174
1-28-74

D. 532

DP-1320

95,395

CALIFORNIUM OXIDE - PALLADIUM CERMET WIRE AS A ^{252}Cf NEUTRON SOURCE FORM

W. C. MOSLEY
P. E. McBEATH
P. K. SMITH

Savannah River Laboratory

Aiken, South Carolina

PREPARED FOR THE U. S ATOMIC ENERGY COMMISSION UNDER CONTRACT AT(07-2)-1

MASTER

Printed in the United States of America
Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151
Price: Printed Copy $4.00; Microfiche $1.45

DISCLAIMER

DP-1320

UC-38

CALIFORNIUM OXIDE - PALLADIUM CERMET WIRE AS A ^{252}Cf NEUTRON SOURCE FORM

by

W. C. Mosley
P. E. McBeath
P. K. Smith

Contributors:

R. M. Harbour
K. W. MacMurdo
W. R. McDonell

Approved by

R. T. Huntoon, Research Manager
Nuclear Materials Division

January 1974

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

CONTRACT AT(07-2)-1 WITH THE
UNITED STATES ATOMIC ENERGY COMMISSION

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

fig

ABSTRACT

An improved ^{252}Cf neutron source form has been developed to enhance containment of ^{252}Cf during production of the sources and to lower the sale price of ^{252}Cf sources by commercial encapsulators. Process steps are described for preparing californium oxide-palladium cermet powder by palladium chemical plating, fabrication of cermet pellets by pressing and sintering, fabrication of bare wire by rolling, and adjustment (reduction) of ^{252}Cf linear concentration by roll cladding. ^{252}Cf is distributed uniformly in the wires, which can be made in concentrations suitable for a full range of industrial source strengths (from 1×10^7 to 2.5×10^{10} n/sec).

These processes were developed in laboratory tests with stand-ins and ^{252}Cf tracer, and were demonstrated with milligram quantities of ^{252}Cf in the Target Fabrication Facility (TFF). Improved wire forming techniques are being developed to manufacture clad wire on a larger scale.

CONTENTS

CONTENTS (continued)

LIST OF FIGURES

LIST OF TABLES

CALIFORNIUM OXIDE – PALLADIUM CERMET WIRE AS A ^{252}Cf NEUTRON SOURCE FORM

INTRODUCTION

^{252}Cf is a valuable source of neutrons for medical and industrial applications.[1] A form of californium, other than the oxide, was desired for supplying commercial encapsulators with bulk ^{252}Cf that could be handled and subdivided simply and with negligible contamination potential. The form should enable the encapsulator to eliminate wet chemistry operations required to prepare sources from californium oxide or oxysulfate forms of bulk ^{252}Cf.[2] Because the new form should simplify encapsulation processes, the finished neutron source should cost less.[3,4] The development of such a new form, californium oxide-palladium cermet wire, is described.

SELECTION OF SOURCE FORM

The chief characteristic desired in a californium neutron source form is the fixation of the ^{252}Cf in an easily divisible matrix to reduce the potential for contaminating handling facilities. Containment of ^{252}Cf in a noble metal matrix, as either an alloy or a cermet, provides this characteristic. Noble metals also offer good resistance to oxidation and corrosion, high melting temperatures, and good ductility for forming. Of the noble metals, palladium (Table I) was chosen as the matrix for ^{252}Cf wire development because it has the lowest cross section for neutron capture, and the least delayed and prompt gamma rays that might interfere in applications of neutron activation analysis. The solubility of palladium in oxidizing acids also facilitates ^{252}Cf recovery.

The ^{252}Cf loading in the palladium is determined by the individual source strength, batch sizes, fabricability, and ability to accommodate decay helium. Industrial sources are required generally in the range of 10 μg to 10 mg of ^{252}Cf (2.3×10^7 to 2.3×10^{10} n/sec). Batch sizes of 30 to 50 mg

TABLE I. PROPERTIES OF PALLADIUM

Atomic Number	46
Atomic Weight	106.4
Stable Isotopes, mass units	102,104,105,106,108,110
Crystal Structure	Face-centered cubic (fcc)
Lattice Constant, a, at 25°C (77°F)	3.8898Å
Density at 20°C (68°F)	12.02 g/cm^3
Melting Point	1552°C (2825°F)
Boiling Point	2900°C (5252°F)
Electrical Resistivity at 0°C (32°F)	9.93 microhm-cm
Temperature Coefficient of Electrical Resistivity at 0 to 100°C (32 to 212°F)	0.0038/°C
Thermal Conductivity at 0 to 100°C (32 to 212°F)	0.18 cal/(sec-cm^2-°C-cm)
Coefficient of Linear Thermal Expansion at 20 to 100°C (68-212°F)	11.1 x 10^6/°C
Specific Heat at 0°C (32°F)	0.0584 cal/(g-°C)
Young's Modulus at 20°C (68°F)	
Static	16.7 x 10^6 psi
Dynamic	17.6 x 10^6 psi
Ductility (Elongation; Vickers Hardness)	30%; 37 to 39
Thermal Neutron Capture Cross Section	8.0 barns

of ^{252}Cf can be accommodated by the shielding in existing cells. The smallest amount of palladium that can be handled in the shielded cells is about 1 g, which is equivalent to 4 inches of wire with about 0.040-in. x 0.040-in. cross section, a conveniently fabricable and easily handled configuration.

