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DP-1094

AEC RESEARCH AND DEVELOPMENT REPORT

SAVANNAH RIVER LABORATORY
ISOTOPIC POWER AND HEAT SOURCES

QUARTERLY PROGRESS REPORT
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SAVANNAH RIVER LABORATORY
ISOTOPIC POWER AND HEAT SOURCES

H. S. Hilborn, Compiler

January 1967

E. I. DU PONT DE NEMOURS & COMPANY
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PREFACE

This report is the second 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 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 present report contains principally data from work in October, November, and December 1966. The first report, DP-1088, presented some background data and reported the data from work in July, August, and September 1966.

Isotopic fuel data sheets on cobalt are included as an appendix to this report, and serve to update DP-1051, Revision 1, "Properties of ^{60}Co and Cobalt Metal Fuel Forms" by W. C. Windley, Jr.

SUMMARY

Cobalt-60

Of the candidate capsule materials tested, "Inconel" 600 and TD Nickel are most compatible with cobalt metal, based on 168-hour tests at 800, 1000, and 1200°C. TD Nickel Chromium has outstanding oxidation resistance, based on 1000-hour tests in air at 1000°C.

Capsules of "Inconel" 600 and "Hastelloy" C containing radioactive cobalt were heated for 100 hours in air at 850°C with no significant changes in appearance or dimensions.

^{60}Co heat sources were shown to require lighter shields than $^{90}SrTiO_3$ heat sources at powers above about 2 kwt.

Curium-244

Reaction of CmO_2 with H_2S in the presence of CS_2 was used to synthesize Cm_2S_3. The sulfides (notably CmS) are potential high melting fuel compounds of ^{244}Cm.

In analogy with the rare earth sesquioxides, Cm_2O_3 exists with increasing temperature in three crystallographic forms: (1) body-centered-cubic C-type, (2) monoclinic B-type, and (3) hexagonal A-type. The B-type Cm_2O_3, can be retained on cooling and resists self-radiation-induced transformation at low temperatures. It thus appears to be the best candidate curium oxide for heat sources. The decomposition of CmO_2 to Cm_2O_3 during heating proceeds through at least one intermediate composition with a fcc cubic structure closely related to the parent CmO_2 structure.

Relatively high losses of Cm_2O_3 due to vaporization through a small hole have been observed during measurements of the vapor pressure of the oxide using the Knudsen technique.

A cermet compact of Cm_2O_3 with tungsten, fabricated by cold pressing and sintering at 1850°C, showed no evidence of deleterious interaction between the oxide and metal particles.

A shipping container for transport of curium oxide in 120 g batches was designed.

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DISCUSSION

COBALT-60

Objectives of the Savannah River Laboratory (SRL) program on ^{60}Co are to develop and establish allowable operating limits for:

- Capsules containing radioactive cobalt metal in an oxidation resistant cladding by the end of FY-1968, and
- Capsules containing a higher temperature fuel form of ^{60}Co in a refractory metal cladding by the end of FY-1970.

The program is a limited one to meet needs of general applicability to heat source designers and users. Development and evaluation of specific concepts are not at present included in the scope of the SRL program.

PRODUCTION OF ^{60}Co FOR HEAT SOURCE DEVELOPMENT

Production of high-activity cobalt for experimental programs and possible heat source demonstrations was continued. As of December 30, about 6 million curies of ^{60}Co, averaging 260 curies per gram of metal, had been produced. Irradiation will continue until about 8 MCi (125 kw), at an average of 350 Ci/g (48 watts/cm^3), have been produced. This will include 6 MCi as 0.745-inch-diameter by 0.040-inch-thick wafers plated with 0.0005 to 0.001 inch of nickel, and 2 MCi as 0.80-inch-diameter wafers and 3-inch-long slabs of various types (nickel-plated, stainless-steel-clad, stainless-steel-bonded).

MATERIALS TECHNOLOGY AND DEVELOPMENT

Properties of Irradiated Cobalt Metal

Changes in dimensions, density, hardness, and microstructure of irradiated cobalt metal are being measured to define the effects of irradiation and radioactive decay.

Other properties will be investigated as required for particular applications.

Specimens of five levels of specific activity have been examined. Measured densities and hardnesses are shown in Table I. These variations from nominal preirradiation values, including the expected increase in hardness, should be negligible in terms of heat source design and operation. No changes in dimensions could be measured. The microstructures were also unaffected, as reported earlier.(1)

TABLE I

Effect of Irradiation and Decay on Density and Hardness of Cobalt

Specific Activity, Ci/g	Composition,(a) % ^{59}Co	^{60}Co	Ni	Density,(b) g/cc	Hardness,(c) Rockwell D Scale
0	100	-	-	8.85	14.7
6	100	-	-		36.5
93	91	8	1	8.85	36.2
100-50(d)	91	4	5	8.72	44.8
300-140(d)	65	13	22	8.77	49.0
700	27	62	11	8.93	42.9

(a) Composition given is that at the time of the examination.
(b) Averages of at least three measurements; ranges were ±0.5%.
(c) Averages of at least five measurements; ranges were ±5%.
(d) First number is initial specific activity and second is activity at the time of the examination.

High-Temperature Fuel Candidates

Alloys and compounds of cobalt that have higher melting temperatures than cobalt metal are being explored for use in high-temperature ^{60}Co heat sources. Cobalt-rhenium (Co-Re) alloys have sufficiently high melting temperatures but would have to be fabricated after irradiation to prevent conversion of the rhenium to osmium and the concurrent formation of a lower-melting alloy.(1) Methods are being developed to obtain Co-Re alloys that can be fabricated from radioactive cobalt, and alternative forms of cobalt are being developed that can be fabricated before irradiation.

Fabrication of Cobalt-Rhenium Alloys

Co-Re alloys formed by sintering cold-pressed compacts have been porous. More complete consolidation by cold-hearth arc-melting of the compacts yielded nonequilibrium alloy structures. Additional attempts to fabricate sound alloys by these techniques have been deferred.

Alternative High-Temperature Forms of Cobalt

Ceramic bodies of cobalt oxide (CoO) or a mixture of cobalt and magnesium oxides (MgO) can be fabricated before irradiation. The solid solutions of the CoO-MgO system have the desired high melting temperatures though at some sacrifice of power density. CoO also melts in the desired temperature range but presents a compatibility problem with encapsulating materials.

The CoO-MgO system has complete solid solubility. As the concentration of MgO is increased the melting temperature increases from 1745 to 2800°C, but the power density decreases. A CoO-MgO alloy with a power density of 12 w/cc with 300 Ci/g ^{60}Co has a melting temperature of 2150°C compared to 2300°C for a Co-Re alloy of the same power density. The solid solutions might be compatible with refractory-metal containers because MgO is one of the most stable oxides. CoO-MgO ceramics will be investigated further.

