar{G}_f^o(ss) = \Delta G_f^o(CoO) + RT \ln N_{CoO} ,$$

where $$\Delta G_f^o(CoO) = 17.389T - 57200^{(3)} .$$

Rhenium oxide (Re_2O_7) and the noble metal oxides do not exist as condensed phases at these temperatures, indicating no potential for reaction of the corresponding metal with CoO.

Cobalt monoxide (CoO) is susceptible to oxidation in air to a higher oxide, Co_3O_4; this reaction might deleteriously affect the behavior of a CoO fuel form under accident conditions. Addition of MgO to the oxide is expected to lower the temperature below which the reaction takes place in air (from about 825°C to

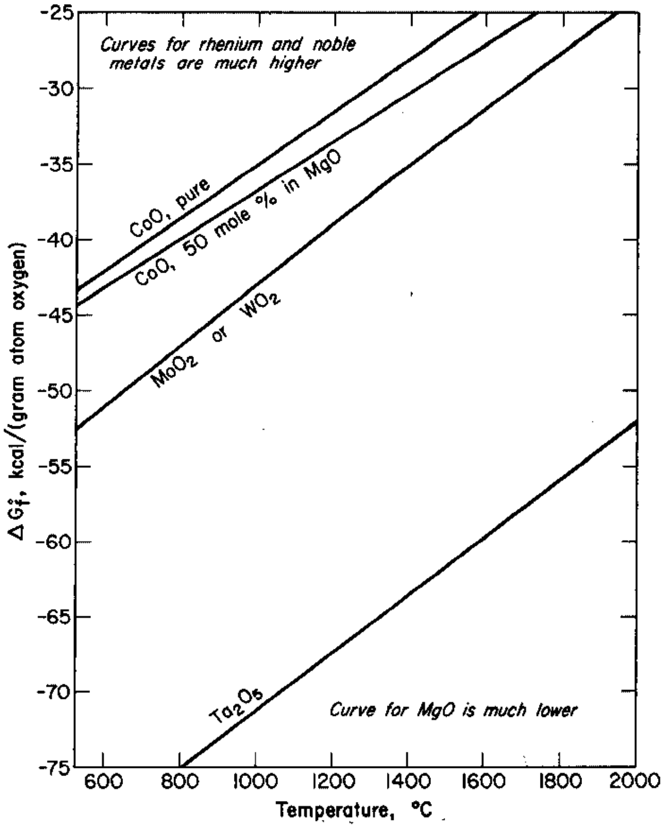


FIG. 3. FREE ENERGY OF FORMATION

about 600°C for 50 mol % CoO-MgO), as shown in Figure 4. This represents a potentially beneficial reduction of the range of instability of the oxide fuel form, since the rate of the oxidation at low temperatures may be relatively slow.

Partial pressures of oxygen (P_{O_2}) shown in Figure 4 for CoO-MgO solid solutions were calculated from

$$-RT \ln P_{O_2} = \Delta G^{\circ} + 6RT \ln N_{CoO} ,$$

where $\Delta G^{\circ} = -2.303\ RT[13,900 - 1.585 \times 10^4/T]$ for the reaction $2Co_3O_4(s) = 6CoO(s) + O_2(g)$, using the data of Aukrust and Muan.(4)