Two milligrams of ^{252}Cf per gram of palladium is about the maximum concentration allowable to prevent significant embrittlement and swelling by decay helium. This concentration, which is equivalent to 500 μg of ^{252}Cf per inch of 0.040-in. x 0.040-in. cermet wire, will produce a volume of helium equal to 2 cc (STP) per cc of palladium after a ten-year decay period. For cermet, two mg of ^{252}Cf per gram of palladium is also the practical limit of fabricability because significant dispersion hardening occurs. This hardening is caused by californium oxide particles. Cermet pellets can be made with higher concentrations (up to 30 mg of ^{252}Cf per gram of palladium) but will be too brittle to permit subsequent fabrication.

The lightest anticipated ^{252}Cf loading of about 20 μg ^{252}Cf per gram of palladium should not cause significant radiation embrittlement or dispersion hardening.

ALTERNATIVE ADMIXING PROCESSES

Initial efforts to develop a wire form were directed toward californium-palladium alloy. Preliminary tests of *carbothermic reduction of oxide* in the presence of molten palladium using samarium as a stand-in resulted in incomplete alloying. Also, at the alloying temperatures required, the volatility of californium metal was considered to be unacceptably high. Therefore, the emphasis was shifted to fabrication of californium oxide-palladium cermet wire by powder metallurgy processes. Several methods to prepare cermet were investigated, including evaporative admixing, freeze-drying, and chemical plating.

Evaporative admixing involved adding ^{252}Cf feed in 0.1N combined nitric-formic acid to palladium powder, and evaporating the mixture to dryness.[4] The palladium powder, coated with californium nitrate, was pressed into a compact, heated at about 800°C to decompose the nitrate to oxide, and then sintered at 1300°C to produce a dense pellet for wire fabrication by rolling. In two demonstrations on a milligram production scale, impurities in the ^{252}Cf feed caused the palladium to stick to the evaporation beaker, and radiation caused undesirable frothing at high ^{252}Cf concentrations during evaporation. Although wires with satisfactory uniformity were produced, evaporative admixing was abandoned because of unacceptable low yields experienced in these demonstrations (Table II).

Preparation of cermet by a *freeze-drying* process was developed with tracer quantities of ^{252}Cf and samarium stand-in, but was not demonstrated on a milligram ^{252}Cf production scale. In this process, a solution of palladium, samarium, and californium nitrates was atomized to a mist and frozen at liquid nitrogen temperature into tiny particles. Moisture was sublimed by vacuum from the particles leaving a mixed nitrate powder, which was heated to form cermet powder with uniform dispersion of samarium-californium oxide in a palladium metal matrix. High integrity, uniform wires were produced by this technique with yields of about 80 to 90%. However, freeze drying was abandoned because of difficulties in handling the powder and the hazards associated with handling cryogenic fluids in a remotely operated containment facility.

A *chemical plating* process outlined in Table III was chosen for cermet preparation because it was insensitive to impurity and radiation effects and was easily adaptable to containment cell operation.[4]

TABLE II. CALIFORNIUM OXIDE - PALLADIUM WIRES FABRICATED DURING PROCESS DEVELOPMENT

Process	Source No.	Invested ^{252}Cf, µg	^{252}Cf Concentration, µg/inch[a]	Yield, %	Process Yield, %[b]	^{252}Cf Not Recovered, %
Evaporative Admixing	SR-Cf-1005C	1352	207 ±4.4	68.9	83.4	13.8
	SR-Cf-1009C	1057	170 ±6.1	60.5	79.1	16.0
	Average:	-		65.2	81.6	14.7
Chemical Plating	SR-Cf-1014C	956	147 ±4.0	88.6	95.3	4.4
	SR-Cf-1020C	41	11 ±3.7	92.7	97.4	2.4
	SR-Cf-1021C	41	11 ±5.8	95.1	100	0
	SR-Cf-1018C	1043	412 ±4.4	73.1	89.3	8.7
	SR-Cf-1022C 1023C	1014	430 ±4.3	70.8	81.2	16.4
	Average:	-		77.7	88.9	9.7
Total or Average		5504		72.2	85.9	11.9

---

a. Deviation in %.
b. ^{252}Cf in wire + reclaimable losses to process.

TABLE III. FLOW SHEET OF CALIFORNIUM OXIDE - PALLADIUM CERMET WIRE PREPARATION BY CHEMICAL PLATING

Operation	Condition
1. Prepare ^{252}Cf feed	20-50 ml of 0.1N HNO_3.
2. Add Tb carrier	10 mg $Tb(NO_3)_2 \cdot 6H_2O$ if $\leqslant$2 mg ^{252}Cf.
3. Precipitate oxalate	40 mg oxalic acid/(mg ^{252}Cf) in ∿40 ml H_2O. Digest $\geqslant$30 minutes.
4. Add reductant	10 ml of 85% hydrazine hydrate per gram of palladium.
5. Pd plating	Add solution containing ∿1 gram palladium per 100 ml solution while stirring.
6. Filter	Pull through glass frit with vacuum.
7. Rinse	$\geqslant$300 ml distilled H_2O.
8. Dry	200°C in argon until moisture is gone.
9. Pulverize	Tap filter cake lightly with chopper rod.
10. Calcine	450°C in 4% H_2-96% He for 30 min; cool below 200°C in argon.
11. Transfer powder	Use transfer vial.
12. Press compact	$\leqslant$15,000 psi.
13. Sinter	$\geqslant$2 hr heatup to 1000°C in 4% H_2-96% He; $\geqslant$2 hr at 1300°C in argon.
14. Assay ^{252}Cf	Neutron counter.
15. Fabricate wire	Roll to ∿30% reduction in area; 10 minute anneal at 850°C in argon.
16. Assay ^{252}Cf	Neutron counter.
17. Assay ^{252}Cf uniformity	Autoradiograph.
18. Subdivide	Cut.
19. Package	
20. Ship	