The melting temperature of CoO is reported to be 1745°C.(2) The power density of the oxide (24 w/cc for 300 Ci/g ^{60}Co) is similar to the 25 w/cc density of the Co-Re alloy of the same melting temperature. The oxide is probably incompatible with refractory metal capsules since the calculated free-energy change for the oxidation of the refractory metals is more negative than that for the oxidation of cobalt. Therefore, the refractory metal would reduce the oxide and liquid cobalt would be formed above 1495°C. Consequently, use of CoO in high-temperature heat sources would have little advantage over use of cobalt metal.

Evaluation of Capsule Materials

Selection of suitable materials and definition of their limiting operating conditions requires the assessment of the compatibility between cobalt and cladding. Necessary data include knowledge of rates of diffusion of ^{60}Co through the cladding, rates of oxidation of the cladding, and effects of these reactions on the mechanical properties of the materials. Direct measurements of these characteristics are supplemented by demonstration tests in which capsules fabricated from the most promising materials and containing unirradiated cobalt (^{59}Co) are annealed for longer than 1000 hr. Effects of the radiation field are being measured in a smaller number of companion tests on identical capsules containing ^{60}Co.

Compatibility

Preliminary evaluations of compatibility have been made by annealing multilayered diffusion couples of cobalt and various nickel- and cobalt-based heat resistant alloys for 168 hr at 800, 1000, and 1200°C.(1) Metallographic examinations and electron microprobe analyses showed that the resultant diffusion zones are regions of solid solution terminating in a band of voids. Of the materials tested, the rate of growth of this diffusion zone was lowest in "Inconel"* 600, and TD Nickel**, followed by TD Nickel Chromium**, "Hastelloy"*** C, and "Haynes"*** 25.

Diffusion of ^{60}Co

The rate of diffusion of ^{60}Co through various cladding materials is being measured by standard radioactive tracer techniques.(1) Preliminary results obtained with "Inconel" 600, "Hastelloy" C, and "Incoloy"* 825 indicate that the rate of diffusion along the grain boundaries and the rate of diffusion through the volume of the grains varied with alloy content. These tests are continuing and will be interpreted in terms of the amount of ^{60}Co that could be present near the surface of a capsule after operation for various lengths of time.

Rate of Oxidation

The oxidation resistance of numerous nickel- and cobalt-based heat-resistant alloys is being measured by exposing test coupons

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* International Nickel Co., Inc., New York, N. Y.

** E. I. du Pont de Nemours & Co., Wilmington, Del.

*** Union Carbide Corp., New York, N. Y.

to still air at 1000°C for times up to 10,000 hr.(1) Examinations after 1000 hr showed that TD Nickel Chromium had outstanding resistance to oxidation and that "Inconel" 600, "Hastelloy" C, and "Hastelloy" X were satisfactory confirming predictions based on literature values. Companion specimens are being tested to total exposures of 5000 and 10,000 hr.

Capsule Fabrication and Testing

Welding of Thoria-Strengthened Alloys

Although TD Nickel and TD Nickel Chromium are prime candidates for encapsulating radioactive cobalt, they are difficult to weld without causing segregation of the thoria dispersion, and are normally joined by brazing. The degree of segregation in welds made by various techniques is currently being evaluated.

Examination of TIG welds of TD Nickel and TD Nickel Chromium showed that thoria segregation occurred in the weld metal. Pockets of thoria-free metal and thoria-free "stringers" were present, predominantly along the original interface between the components. The reduced strength of these stringers may not be detrimental to this particular application because of the low level of stress expected in a capsule.

Electron-beam welded sections, which should have little or no segregation because of the shorter fusion time and increased agitation of the molten metal pool, will be evaluated in future tests.

Heating Tests of Inactive Capsules

Reliability and durability of prototype capsules are being evaluated by heating for 1000 hr at 1000°C in still air. The first test demonstrated that "Inconel" 600 and "Hastelloy" C were compatible with the unirradiated nickel-plated cobalt wafers and were reasonably resistant to oxidation; "Incoloy" 825 had inadequate resistance to oxidation.(1)

The second and third tests have been completed. In the second test, the three capsule materials oxidized extensively, probably as a result of reaction with the firebrick that supported the capsules during the heating. A third test with capsules of "Inconel" 600 and "Hastelloy" C confirmed that these materials were compatible with the cobalt and that "Inconel" 600 was more resistant to oxidation than "Hastelloy" C. The degree of oxidation for both materials was greater than in the first test due to thermal cycling caused by furnace failures during the 1000-hr exposure period. None of the cobalt wafers could be removed from either of the capsules after the tests because the wafers bonded to each other and to the capsules.

Similar tests of other encapsulating materials, such as TD Nickel, TD Nickel Chromium, and "Hastelloy" X, will be completed next quarter. Additional tests of "Inconel" 600 capsules at 850°C for times up to 10,000 hr are in progress; these capsules will be compared with companions filled with radioactive cobalt and annealed under identical conditions.

Heating of ^{60}Co Capsules

Prototype capsules filled with radioactive cobalt are being heated to demonstrate the reliability of the remote encapsulation procedures and to measure the effects of the radiation on oxidation and compatibility. Annealing conditions range between 850 and 1000°C for 1000 to 10,000 hr.

Two capsules, one of "Hastelloy" C containing 9000 Ci and one of "Inconel" 600 containing 16,000 Ci, have been annealed for 100 hr at 850°C in still air. Helium leak tests before and after the anneal showed that the integrity of the capsules was maintained. No significant changes occurred in the appearance of the capsules. Metallographic examination for oxidation and interdiffusion is in progress.

Heat Source Design

Shield Weight for Practical ^{60}Co Heat Sources

To assess the effects of engineering realities such as fuel encapsulation on heat source shield weights, ^{60}Co and ^{90}Sr sources of 1 to 20 thermal kilowatts were compared. The diameter of a spherical $^{90}SrTiO_3$ source is about 3-1/2 times the diameter of a 300 Ci/g ^{60}Co source of equal power. Because the inner diameter is much smaller, uranium shielding for ^{60}Co weighs less than for $^{90}SrTiO_3$ at powers above $\sim$2 kwt. Biological shielding weighs less for ^{60}Co than for ^{90}Sr at initial powers above about 2 kwt for a concentric sphere configuration with uranium shielding, Figure 1. ^{60}Co is even more favorable for large heat sources consisting of cylindrical arrays of encapsulated fuel with tungsten shielding, Figure 2, although shield weights for practical heat sources are at least 40% heavier than for spherical sources. Tungsten shielding for an initial heat source power of 20 kwt weighs about 2000 lb for ^{60}Co and about 4000 lbs for ^{90}Sr (as $SrTiO_3$).