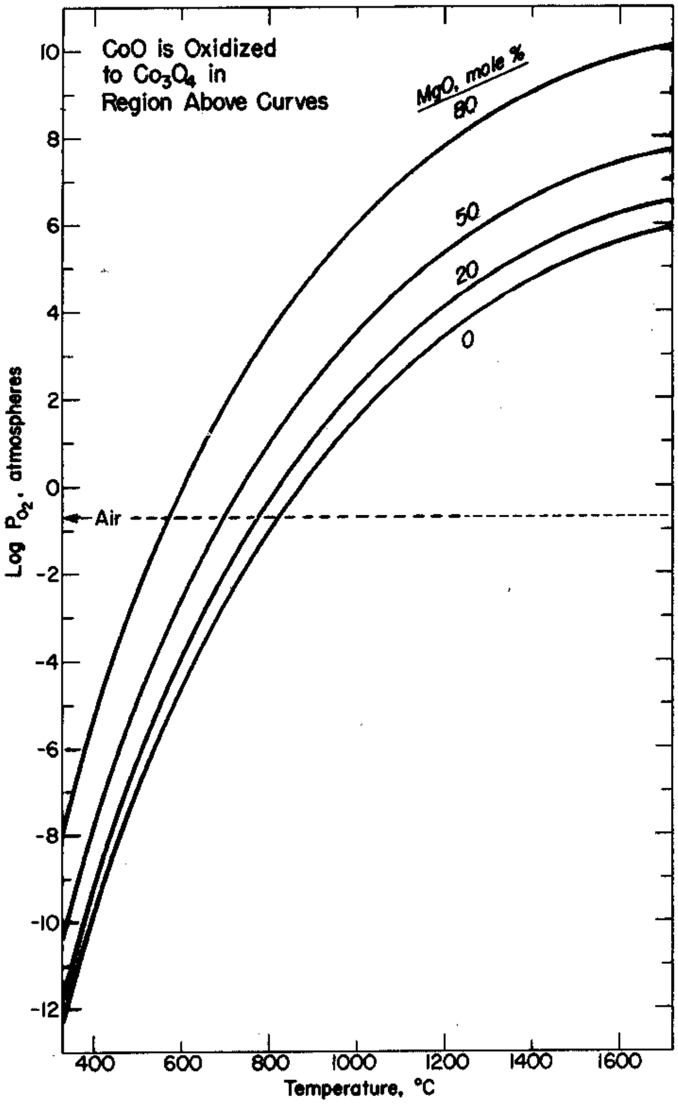


FIG. 4 MgO STABILIZES CoO

CoO and CoO in MgO solid solution are expected to vaporize to gaseous elements, cobalt and oxygen, rather than decompose to solid cobalt metal. Since CoO vaporizes about 10 to 50 times faster than does MgO, control of composition of CoO-MgO fuel forms during fabrication may be difficult and concentration of CoO at cooler regions in temperature gradients of a high-temperature heat source is expected. Total pressures over CoO and CoO-MgO solid solutions, as well as over cobalt metal, are compared in Table II with pressures over $^{244}Cm_2O_3$, a relatively stable high-temperature fuel material.

TABLE II

VAPOR PRESSURES OF HIGH TEMPERATURE FUELS

Material	Predominant Species	Total Pressure at 1500°C, atm	Total Pressure at 1000°C, atm
CoO	Co, O_2	$10^{-5.3}$	$10^{-10.3}$
50 mol % CoO-MgO	Co, O_2	$10^{-5.5}$	$10^{-10.5}$
Co	Co	$10^{-4.8}$	$10^{-9.4}$
Co/CoO	O_2	$10^{-6.3}(P_{O_2})$	$10^{-11.7}(P_{O_2})$
Cm_2O_3	CmO, O_2	10^{-9}	10^{-15}

The vapor pressure of CoO, 10^4 greater than Cm_2O_3, is only slightly lower than that over cobalt metal. However, because the oxygen partial pressure is greater than that over a cobalt metal-CoO mixture, significant decomposition of CoO (or CoO in MgO solid solution) to cobalt metal in a closed capsule is not expected. In a vacuum or inert gas environment with oxygen pressure less than 10^{-6} to 10^{-7} atm at 1500°C (such as a leaky capsule in space), decomposition of the CoO to cobalt metal would occur. Dilution of CoO in MgO solid solution does little to lower the cobalt vaporization rate.

A consequence of the relatively high vaporization rate of CoO, with or without MgO, is that relatively small temperature gradients (~25°C) may cause vapor-phase redistributions and composition gradients in CoO-MgO fuels, and produce preferential deposition of CoO at colder regions over long operating times at high temperature. Further evaluation of the effects of temperature gradients on composition and properties of the solid solution fuels will be made in future work, and the effect of the nickel decay product, whose oxide has a stability similar to CoO, on ^{60}Co oxide fuel will be assessed.

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 cobalt-capsule compatibility reactions,(5,6) diffusion of ^{60}Co,(6-10) and oxidation,(8,10,11) 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 years). Limiting operating conditions are defined by the time and temperature dependency of each of the reactions. Published data on mechanical properties (such as creep) have been evaluated, and will be confirmed if necessary by tests with pressurized capsules. The predicted behavior of the materials is being verified by 1000-, 5000-, 10,000-, and 50,000-hr (5.7-yr) heating tests of experimental capsules, Tables III and IV. Tests of companion capsules containing unirradiated or irradiated cobalt 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