DEVELOPMENT OF CHEMICAL PLATING AND WIRE FABRICATION

The cermet prepared by chemical plating consists of finely divided oxides containing Cf_2O_3 distributed uniformly in a palladium matrix. The chemical plating process to prepare cermet is similar to that used by Fuschillo and Gimpl[5] to dispersion-strengthen platinum, gold, and copper.

Californium is precipitated as oxalate particles that are chemically coated with palladium metal. These coated particles are calcined to convert the oxalate to oxide and to form the cermet powder. Pressing and sintering are used to consolidate the cermet powder into a pellet, which is fabricated into wire form by rolling. The linear ^{252}Cf concentration can be reduced by inserting a piece of bare cermet wire into a palladium tube and rolling to appropriate cross section and length. Recovery of ^{252}Cf from californium oxide-palladium cermet is accomplished by dissolving in concentrated nitric acid (with a trace of hydrochloric acid), adjusting the acidity to 0.1N HNO_3, and separating the ^{252}Cf from the palladium by anion exchange techniques.

Laboratory tests of chemical plating with samarium stand-in and ^{252}Cf tracer (10^{-9} g) indicated that 80 to 90% of the ^{252}Cf in the feed solution was incorporated into the finished cermet wires. The ^{252}Cf tracer was distributed uniformly throughout the cermet with the ^{252}Cf concentration in 0.5-in. pieces of subdivided 0.040-in. x 0.040-in. square wire deviating less than 5% from the average. Dense pellets (90% of theoretical density) of samarium sesquioxide (Sm_2O_3)-palladium cermet containing up to 2.5 vol % oxide were successfully fabricated into wires with square cross sections in a rolling mill. The final wire cross sections were 0.030-in. x 0.030-in. However, cermet pellets with >5 vol % oxide splintered during rolling.

Fabrication of californium oxide-palladium cermet wire has been demonstrated on a production scale with milligram quantities of ^{252}Cf in the Target Fabrication Facility (TFF). The wires listed in Table II are expected to be typical of production sizes required to accommodate the demand for this form for several years. Yields from chemical plating were significantly higher than for evaporative admixing, but were lower than the expected 80 to 90% for attempted loadings of 500 µg ^{252}Cf/inch. Principal losses occurred during handling of cermet powder and compacts. These losses are expected to be reduced by modification of the equipment.

Uniformity of bare californium oxide-palladium cermet wires was determined by densitometer analyses of gamma autoradiographs. The ^{252}Cf content at 1/8-in. intervals along the wires generally deviated about ±5% from the average. Several pieces of bare wire were sheathed in palladium and rolled to reduce the linear ^{252}Cf concentrations up to 25 times without affecting uniformity (Table IV). One piece of bare wire containing about 3 µg of ^{252}Cf (6×10^9 alpha d/min) was roll-sheathed in an uncontaminated facility and subdivided by a pinch cutting process with no detectable smearable contamination (less than 20 alpha d/min).

TABLE IV. ROLL-SHEATHED CALIFORNIUM OXIDE - PALLADIUM CERMET WIRE

^{252}Cf Content		Dimensions, in.		
Total, µg	µg/in.[a]	Length	Core	Clad
43	57.8 ±3.7	0.75	0.019	0.083
51	13.0	4.0	0.010	0.042
10	1.2 ±7.8	8.0	0.015	0.062

---

[a] Deviation in %.

Product Specifications

Standard californium oxide-palladium cermet wire will be produced for sale to encapsulators with nominal 0.040-in.^{2} cross section and loadings of 5, 50, and 500 µg ^{252}Cf/in. These linear loadings are equivalent to 16.9, 169, and 1688 µg ^{252}Cf per gram of palladium. Product specifications for bare wire are shown in Table V. Combinations of the three concentration levels should allow fabrication of sources of the SR-Cf-100 design[3] from about 2 µg to 2000 µg ^{252}Cf (or larger) within ±10% of the desired ^{252}Cf content. The ^{252}Cf content and uniformity in lengths of wire shorter than 0.5 in. do not meet specifications because of cutting precision and end effects.

Cermet wire lengths and loadings that do not meet standard specifications can be accommodated on special order. Also, different shapes such as clad wire, cermet powders, sintered pellets or discs, square rod, or larger wire may be fabricated fairly easily.