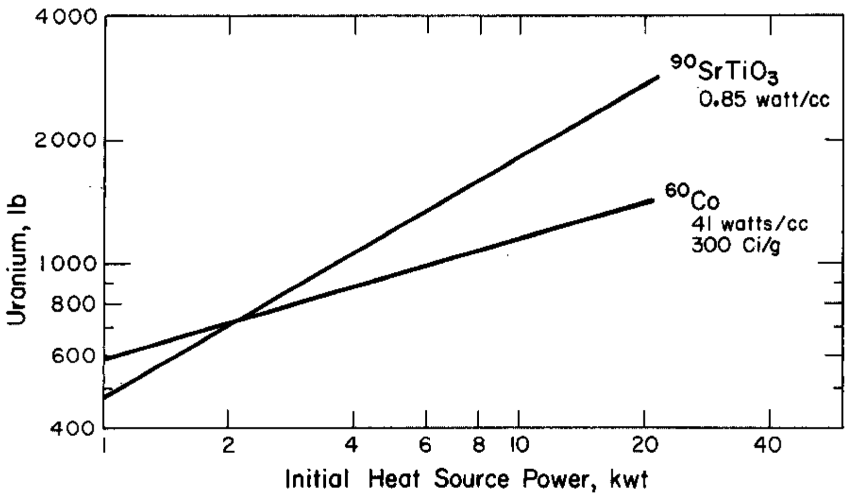


FIG. 1 URANIUM SHIELD WEIGHT REQUIRED TO REDUCE RADIATION FROM SPHERICAL SOURCES OF ^{90}Sr AND ^{60}Co TO 10 mr/hr AT 1 METER FROM CENTER OF SOURCE

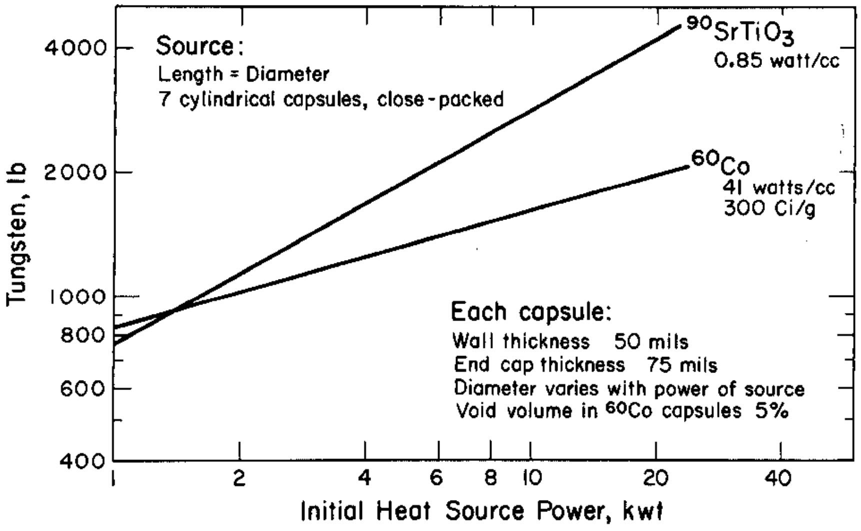


FIG. 2 TUNGSTEN SHIELD WEIGHT REQUIRED TO REDUCE RADIATION FROM ARRAYS OF ^{90}Sr AND ^{60}Co CAPSULES TO 10 mr/hr AT 1 METER FROM CENTER OF SOURCE

Figure 2 compares the weight of tungsten shields for a heat source consisting of a 7-capsule close-packed array, each capsule having a 0.050-inch-thick wall and 0.075-inch-thick end caps. L/D of the capsule array is 1. Capsule diameters vary with power over the reasonable ranges of 0.6 to 1.1 inches for ^{60}Co and 1.8 to 3.7 inches for ^{90}Sr from 1 to 10 kw. If capsules must be spaced apart instead of close-packed, e.g. to allow for gas coolants, total shield weight increases and the advantage of ^{60}Co is even more pronounced. Figure 2 is based on initial heat source power. A comparison based on average or end-of-life power would be only slightly less favorable for ^{60}Co. For equal powers after one half-life of ^{60}Co the power level at which the ^{90}Sr and ^{60}Co shield weights are equal is increased to about 2-1/2 kwt for practical heat sources.

REFERENCES

1. H. S. Hilborn (compiler), Savannah River Laboratory Isotopic Power and Heat Sources, Quarterly Progress Report, July-September 1966, USAEC Report DP-1088, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, S. C. (Confidential).

2. D. P. Masse and A. Muan, "Phase Relations in the System CoO-SiO_2", Trans. AIME, 233, 1448 (1965).

CURIUM-244

Approximately 4.5 kg of ^{244}Cm is now being produced in the Savannah River Reactors to provide material for the development of ^{244}Cm heat sources. ^{244}Cm, which decays with a half-life 18.1 years principally by the emission of alpha particles, generates 2.65 watts/g in pure form. The isotopes can thus be utilized in applications requiring high power-to-weight ratios, with operating temperatures in the 1500-2000°C range required for thermionic conversion systems as well as in the lower temperature ranges required for thermoelectric and thermodynamic conversion systems. Study of refractory forms of the isotope and development of fuel capsules for these applications is underway at Oak Ridge National Laboratory (ORNL) and at the Savannah River Laboratory (SRL).

The specific objective of the SRL program is to acquire the technology needed for large-scale manufacture of ^{244}Cm fuel capsules. Pending definition of specific product goals, both basic and development studies of candidate systems have been initiated. Close liaison is maintained with ORNL. Work is currently being done in the following areas:

- Synthesis and measurement of properties of refractory ^{244}Cm compounds
- Development of techniques for preparing dense fuel forms
- Testing of the compatibility of the fuel forms with candidate encapsulation materials
- Design of facilities for encapsulation of 100-500 watt fuel forms

MATERIALS DEVELOPMENT

Synthesis of Curium Sulfides

Refractory compounds of curium are being synthesized as alternatives to curium oxide for high temperature heat source applications. Curium monosulfide (CmS) is a promising candidate. By analogy with other sulfides, CmS is expected to have a high melting temperature (estimated >2300°C) and good thermal stability. A procedure has been devised for preparation of curium sesquisulfide (Cm_2S_3), from which CmS might be obtained by thermal decomposition.