Diffusion of ^{60}Co through prospective encapsulation materials is being measured to determine whether it will be a limiting factor in the design of heat sources. Earlier calculations showed that diffusion would not be a limiting factor for "Haynes"* 25, "Hastelloy"* C, or "Hastelloy"* X during operation for 5 yr (half-life of ^{60}Co = 5-1/4 yr) because the maximum specified concentration of 1 ppm ^{60}Co in the capsule material does not occur beyond 0.080 inch from the surface of the cobalt -- a typical capsule wall is 0.100-inch thick. Use of "Inconel"** 600 for 5 yr would be limited by diffusion at 1000°C, but not at 800°C, in situations where the capsule wall is exposed to a flowing coolant.(9)

All measurements of diffusion kinetics have been completed for times up to 100 hr at temperatures between 800 and 1200°C. Correlation of calculated diffusion coefficients with time, temperature, alloy composition, and grain size was deferred until next quarter due to emphasis on examination of ^{60}Co capsules (see below). Future experimental work will emphasize measurement of the ^{60}Co concentrations in capsule walls and special samples heated for 5000 hr or more at 850 to 1000°C.

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* Trademark of Union Carbide Corp.

** Trademark of International Nickel Co.

TABLE III

SUMMARY OF ^{59}Co CAPSULE HEATING TESTS

Capsule Material	Heating Time, hr	Heating Temp, °C	Wall, mils	No. of Capsules	Approx. Starting Date	Approx. Completion Date	Remarks
"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	Capsule intact
	→ 10,000	850	95	1	7-67	9-68	Capsule intact
	50,000	850	95	1	7-67	3-73	
	→ 1,000	900	95	1	11-68	12-68	Examination in progress
	→ 5,000	900	95	1	11-68	6-69	
	→ 10,000	900	95	1	11-68	1-70	
	→ 10,000	900	95	1	11-68	1-70	
	→ 50,000	900	95	1	11-68	7-74	
	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
	1,000(d)	1,000	95	1	2-68	4-68	No oxidation of Co or capsule
	→ 5,000(d)	1,000	95	1	2-68	9-68	No oxidation of Co or capsule
	5,000	1,000	95	1	8-67	2-68	Capsule intact
	→ 10,000	1,000	95	1	8-67	10-68	Capsule intact
	→ 50,000	1,000	95	1	10-67	6-73	
	→ 10,000(d)	1,000	95	1	11-68	1-70	
"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	Capsule intact
	→ 10,000	1,000	95	1	10-67	12-68	Examination in progress
	→ 10,000+	1,000	95	1	10-67	12-68+	
	10,000+	1,000	95	1	5-68	7-69+	
TD Nickel	1,000	850(c)	95	1	10-67	12-67	Capsule intact
	5,000	850	95	1	10-67	5-68	Capsule intact
	→ 10,000	850	95	1	10-67	12-68	Examination in progress
	→ 10,000+	850	95	1	10-67	12-68+	
	1,000	1,000	50	1	12-66	2-67	Capsule intact
	1,000(a)	1,000	95	2	10-67	12-67	No severe oxidation of Co
TD Nickel Chromium	1,000(a)	1,000	95	2	10-67	12-67	Co near pinhole oxidized
	1,000	1,000	95	1	10-67	12-67	Capsule intact
	5,000	1,000	95	1	10-67	5-68	Capsule intact
	→ 10,000	1,000	95	1	10-67	12-68	Examination in progress
	→ 10,000+	1,000	95	1	10-67	12-68+	
"Haynes" 25	10,000	850	95	1	11-68	1-70	
	1,000	1,000	95	1	10-67	12-67	Capsule intact
	5,000	1,000	95	1	10-67	5-68	Capsule intact
	→ 5,000	1,000	95	1	5-68	12-68	Examination in progress
	→ 10,000	1,000	95	1	10-67	12-68	Examination in progress
	→ 10,000+	1,000	95	1	10-67	12-68+	
	10,000+	1,000	95	1	5-68	7-69+	
"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
	→ 5,000	1,000	95	2	2-68	9-68	Capsules intact
	→ 10,000	1,000	95	1	2-68	4-69	
	→ 10,000+	1,000	95	1	2-68	4-69+	
	10,000+	1,000	95	2	5-68	7-69+	

(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) Internal atmosphere air instead of helium.

→ New information reported.