TABLE V. PROPOSED SPECIFICATIONS FOR CALIFORNIUM OXIDE - PALLADIUM CERMET WIRE

^{252}Cf Concentration	Nominally 5, 50, or 500 μg/in.
Total ^{252}Cf	Within 10% of order, assayed to ±3% for pricing.
Thickness	0.040 ±0.002-in.-square cross section.
Length	0.5 to 2.5 inches.
Uniformity	1/8-inch segments within ±10% of average concentration.
Metallurgical Condition	Annealed.
Chemical Purity	Oxide: As $Cf_2O_2SO_4$ or Cf_2O_3;[a] Tb_2O_3 carrier may be added to a maximum of 2 vol % total oxide in the cermet. Palladium: 99.9% Pd.
Isotopic Purity	Typically 2 wt % ^{249}Cf, 15 wt % ^{250}Cf, 4 wt % ^{251}Cf, and 79 wt % ^{252}Cf.[a]
Neutron Emission	To customer's specifications. Determined by manganese sulfate bath and electronic calibration techniques.[a]
Gamma Spectrum	Similar to oxide in platinum-rhodium capsules;[b] typical spectrum for cermet wire available on request.

---

[a] *Californium-242. Guide for Fabricating and Handling* ^{252}*Cf Sources.* USAEC Report SRO-153. Savannah River Operations Office, Aiken, South Carolina 29801 (1971).

[b] W. R. McDonell, A. R. Boulogne, and J. P. Faraci. "Preparation of Cf-252 Sources at Savannah River Laboratory." *Neutron Sources and Applications: Vol. II. Proceedings of the American Nuclear Society National Topical Meeting, April 19-21, 1971, Augusta, Georgia.* USAEC Report CONF-710402. E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, South Carolina 29801. Vol II., I-182 (1971).

Process Description

The process flow sheet for production of wire is described in Table III. The process steps described below apply for production batches of less than 2 mg ^{252}Cf. Anticipated changes for larger batches are described in a later section.

^{252}Cf Feed Preparation

The ^{252}Cf feed should meet the same purity specifications as that used for the SR-Cf-100 sources and SR-Cf-1000 shipping packages:[3]

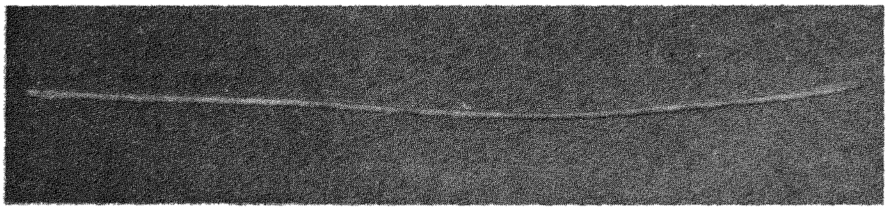
- ^{244}Cm content $\leqslant$ 1000 ppm
- Actinide and lanthanide content $\leqslant$ Cf content
- Content of nonradioactive cations $\leqslant 4 \times$ Cf content

The oxide content in californium oxide-palladium cermet will therefore consist mainly of oxides of impurities in the ^{252}Cf feed that precipitate as oxalates. Preliminary tests with simulated feed indicated that lanthanides, actinides, iron, zinc, copper, lead, and possibly calcium and barium will be the major feed impurities retained in cermet produced by the chemical plating process. The volume of the oxide from these impurity elements could be as much as ten times the californium oxide content in the cermet. The ^{252}Cf concentrations along a length of cermet wire are shown in Figure 1.

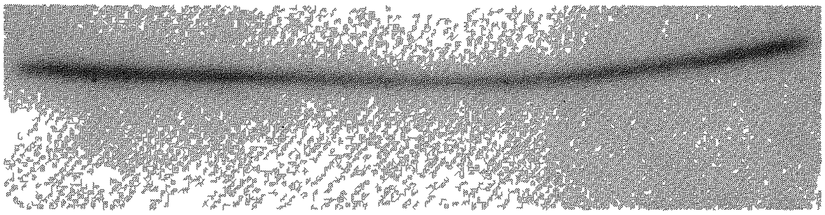
Precipitation of ^{252}Cf Oxalate

Because ^{252}Cf is to be precipitated as the oxalate, the nitric acid content of the ^{252}Cf feed in solution should be $<$0.3N to keep the solubility of the californium oxalate low. If ^{252}Cf feed is received in an SR-Cf-1000 shipping package, the ^{252}Cf should be leached from the package with 10 ml of 0.1N HNO_3.

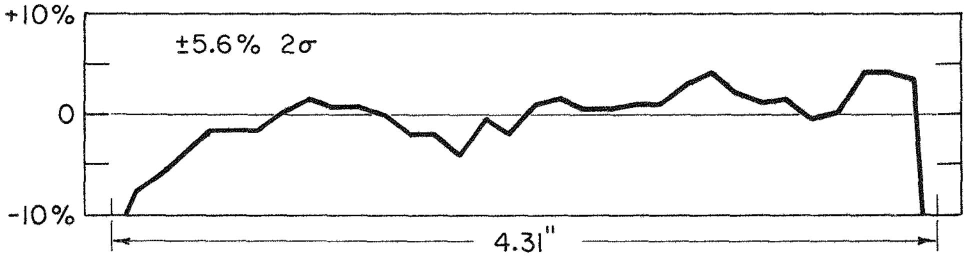
Terbium carrier is needed for quantitative oxalate precipitation when less than 2 mg of ^{252}Cf is to be used; 3.4 mg of terbium (10 mg terbium nitrate) is sufficient. The terbium can be added to the ^{252}Cf feed during preparation of the SR-Cf-1000 shipping package, or it can be added as 10 mg of terbium nitrate in 10 to 20 ml of distilled water when the ^{252}Cf feed is put into the chemical plating apparatus.