The sulfides are generally readily prepared from the oxides. Previous attempts to prepare Cm_2S_3 were made by exposing the oxide to H_2S at 1400°C in a graphite boat for 4 to 5 hours - a method used successfully to prepare Pu_2S_3. However, the graphite boat was attacked and the products contaminated so heavily with carbon that no clear evidence of the curium sesquisulfide could be obtained by X-ray diffraction. The problem was aggravated by the small scale of the experiments.

An improved procedure was developed and tested using cesium oxide (CeO_2) as a stand-in for the curium oxide. A ceramic combustion boat was used as reaction vessel, and the reactant hydrogen sulfide (H_2S) was saturated with carbon disulfide (CS_2) vapor; the presence of carbon has been reported necessary to reduce an intermediate product Ce_2O_2S. In several tests at 1300°C the conversion of CeO_2 to sulfide was essentially complete after seven hours. Analysis of the cerium sulfide indicated a S/Ce atm ratio of 1.4, with 0.7% residual oxygen still present, indicating the reaction product to be a mixture of Ce_2S_3 and Ce_3S_4.

During the current quarter, the new procedure was employed to synthesize a 100 mg sample of $^{244}Cm_2S_3$. CmO_2 in a ceramic combustion boat was exposed for five hours at 1300°C to H_2S saturated with CS_2 vapor. The product was a dark brown solid which was soluble in dilute acids. Chemical analysis showed S/Cm atm ratio to be 1.56, indicating a composition approximating the sesquisulfide was obtained.

X-ray analysis of the product showed only a few weak diffraction lines which could not be interpreted; self-radiation damage apparently produced a poorly defined crystal structure within the time (1 week) between synthesis and X-ray examinations. Fresh specimens will be prepared for prompt X-ray examinations in future work.

Identification and Stability of Curium Oxides

The various phases in the curium-oxygen system are being studied to define a suitably refractory oxide fuel form and to establish conditions for obtaining it.

As described previously,(1) curium dioxide (CmO_2), a product of the chemical separations, decomposes on heating to curium sesquioxide (Cm_2O_3). In analogy with rare earth sesquioxides, Cm_2O_3 may exist at progressively higher temperatures in three crystallographic structures, (1) a body-centered-cubic (bcc) C-type, (2) a monoclinic B-type, and (3) a hexagonal A-type. The C-type oxide may contain excess oxygen, and on standing several weeks at room temperature transforms because of self-radiation damage to a phase that closely resembles hexagonal A-type oxide.(2) The B-type and A-type oxides most probably represent stoichiometric Cm_2O_3, which as a solid will not undergo further thermal decomposition. However, the A-type oxide formed at high temperature reverts to the B-type oxide on cooling. The monoclinic B-type oxide, which can be retained on cooling and which resists irradiation-induced transformation at room temperature,(3) is thus the best candidate curium oxide for heat sources.

As shown in Figure 3, crystal structures and temperature ranges of stability of the various oxides were established by X-ray diffraction analysis of curium oxide samples during and after heating to successively higher temperatures in two oxidizing atmospheres (0.1% O_2/He and 1% O_2/He). The starting CmO_2 was prepared typically by calcination of curium oxalate on an iridium filament in oxygen at 600°C and slowly cooling to room temperature; in some cases platinum powder was added to the specimen to serve as an internal standard for temperature measurement.

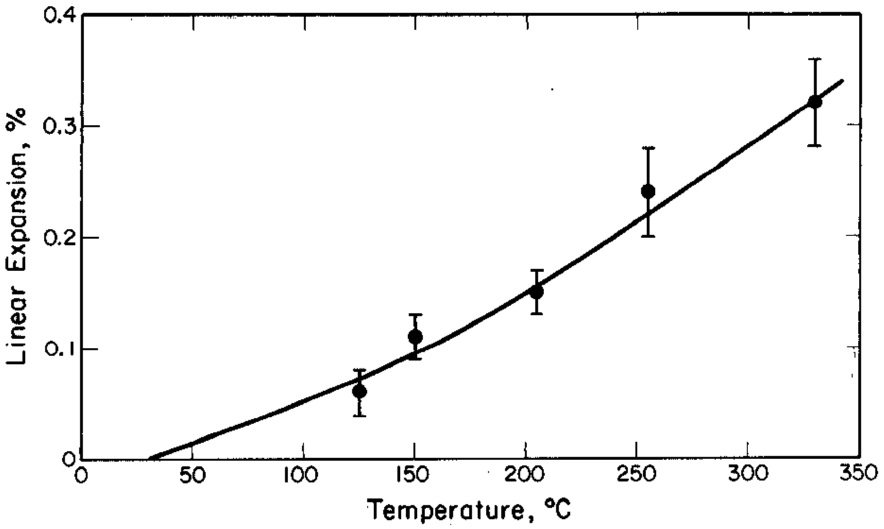
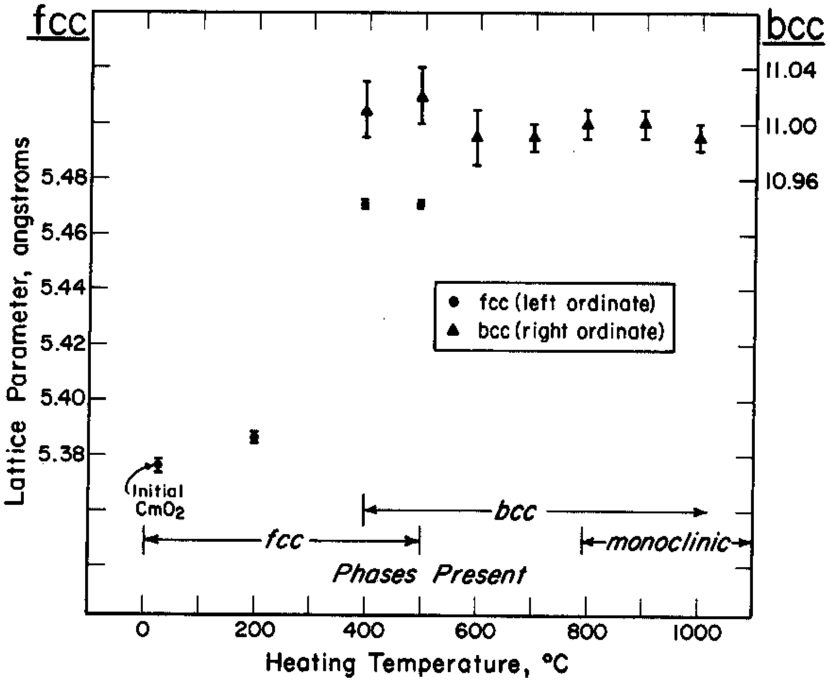