TABLE IV

SUMMARY OF ^{60}Co 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
"Inconel" 600	130	850(a)	50	1	120	16,000	2-67	2-67	Swelled due to overheating
	1,000	~900	50	1	100	5,000	4-67	6-67	Capsule intact
	5,000	~900	50	1	150(b)	15,000	4-67	10-67	Capsule intact
	10,000	~900	50	1	150(b)	15,000	4-67	6-68	Increased Co/capsule reaction
	→ 10,000	~900	50	1	150(b)	9,000	5-67	10-68	Increased Co/capsule reaction
	10,000	900	95	1	255(c)	36,500	2-68	8-69	
	$10,000^+$	900	95	1	288(c)	13,700	7-68	$8-69^+$	
	50,000	900	95	1	282(c)	13,400	7-68	3-74	
	5,000	1,000	95	1	295(c)	14,000	9-68	4-69	
	10,000	1,000	95	1	288(c)	13,700	9-68	11-69	
	$10,000^+$	1,000	95	1	263(c)	12,500	9-68	$11-69^+$	
	50,000	1,000	95	1	255(c)	12,100	9-68	5-74	
	10,000	850	95	1	(d)	-	9-68	11-69	
"Hastelloy" C	100	850	50	1	120	9,000	1-67	1-67	Capsule intact
	10,000	900	95	1	276(c)	13,100	7-68	8-69	
	10,000	1,000	95	1	282(c)	13,400	9-68	11-69	
	50,000	1,000	95	1	270(c)	12,800	9-68	5-74	
"Haynes" 25	5,000	1,000	95	1	263(c)	12,500	9-68	4-69	
	10,000	1,000	95	1	288(c)	13,700	9-68	11-69	
	$10,000^+$	1,000	95	1	282(c)	13,400	9-68	$11-69^+$	
	50,000	1,000	95	1	295(c)	14,000	9-68	5-74	
	10,000	850	95	1	(d)	-	9-68	11-69	
"Hastelloy" X	5,000	1,000	95	1	250(c)	11,900	9-68	4-69	
	10,000	1,000	95	1	263(c)	12,500	9-68	11-69	
	$10,000^+$	1,000	95	1	263(c)	12,500	9-68	$11-69^+$	
	50,000	1,000	95	1	301(c)	14,300	9-68	5-74	

(a) Excursion to >1100°C for 3-6 hr.
(b) Activity as of 2-67.
(c) Activity as of 6-68.
(d) Capsule contains ^{59}Co but is being heated along with ^{60}Co capsules.
→ New information reported.

Oxidation Resistance

Oxidation characteristics of two groups of encapsulating alloys have been defined at 1000°C for periods up to 10,000 hr.(8,10,11) The amount of oxidation observed in specimens of "Inconel" 600, "Hastelloy" C, "Hastelloy" X, "Haynes" 25, TD Nickel Chromium,* GE 2541,** and "Tophet"† C exposed to still air indicated that these alloys were sufficiently resistant to oxidation for use in air-cooled heat sources. The amount of oxidation was proportional to the square root of the exposure time. The temperature dependence of oxidation was found from 500-hr tests at 850 to 1150°C.

The acceptable oxidation behavior of "Inconel" 600, "Hastelloy" C, and "Hastelloy" X was also demonstrated in an accelerated test in still air at 1150°C for 3000 hr.(12) The observed oxidation was equivalent to that predicted for reference service conditions of a heat source capsule (50,000 hr at 1000°C). In the same test higher rates of oxidation than expected were observed over the entire surface of a "Haynes" 25 specimen and in a localized area of a TD Nickel Chromium specimen.

No additional measurements of oxidation resistance are planned for candidate superalloys. A topical report summarizing the above results is being written. In the future, any long-term oxidation data that become available from capsule heating tests will be reported under Capsule Fabrication and Testing.

Mechanical Properties of Capsule Materials

Long-term stress-rupture data are necessary to compare superalloy capsule life expectancies in the anticipated operating temperature range of 850-1000°C. Since data to 50,000 hr (the desired ^{60}Co heat source lifetime) are not available, literature data were extrapolated using the Manson-Haford time/temperature parameter, Figure 5. This extrapolation method is discussed in References 13 and 14. The superalloys investigated included "Haynes" 25, "Inconel" 600, "Hastelloy" C, and "Hastelloy" X.

For a rupture life of 10^4-10^5 hours, "Haynes" 25 can sustain the highest stress throughout the temperature range under consideration. Constant capsule wall thicknesses for 0.750-inch-ID capsules required to prevent rupture in 50,000 hr, with a pressure of 60 psi across the capsule wall, are given in Figure 6 as a function of operating temperature.

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* Product of Fansteel Metallurgical Corp.