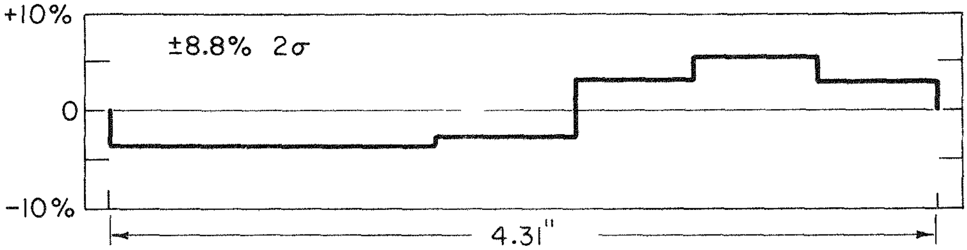
Wire



Autoradiograph



Densitometer Analysis of Radiograph



Neutron Counting Analysis

Figure 1. LINEAR ^{252}Cf CONCENTRATION IN CERMET WIRE

Chemical Plating of Palladium onto Oxalate Particles

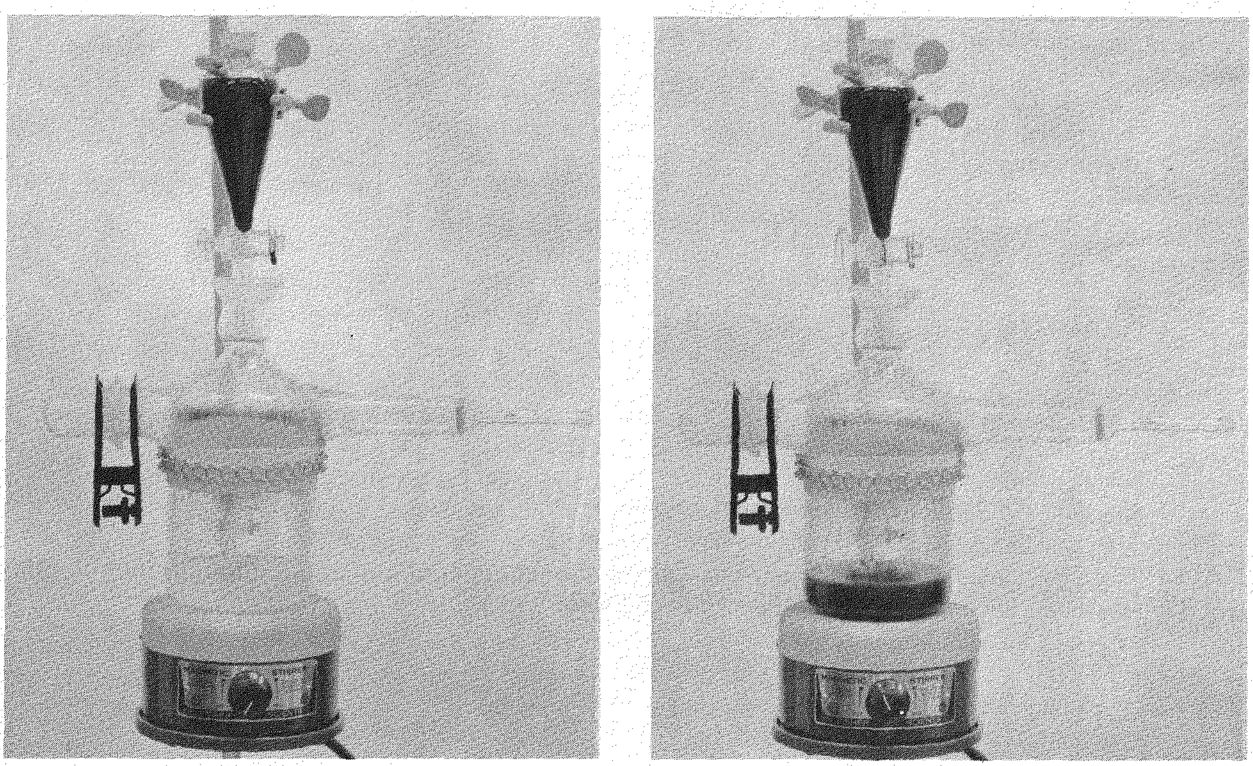
A special chemical plating apparatus consisting of an enclosed beaker having a filter arm with a medium-porosity glass frit (Figure 2) is used to prepare the californium oxide-palladium cermet powder. A magnetic stirplate with a 1-1/2-in.-long glass-covered magnetic stirring bar is used to stir the beaker contents during the plating process. The ^{252}Cf feed is leached from the shipping package with 10 ml of 0.1N HNO_3, the terbium carrier is added, and the feed solution is poured into the beaker. An oxalic acid solution is added while the solution is being stirred. The oxalate solution contains 40 mg of $H_2C_2O_4.2H_2O$ in 40 ml of distilled water for about a fourfold excess of oxalate over the total californium-terbium-impurity metal ions. A higher ratio of oxalate ions to feed-metal ions causes Pd^{2+} to precipitate as oxalate. A cloudy suspended precipitate should form within several minutes (Figure 2a). Stirring should continue for approximately 30 minutes. Agglomerates of oxalate particles may form to coarsen the precipitate.