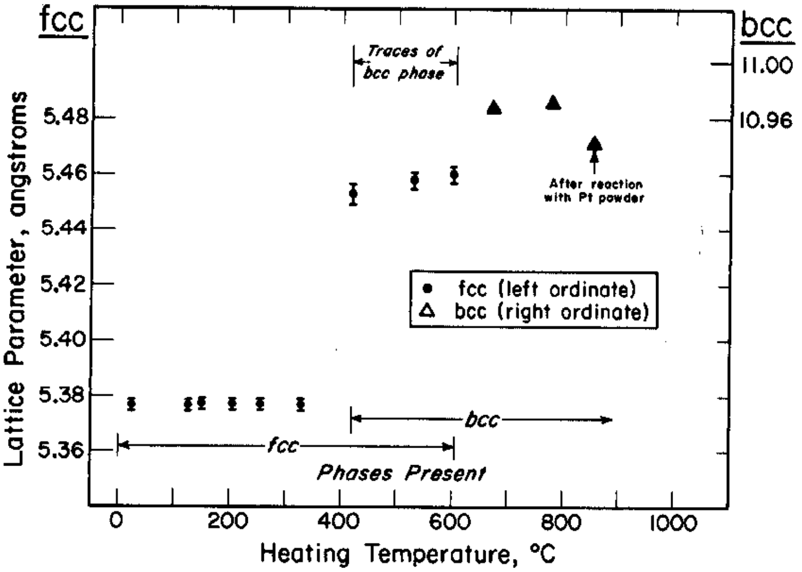
FIG. 3 LINEAR THERMAL EXPANSION OF NEAR STOICHIOMETRIC CmO_2

CmO_2 has a face-centered-cubic (fcc) structure, with lattice parameter a = 5.377 ± 0.003Å, which changed little on heating to 200-300°C. Thermal expansion of the fcc CmO_2 as indicated by lattice parameters at elevated temperatures is shown in Figure 3.

As shown in Figure 4, however, heating to above 400°C increased the lattice parameter from 5.377Å of CmO_2 to 5.45-5.47Å, which was attributed to the formation of a new fcc phase of lower



a. Oxide Heated in 0.1% O_2-He, Then Quenched



b. Oxide Heated in 1% O_2-He, Then Quenched

FIG. 4 CURIUM OXIDE LATTICE PARAMETERS

oxygen content. The new phase persisted to higher temperatures in 1% O_2/He atmosphere (600°C) than in the 0.1% O_2/He atmosphere (500°C).

Heating above 400°C also produced diffraction peaks of the bcc C-type Cm_2O_3, which were resolved above 600°C into a well-defined bcc pattern with lattice parameter a = 10.97Å. The lattice parameter remained relatively constant to over 1000°C (in the absence of platinum powder), which indicated that the C-type Cm_2O_3 has a fixed composition (not necessarily stoichiometric Cm_2O_3) with a very limited range of oxygen content.

In a sample containing platinum (Pt) powder heated to 850°C in 1% O_2/He atmospheres, the bcc lattice parameter of the C-type Cm_2O_3 was reduced to 10.94Å, probably because of reaction with the Pt powder at these temperatures. The lattice parameter of the cubic Pt powder decreased from 3.923Å to 3.916Å and several extra peaks occurred in the diffraction record near positions expected for the compound $Cm_2O_3 \cdot 2PtO_2$. Heating to 1300°C in nitrogen, at which temperature the complex compound would be expected to decompose, caused the extra peaks to vanish, and the lattice parameter of the small amount of bcc oxide that persisted to this temperature reverted to its previous value (10.97Å).

On heating to 800°C the monoclinic B-type Cm_2O_3* pattern appeared in the diffraction record, though temperatures up to 1300°C (in nitrogen) were required in some cases to achieve complete transformation. Preliminary evidence suggests that rapid heating promotes formation B-type Cm_2O_3 at lower temperatures; the kinetics of the C-type to B-type oxide transformation require further study.

The B-type oxide produced at elevated temperatures was retained at room temperature, and cooling in nitrogen in steps of 200-450°C did not cause a reversion to the C-type oxide to any significant degree. The transformation thus appears irreversible in the absence of oxygen, indicating the C-type Cm_2O_3 may contain excess oxygen.

Heating in inert atmosphere in the range 1400-1750°C transformed the oxide to the high temperature form, most probably the hexagonal A-type Cm_2O_3 (a = 3.88Å, c = 6.20Å at 1750°C). This form persisted up to the melting point of the oxide, remeasured at about 1950°C in agreement with previous ORNL results.(4) On cooling to below 1400°C, the high temperature form generally reverted to the B-type Cm_2O_3, though on rapid quenching to room temperature, the diffraction record indicated a small fraction of the high temperature form persisted.

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* a = 14.27Å, b = 3.65Å, c = 8.92Å, β = 100°16'

A hexagonal form of Cm_2O_3 can be produced by self-radiation damage of the bcc C-type oxide during several weeks at room temperature.(2) This hexagonal form may be the same as the high temperature form observed above 1500°C, though the relative intensities of the diffraction peaks differ somewhat.

Vapor Pressure of Curium Oxide

Relatively high losses of Cm_2O_3 have been observed during studies of the vaporization characteristics of the oxide at high temperatures using the Knudsen effusion technique. In a first experiment, a total of 19 mg of Cm_2O_3 was vaporized through a 0.976-mm diameter hole in the lid of a tungsten (W) crucible during seven hours at temperatures of between 1640-1850°C. Vaporization rates varied from 10^{-6} to 10^{-4} g/cm^2-sec over this temperature range; corresponding vapor pressures were calculated assuming the varporization reaction $Cm_2O_3(s) = CmO_2(g) + CmO(g)$, as given in Table II. The heat of vaporization at temperature was about 150 kcal/mole Cm_2O_3.

TABLE II

Vaporization Rate of Cm_2O_3*

Temp., °C	Rate, g/(cm^2)(sec)	P(CmO_2), atm
1641	4.00×10^{-6}	1.19×10^{-7}
1656	9.00×10^{-6}	2.68×10^{-7}
1682	15.9×10^{-6}	4.78×10^{-7}
1713	17.0×10^{-6}	5.15×10^{-7}
1750	59.8×10^{-6}	18.3×10^{-7}
1768	76.5×10^{-6}	23.5×10^{-7}
1836	$119. \times 10^{-6}$	37.1×10^{-7}
1849	$221. \times 10^{-6}$	69.2×10^{-7}

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* Assuming $Cm_2O_3(s) = CmO_2(g) + CmO(g)$

In a second experiment, about 9 mg of Cm_2O_3 sample left over from the first experiment was vaporized through the 0.976-mm-diameter hole in the lid of the crucible during 7.5 hours over a temperature range 1560-1930°C. The heat of vaporization calculated from the data of the second experiment was the same as for the first experiment within the precision of the highly scattered data points. The measured vaporization rate was, however, lower by a factor of 15 in the second experiment than in the first experiment. Test data are being further analyzed and experimental parameters are being evaluated to resolve the discrepancies between the first and second experiments and to reduce scatter in the data.