** Product of General Electric Co.

† Trademark of W. B. Driver Co.

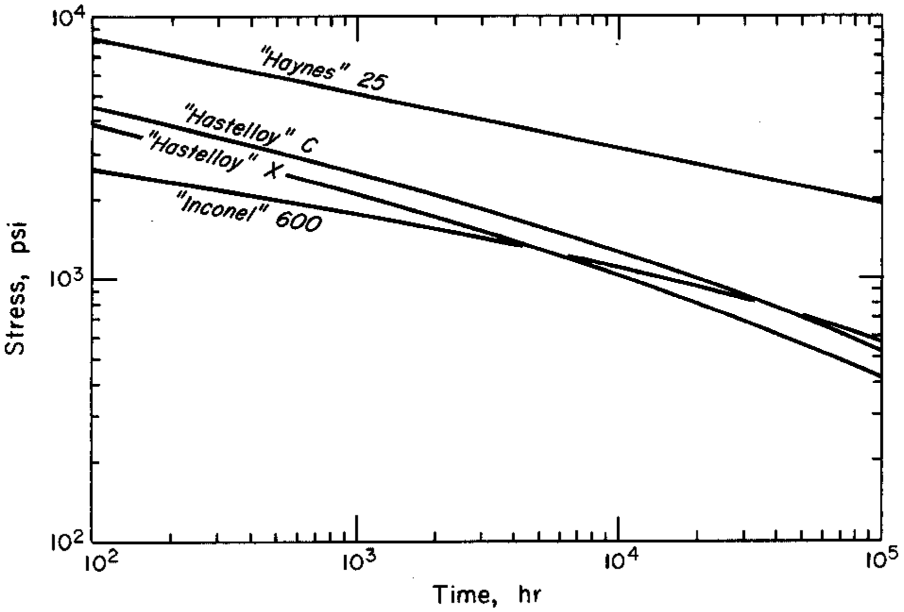


FIG. 5 EXTRAPOLATED STRESS VS. TIME TO RUPTURE
T = 1800°C (~982°C)

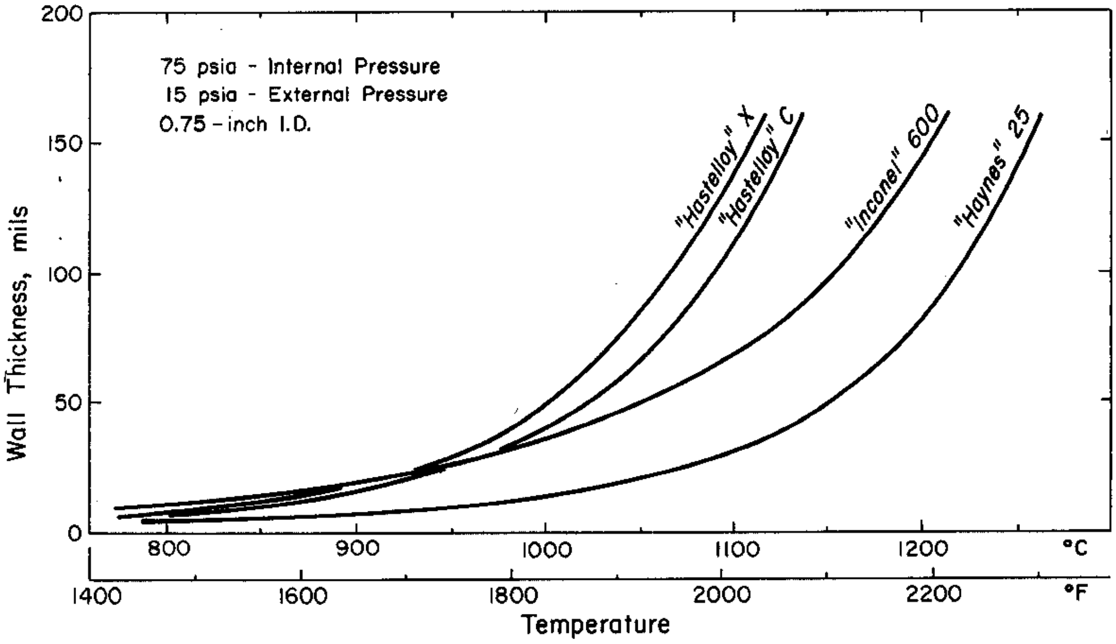


FIG. 6 CONSTANT WALL THICKNESS FOR STRESS-RUPTURE
@ 50,000 hr (5.7 yr)

In an actual capsule, effective wall thickness will decrease and stress will increase with time if there is significant oxidation and/or void formation by cobalt diffusion. Thus the initial capsule wall thickness would be higher than those shown in Figure 6, but the final sound wall thickness could be lower. In certain applications the temperature decay of the capsule may compensate for wall thickness reduction, because of the increase in rupture stress and the decrease in oxidation and diffusion rates with decreasing temperature.