An 85% aqueous solution of hydrazine hydrate is poured into the plating beaker, and stirring is continued to keep the oxalate particles suspended. The solution will change from acid to basic with a pH near 10. Ten ml of hydrazine hydrate solution is sufficient to reduce 1 g of palladium to metal by the reaction:

$$Pd^{2+} + 2N_2H_4.H_2O \rightarrow Pd^{\circ} + 2H^{+} + 2NH_3\uparrow + N_2\uparrow + H_2O$$

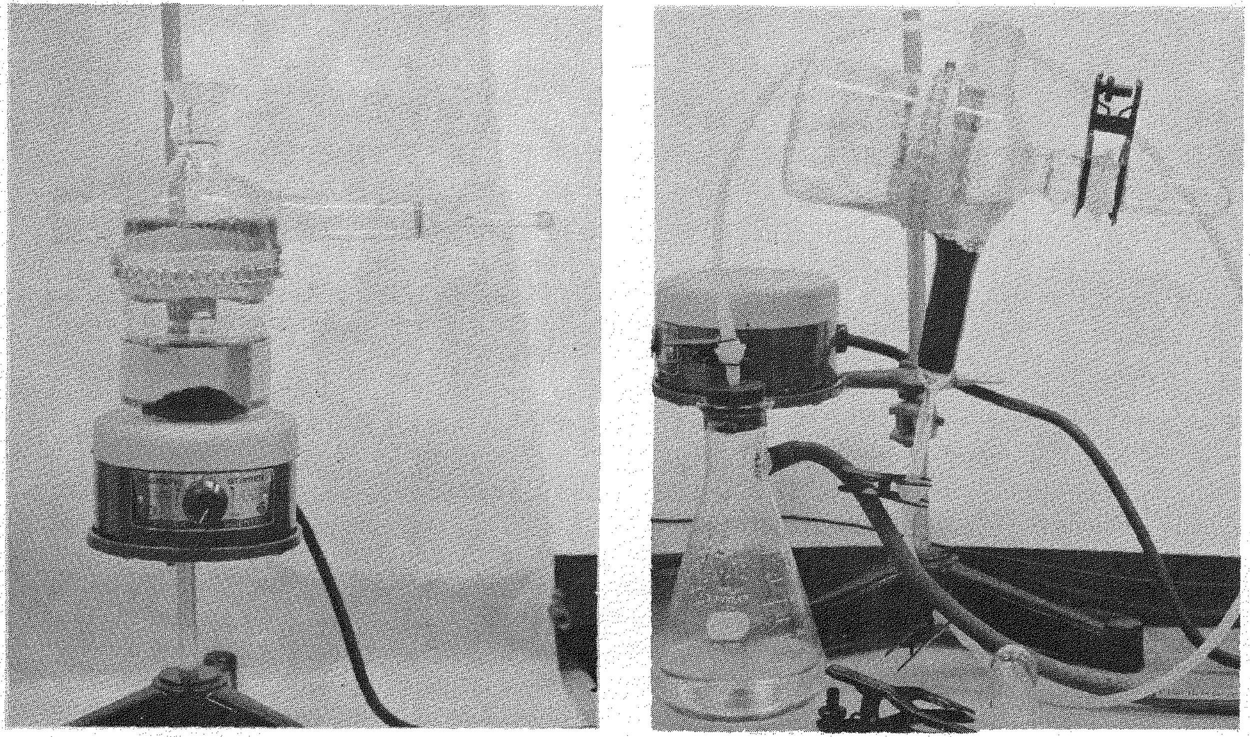
Excess hydrazine hydrate will cause bubbling and should be avoided. The addition of hydrazine hydrate will cause the agglomerates of oxalate particles to disperse. Chemical reduction of transition element impurities in the ^{252}Cf feed may cause a noticeable change in color of the liquid in the plating apparatus as hydrazine hydrate is added.

After the addition of hydrazine, a solution of palladium salt e.g., tetramine dinitrate (1 g Pd^{2+} equivalent in 50 ml of distilled water), is poured into a dropping funnel above the plating apparatus (Figure 2b). The desired quantity of palladium solution is added dropwise (10 to 20 ml/min) to the plating apparatus while the oxalate particles are suspended by stirring. The hydrazine reduces the palladium ion to palladium metal, which plates onto the suspended oxalate particles. The coated particles form agglomerates, which settle to the bottom of the plating apparatus when stirring is stopped (Figure 2c). When all the palladium is reduced to metal, the liquid appears clear. Some bubbling and agitation