No reaction was observed between the curium oxide and the 100% dense tungsten crucible after the first experiment. All oxide residues and vapor deposits were easily scraped from the tungsten, and the knife-edge orifice in the crucible lid had not been enlarged within a precision of 1%.

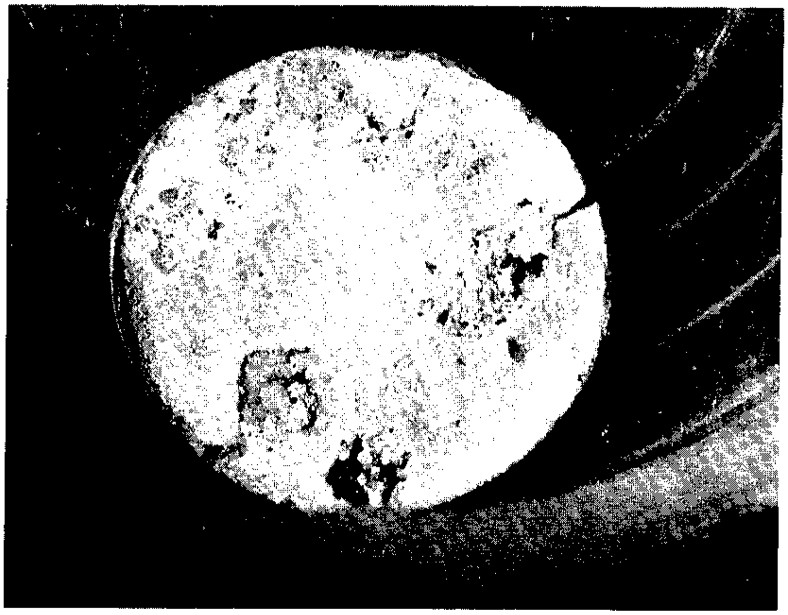
After the second experiment, however, the residual oxide in the crucible had a slight yellow color, and a substantial deposit had built up around the periphery of the orifice in the crucible lid. This deposit proved to be readily soluble in water. X-ray diffraction analysis of the residual oxide yielded a complex pattern which has not been resolved. It is suspected that a complex compound of curium oxides and tungsten oxide had been formed, possibly aided by alpha-radiation induced spalling of the crucible wall, during about four months standing at room temperature in air between the first and second experiments. The experiment will be repeated using a freshly made Cm_2O_3 sample.

Curium Oxide-Refractory Metal Cermets

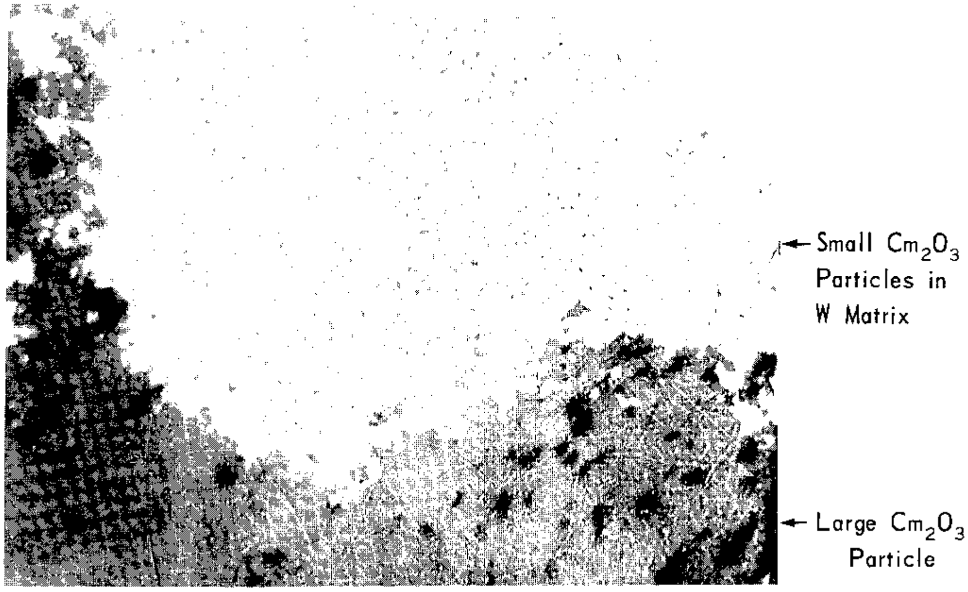
Cermet pellets of Cm_2O_3 and several refractory metals that could be employed as matrix or capsule materials for ^{244}Cm heat sources are being fabricated. The primary objective of the work is to determine the nature and extent of interaction between Cm_2O_3 and the candidate metals at high temperatures. In a first experiment, a 25 vol % Cm_2O_3-75% vol % W cermet pellet was fabricated by cold pressing and sintering. A high quality cermet was not achieved because of inadequate mixing of the component powders but no evidence of deleterious interaction between Cm_2O_3 and tungsten at 1850°C was observed.

Monoclinic (B-type) Cm_2O_3 powder was prepared from CmO_2 by heating in 4% H_2/He at 1300°C. About 50 mg of the Cm_2O_3 powder was mixed with 250 mg of tungsten powder and cold compacted at 50,000 psi to a pellet 0.31-inch diameter by 0.025-inch thick. The pellet was sintered in an induction furnace at 1850°C (with three short excursions to 1900°C) for 5 hours and 40 minutes, then quenched to about 700°C in 3 minutes.

Visual examination of the pellet showed surface craters evidently caused by evolution of curium oxide vapor from relatively large Cm_2O_3 particles, Figure 5A. Deposits of the evolved oxide on the top of the tungsten container used to hold the pellet



a. Surface Appearance (10X)



b. Microstructure (500X)

FIG. 5 SURFACE APPEARANCE AND MICROSTRUCTURE OF SINTERED Cm_2O_3-W CERMET PELLET. Surface craters were formed by vaporization from large Cm_2O_3 particles shown in microstructure.

yielded a well-defined diffraction pattern for predominantly monoclinic B-type Cm_2O_3.