Although "Hastelloy" C appears to perform somewhat better than "Hastelloy" X, the certainty of the "Hastelloy" C extrapolation is in doubt due to a lack of data at temperatures above 1600°F (871°C).

CAPSULE FABRICATION AND TESTING

Heating Tests of Capsules Containing Unirradiated Cobalt

Heating tests are continuing on 18 capsules containing unirradiated cobalt to demonstrate structural integrity for 10,000 hr or more at typical heat source conditions (850 to 1000°C), Table III. During the quarter, six new "Inconel" 600 capsules were placed in test at 900 and 1000°C, and one new "Haynes" 25 capsule was placed in test at 850°C; the heating conditions of these capsules duplicate those of capsules containing irradiated cobalt.

Also during the quarter, a total of eleven capsules reached their goal exposures and were removed from test for examination. This examination was completed on five of the capsules, as described below. Examination is in progress on the remaining six capsules, which include one "Inconel" 600 capsule heated 1000 hr at 900°C, one "Haynes" 25 capsule heated 5000 hr at 1000°C, and one capsule each of "Haynes" 25, "Hastelloy" C, TD Nickel, and TD Nickel Chromium heated 10,000 hr at 1000°C. An additional capsule of each of the four latter alloys achieved 10,000 hr exposure at 1000°C. If the examinations of their companion capsules reveal satisfactory performance, the exposures will be extended to 20,000 hr or more.

Satisfactory performance for 10,000 hr was demonstrated with two "Inconel" 600 capsules, one at 850°C and the other at 1000°C. Similar performance was demonstrated for 5000 hr at 1000°C with two "Hastelloy" X capsules. The integrity of each capsule was maintained and there were no significant dimensional changes. The depths affected by the reaction at the cobalt-capsule interface and the oxidation of the exterior capsule surfaces were in agreement with previous shorter-term capsule and screening tests.

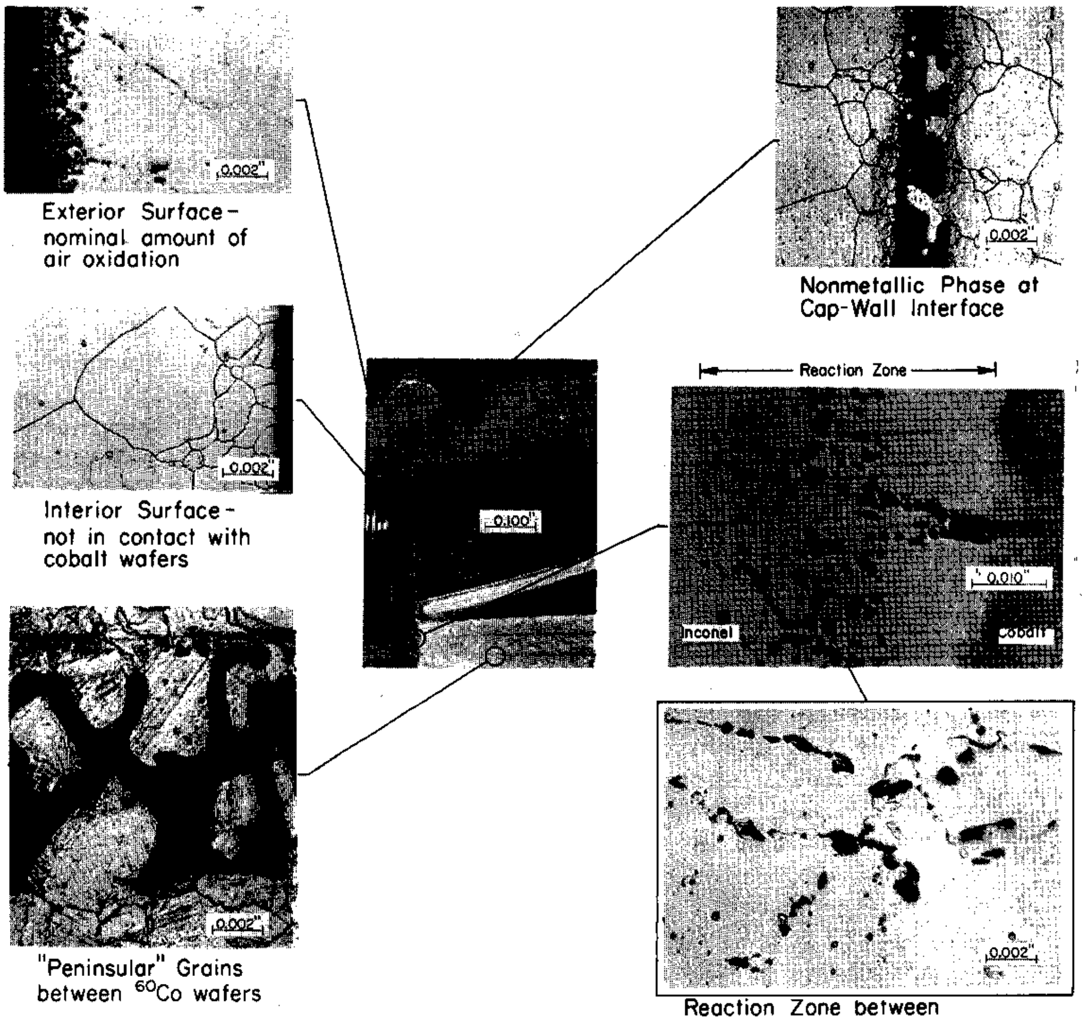
No detrimental effects of an air atmosphere inside an "Inconel" 600 capsule were observed after heating for 5000 hr at 1000°C. No oxide scale was observed on either the cobalt wafers or the inside surfaces of the capsule at the void space. The extent of reaction at the cobalt-capsule interface and the oxidation of the exterior capsule surface were in accord with previous results on other "Inconel" 600 capsules heated at 1000°C.