a. Precipitate Cf-Sm oxalate

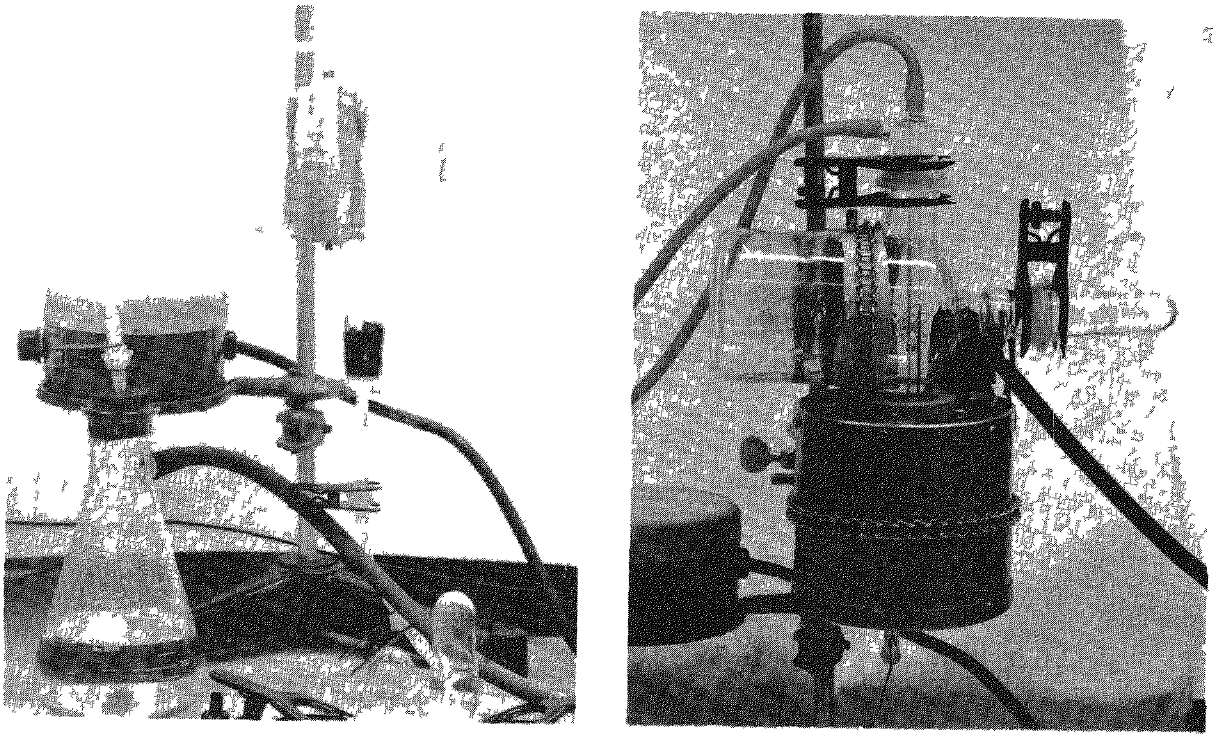
b. Chemically coat with Pd



c. Allow coated particles to settle

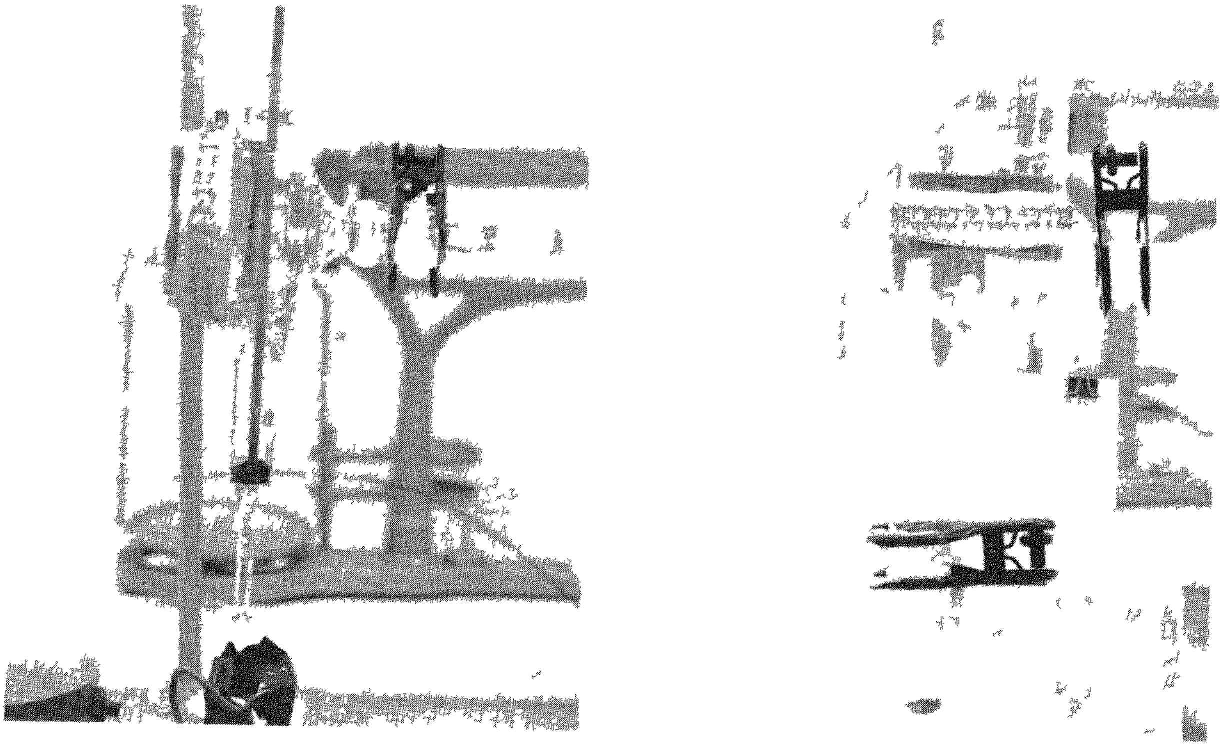
d. Filter

Figure 2. PALLADIUM COATING PROCESS



e. Wash powder

f. Dry powder at ∿200°C



g. Break up filter cake

h. Transfer to die after calcining at 400-500°C

Figure 2 contd. PALLADIUM COATING PROCESS of the coated particles may occur because of continuing hydrazine decomposition.