Metallographic examination of the pellet showed a coarse distribution of large Cm_2O_3 particles in some regions and a fine distribution of small Cm_2O_3 particles in grain boundaries of the tungsten matrix in other regions, Figure 5B. The tungsten matrix was well sintered with very little residual porosity. No reaction between the Cm_2O_3 particles and the tungsten matrix was observed.

X-ray analysis of the sintered pellet yielded only broad, low intensity peaks tentatively identified as monoclinic Cm_2O_3, and characteristic tungsten peaks. No evidence of any interaction product was detected.

ENGINEERING DEVELOPMENT

Curium Oxide Shipping Container

A shipping container for transport and storage of curium oxide in 120 gram batches was designed and two prototype containers fabricated. The container, shown in Figure 6, was designed to comply with ICC shipping regulations, which require no loss of containment after exposure to an 800°C fire for 1/2 hour.

Curium oxide is loaded into a 1/8-inch annular cavity in the type 316 stainless steel container designed to maintain low oxide temperatures. Final closures will be made by welding. A large central chamber containing an oxygen getter material is provided for collection of gases evolved by radioactive decay and possible thermal decomposition of the curium oxide after loading. Internal pressure generated within the container will not exceed 200 psia at 800°C. Product temperatures are expected to be much less than 800°C, though packing density tests will be necessary to establish actual temperature values.

To eliminate contamination of the curium oxide with iron, nickel, and chromium by reaction with the 316 stainless steel container, the inside annulus walls will be lined with platinum. Tests will be run to determine minimum platinum liner thickness required, and the degree of platinum contamination of the oxide to be expected due to spalling resulting from alpha particle bombardment.

The prototype containers, fabricated without platinum lining, will be used for discussions with Oak Ridge, handling and loading tests, platinum liner development, and structural integrity tests. One of the containers will be hydrostatically loaded to rupture at room temperature to evaluate the basic design.

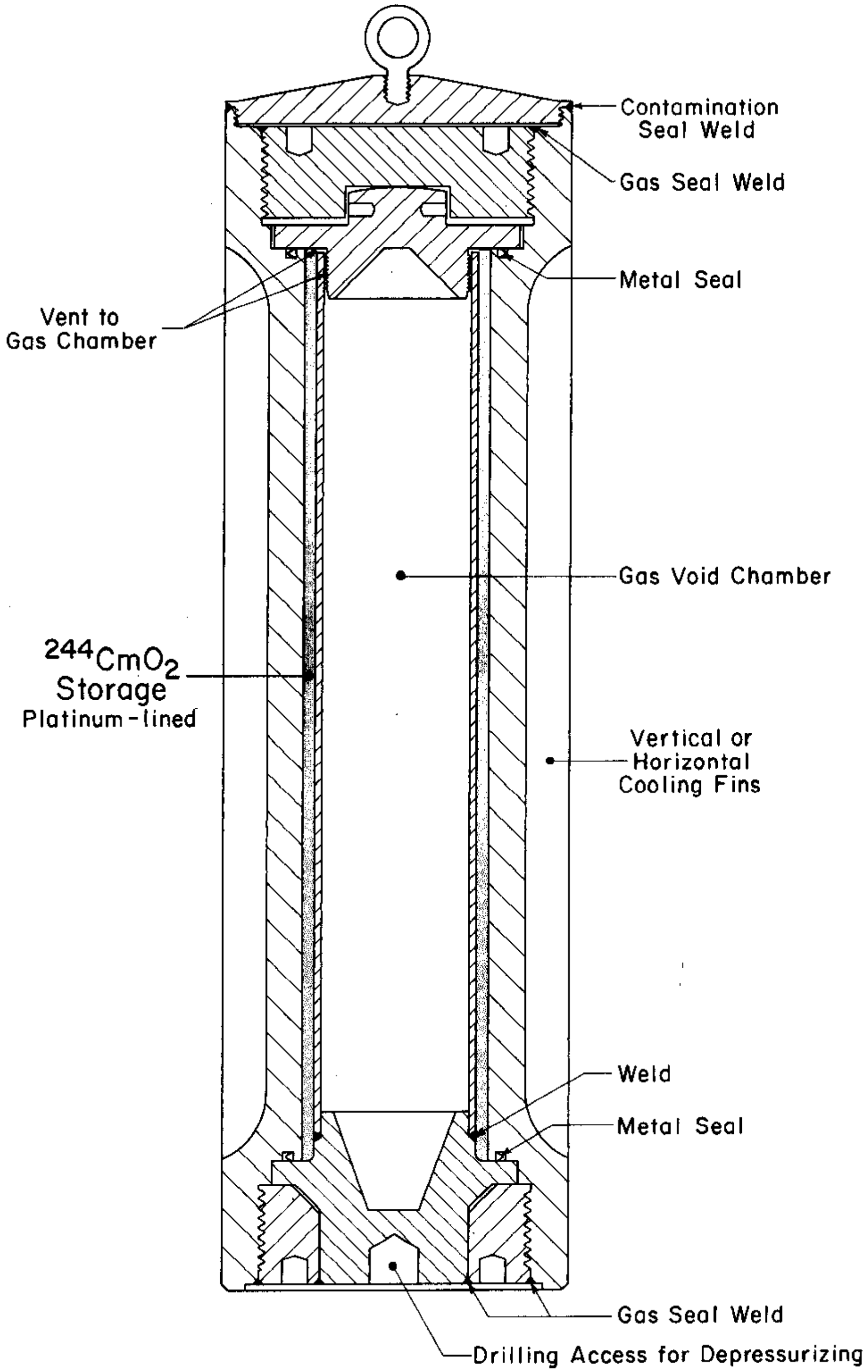


FIG. 6 CURIUM OXIDE SHIPPING CONTAINER
3.5" O.D. x 12.6" long

REFERENCES

1. H. S. Hilborn (compiler), Savannah River Laboratory Isotopic Power and Heat Sources, Quarterly Progress Report, July-September 1966, USAEC Report DP-1088, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, S. C. (Confidential).

2. J. C. Wallman, "A Structural Transformation of Curium Sesquioxide," J. Inorg. Nucl. Chem. 26, 2053 (1946).

3. Private communication, Herman Haug, Argonne National Laboratory, Argonne, Illinois.

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APPENDIX

Isotopic Fuel Data Sheet for Cobalt

This supersedes similar material included in the corresponding section (section I.A.5., pages 7, 8, and 9) of DP-1051, Revision 1, "Properties of ^{60}Co and Cobalt Metal Fuel Forms" by W. C. Windley, Jr.