Heating Tests of Capsules Containing Irradiated Cobalt

Twenty superalloy capsules, 18 containing irradiated and 2 containing unirradiated cobalt metal, are being heated in air at 900 to 1000°C in the High Level Caves (HLC), Table IV. The superalloys include "Inconel" 600, "Hastelloy" C, "Haynes" 25, and "Hastelloy" X. During the quarter, one "Inconel" 600 capsule reached its goal exposure of 10,000 hr at 900°C. Examination was completed on this capsule and another "Inconel" 600 capsule that was heated under the same conditions and removed from test in June.(10) The examination revealed more than twice the expected thickness of reaction at the interior cobalt-capsule interface. External effects were normal: oxidation of the "Inconel" 600 was proportional to the square root of the exposure time extrapolated from all previous tests, and dimensional changes were less than 0.002 inch.

The two capsules have similar histories. The cobalt wafers were initially encapsulated together in one capsule that had a defective weld, and were subsequently re-encapsulated separately in the two capsules that were heated for 10,000 hr. The increased reaction between cobalt and "Inconel" is attributed tentatively to foreign material -- either a surface film or an impurity in the cobalt.

The thickness of the cobalt-"Inconel" reaction zone within the two capsules averaged 0.030 inch after 10,000 hr at 900°C in contrast to the 0.013 inch expected from previous 1000- and 5000-hr tests. The deepest portion of the reaction zone in the "Inconel" comprised a gray, nonmetallic phase in the "Inconel" grain boundaries, illustrated in Figure 7 for the 15,000-Ci capsule. Portions of the reaction zone closer to the cobalt wafers contained principally Kirkendall voids and a solid solution, both of which are typical of cobalt-"Inconel" reaction; little of the nonmetallic phase was evident. The nonmetallic, grain-boundary phase was present in the capsule wall and spacers, but was not seen in the "Inconel" 600 surfaces of the void space at the top of the capsule.



Exterior Surface - nominal amount of air oxidation

Interior Surface - not in contact with cobalt wafers

"Peninsular" Grains between ^{60}Co wafers

Nonmetallic Phase at Cap-Wall Interface

Reaction Zone between "Inconel" 600 and Cobalt wafers.

FIG. 7 MICROSTRUCTURE OF "INCONEL" 600 CAPSULE
Containing 15,000 Ci of ^{60}Co after 10,000 hr at 900°C

A gray, nonmetallic phase of unknown origin was also found in the 15,000-Ci capsule as a surface scale in one region of the interface between the cap and the capsule just below the weld zone, Figure 7; whether this is the same material as the intergranular phase is not known.