5. Compatibility with Materials of Encapsulation

The principal aspect of compatibility between cobalt and cladding is interdiffusion at heat source temperatures. Of particular concern in diffusion are (1) penetration rate of ^{60}Co through the cladding, (2) formation of brittle and highly corrodable intermetallic compounds at the cobalt-cladding interface, and (3) changes in mechanical and physical properties of the cobalt or cladding.

The rate of ^{60}Co penetration has been estimated from reported ^{60}Co diffusion rates through pure nickel and cobalt. The table below shows the rate at which a plane parallel to the original interface corresponding to a ^{60}Co concentration of 0.01 wt % would move into the cladding (same in both metals since diffusion coefficients are nearly identical).

Temperature, °C	Rate of Penetration, mils^2/hr$^{(a)}$
600	1.3×10^{-7}
800	2.1×10^{-4}
1000	4.6×10^{-2}
1200	2.1

(a) From parabolic relationship $x^2 = kt$, where x = penetration and t = time.

These data are for volume diffusion. Current measurements at SRL for both nickel- and cobalt-based alloys indicate that grain boundary diffusion also occurs which would lead to deeper penetrations than shown above. Both volume and grain boundary diffusion rates vary with alloy content.

Of nickel- and cobalt-based heat-resistant alloys, "Inconel"* 600, TD Nickel**, TD Nickel Chromium**, "Hastelloy"*** C, and Haynes*** 25 have the highest degree of compatibility with cobalt, Figure 3. These results were calculated from measured widths of diffusion zones formed in multilayered diffusion couples annealed

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* International Nickel Co., New York, N. Y.

** E. I. du Pont de Nemours & Co., Wilmington, Del.

*** Union Carbide Corp., New York, N. Y.

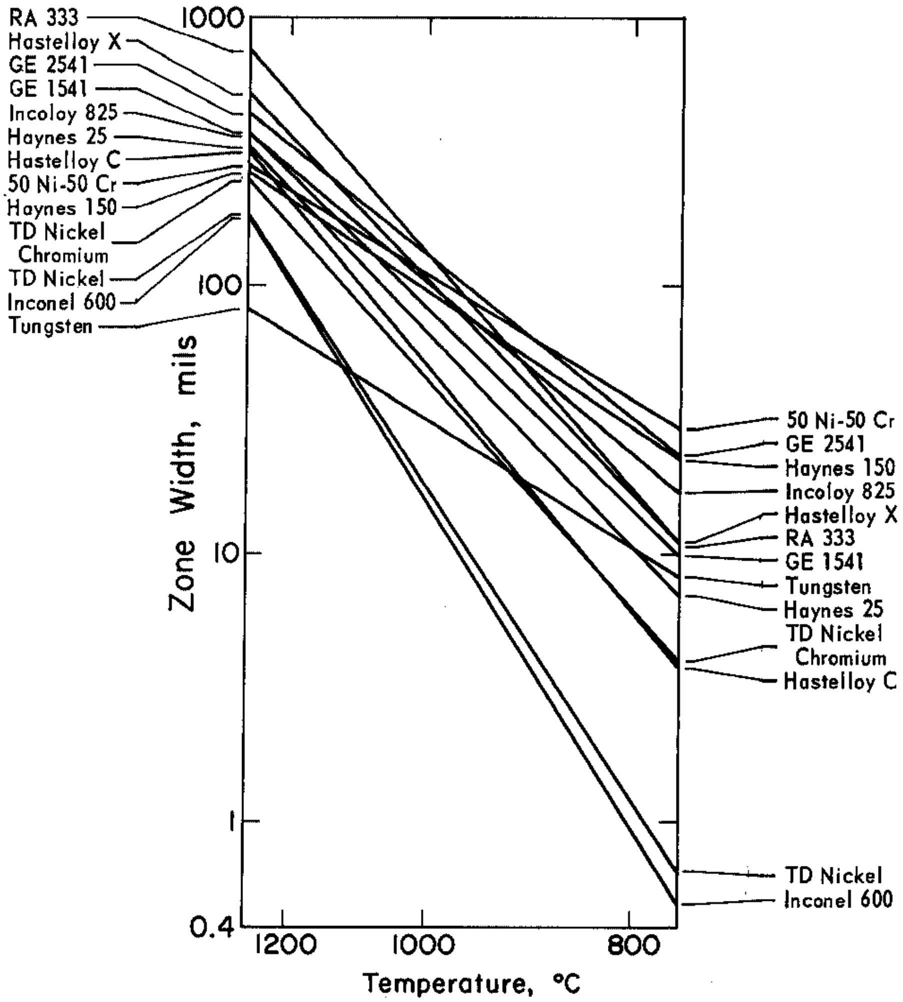

FIG. 3 CALCULATED DIFFUSION ZONE WIDTHS AFTER ONE HALF-LIFE OF ^{60}Co
(Based on 168 hr Anneal)

for 168 hr at 800, 1000, and 1200°C, see the accompanying table. Metallographic examinations and electron microprobe analyses showed that the diffusion zone formed between each of these alloys and cobalt is a region of solid solution terminating in a band of voids. These voids are less prevalent in the cobalt-based alloys and non-existent in pure nickel. The compatibility of pure nickel depends on the rate of diffusion of ^{60}Co atoms at the expected operating temperature.

Of the refractory metals, rhenium should be the most compatible since it forms a continuous series of solid solutions with cobalt; the diffusion rate of ^{60}Co atoms is the governing factor as with pure nickel. The compatbility of tungsten has been measured as shown in Figure 3; the diffusion zone consists of two intermetallic compounds. Tantalum and molybdenum would be incompatible above 1200 and 1300°C, respectively, due to eutectic melting.

Microhardness measurements indicate that the strength of the diffusion zone in nickel- and cobalt-based alloys will be no more than 25% lower than the unreacted cladding material.

Widths of Diffusion Zones After 168 Hours (mils)

Alloy	Annealing Temperature, °C 800	1000	1200
Ni-based Alloys			
Inconel 600	0.05	1.0	7.3
TD Nickel	0.06	1.1	7.0
TD Nickel-chromium	0.4	3.8	10.5
Hastelloy C	0.4	3.2	16.4
RA-333	0.8	7.8	31.0
Hastelloy X	0.8	5.8	22.5
Incoloy 825	1.0	6.4	19.0
50 Ni - 50 Cr	2.0	6.5	17.0
Co-based Alloys			
Haynes 25	0.5	3.8	14.4
Haynes 150	1.6	5.7	13.4
Fe-based Alloys			
GE 1541	0.6	4.8	16.2
GE 2541	1.7	7.7	20.5
Others			
Tungsten	-	2.0	4.2