"Peninsular" single crystals of cobalt protruded from the surface of some cobalt wafers into gaps between adjoining wafers, Figure 7. The top cobalt wafer of the 15,000-Ci capsule bonded to the capsule wall in a tilted position and grew peninsular grains only on its bottom surface; its upper surface was presumably in contact with the top "Inconel" spacer, which fell out when the capsule was cut. Single-grain deposits, but not the increased cobalt-capsule reaction, were also observed in an "Inconel" 600 capsule containing 15,000 Ci of ^{60}Co that was heated for 5000 hr at ~900°C. Therefore these two reactions are probably not related.

The oxidation of the exterior capsule surface, Figure 7, was the same as that seen in previous capsule and screening tests. The total affected depth averaged 0.0055 inch, in accord with a $(\text{time})^{\frac{1}{2}}$ extrapolation of previous results.

Because of the similarities in wafer histories the internal attack on the capsule walls was most probably caused by foreign material, either a surface film on the cobalt wafers or an impurity in the cobalt, rather than variance in test conditions such as temperature. For example, previous data indicate that 10,000 hr at 1150°C would be required to produce the observed thickness of cobalt-"Inconel" reaction zone; under these conditions, the surface oxide on the "Inconel" capsule would have been ~0.065-inch thick rather than the observed 0.0055 inch. Similarly, the attack was not caused by general contamination of the helium fill gas; such contamination would have affected the interior surfaces bounding the void space -- no attack of these surfaces was found.

In all ^{60}Co capsules, a thermal gradient exists between the surface and center of the capsule because of the self-absorption of the radiation. Reactions that depend on this thermal gradient could explain the increased reaction between cobalt and capsule and the deposition of the single grains between cobalt wafers, but these reactions have a low probability because of the smallness of the thermal gradient. For example, the gradient could assist diffusion of oxygen from the surrounding atmosphere into the capsule wall where it would react with the iron and chromium constituents of the "Inconel" to form the gray phase characteristic of the increased reaction zone. Also, the single-grain deposits could result from the formation of nickel or cobalt carbonyl and its subsequent decomposition in the thermal gradient.

Two sets of capsules containing ^{59}Co will be fabricated and heated in an attempt to duplicate reactions observed in the ^{60}Co capsules. In one set the wafers will be intentionally contaminated with potential sources of foreign materials, such as the NaOH used to recover the wafers from the aluminum target slugs. In the other set, the capsules will be heated in a thermal gradient.

Failure of Thermocouples Attached to ^{60}Co Capsules at 1000°C

Thermocouples spot welded to four capsules containing ^{60}Co failed after 240 to 840 hr of operation at a capsule temperature of 1000°C. However, these thermocouples performed long enough at equilibrium temperature to permit setting the temperature controllers and correlating the furnace atmosphere temperatures with the indicated capsule surface temperatures.

Six capsules containing ^{60}Co had 0.040-inch sheathed thermocouples spot welded to the outer surface to measure the surface temperature. One instrumented capsule is included in each of two 900°C furnaces and a small 1000°C furnace; the other three instrumented capsules are in a large 1000°C furnace. The thermocouples on the capsules at 900°C are operating satisfactorily. The 1000°C furnaces have not been opened to allow observation of the failed thermocouples; therefore, the physical appearance of the thermocouples is unknown. The failures probably occurred because of oxidation through the "Inconel" sheaths leading to oxidation of the chromel and alumel wires inside the sheath. The sheaths (wall thickness of 0.006 inch prior to welding) were slightly pitted at each spot weld by the discharge from the welder electrodes. The nominal diameters of the chromel and alumel wires are 0.005 inch.

As the ^{60}Co decays and as capsules are removed from test, the internal heat generation in the remaining capsules will decrease, and power input to the furnaces must be increased to maintain the desired capsule temperatures. Replacement thermocouples will be attached to selected capsules, probably at inspection intervals of 5000 hr, to allow resetting the temperature controllers. The capsule surface temperature decrease during a 5000-hr period of ^{60}Co decay is small.

SAVANNAH RIVER LABORATORY ^{60}Co PUBLICATIONS

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DP-1094	October - December 1966
DP-1105-I	January - March 1967, Part I - Cobalt
DP-1120-I	April - June 1967, Part I - Cobalt
DP-1129-I	July - September 1967, Part I - Cobalt
DP-1143-I	October - December 1967, Part I - Cobalt
DP-1155-I	January - March 1968, Part I - Cobalt
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