A standard palladium plating salt, the tetrammine dinitrate, $Pd(NH_3)_4(NO_3)_2$, is preferred for the chemical plating process. This salt, which contains 36% palladium equivalent, is completely soluble in water and forms a pale yellow solution. During plating of the oxalate particles using this salt, noticeable plating of the apparatus and stirring bar occur. However, the weight fraction of this palladium is insignificant, and most of the thin coating on the glassware peels off during stirring and is processed along with the coated particles.

Chemical plating is possible using palladium dinitrate, $Pd(NO_3)_2$, in water. This salt decomposes with time, apparently stimulated by exposure to light in moist air and water, leaving varying amounts of an insoluble palladium compound, probably oxide, which does not enter into the plating process. This insoluble material is reduced to palladium metal by the hydrazine hydrate or calcining and apparently does not interfere with subsequent fabrication. However, use of the palladium tetrammine dinitrate plating salt is recommended over palladium dinitrate because of the former's better chemical stability and complete solubility, which facilitates better control of plating and palladium content of the cermet.

Other water-soluble palladium salts exist but these have not been tested. Soluble salts which contain halides or sulfur should not be used because of possible formation of volatile oxyhalides or embrittlement of palladium by sulfur. Palladium oxide hydrate, $PdO \cdot H_2O$, may serve as an alternative to palladium tetrammine dinitrate. Plating with noble metals other than palladium can be accomplished, if needed, by substituting water-soluble salts of the desired noble metals for the palladium compounds.

Filtering and Drying

The coated particles are separated from the liquid by filtering. The stirring bar is removed, and the apparatus is turned so the coated particles flow into the filter (Figure 2d). Distilled water (>300 ml) is used to rinse all the powder onto the filter and remove oxalic acid and hydrazine hydrate. The liquid is drawn by vacuum through the filter into a flask (Figure 2e). The combined filtrate and wash solution is analysed for ^{252}Cf.

The powder on the filter is dried by heating at 200-220°C in argon flowing at 100 cc/min. A tube furnace is brought to the filter arm so that the powder cake is in the center of the heat zone (Figure 2f). A chromel-alumel thermocouple to measure the temperature is inserted from below through the filter outlet until it touches the bottom of the filter frit. The ports on the plating apparatus are capped. Then the system is swept with argon at about 1 cfh and purged for about 30 minutes before heating is begun. Moisture driven off by heating will condense inside the apparatus and gradually disappear as it is carried off in the argon flow. The gas flow is exhausted through an anti-feedback bubbler. Heating is continued until all moisture has been removed from the apparatus. Drying usually takes 8-16 hours.

The friable dried powder cake on the filter frit is broken up to ensure subsequent passage of the powder through the die-loading funnel. The furnace should be removed so this operation may be observed. A stainless steel rod with a chopper blade on one end ("chopper rod"), is inserted into the filter arm through the gas inlet port and repetitively pressed through the filter cake until sufficiently small particles are obtained (Figure 2g). Generally the filter cake crumbles when touched. Moisture in the powder may cause the powder to stick to the chopper rod. If this occurs, the powder should be redried.

Fine particles caused by high acid content (greater than 0.3N) of the ^{252}Cf feed or by a high drying temperature (above 250°C) may cause a hard filter cake to form. In this case, the filter cake should be pulverized in the beaker portion of the apparatus rather than on the filter frit.

Calcining Oxalate Cermet to Oxide Cermet

The oxalate in the pulverized filter cake is converted to oxide by heating at 15°C/min to 450-500°C. The cake is held at this temperature for 30 minutes in a 4% H_2 - 96% He atmosphere. The mixed gases flow at 100 cc/min through an anti-feedback bubbler. The conversion equation is:

$$M_x(C_2O_4)_y \cdot ZH_2O \rightarrow M_xO_y + yCO\uparrow + yCO_2\uparrow + ZH_2O\uparrow$$

The furnace and thermocouple are used as in the drying step (Figure 2e). After calcining, hydrogen absorbed in palladium during cooling below 200°C can react exothermally with oxygen when the cermet powder is subsequently exposed to air. This reaction can heat the powder high enough to oxidize some of the palladium:

$$Pd \cdot xH_2 + 1/2(x+y)O_2 \rightarrow xH_2O + yPdO + (1-y)Pd$$

(This reaction will not occur in the inert atmosphere in the TFF.) Since palladium oxide (PdO) will interfere with densification of the cermet during pressing and sintering, this hydrogen-oxygen reaction is avoided by changing to argon flow on cooling to 200°C after calcining. This prevents hydrogen absorption in the palladium powder.

Pressing and Sintering into a Billet

The chopper rod is used to loosen the calcined cermet powder on the filter frit. The plating apparatus is rotated and gently shaken so that the loosened powder flows into the transfer tube (Figure 2h). The calcined powder should be pressed into a pellet within 6-8 hours of heating because the fine particles tend to absorb moisture, which interferes with subsequent compaction and sintering. The powder should be kept at 100°C in dry argon if it must be stored for more than 8 hours before pressing into a pellet.

The cermet powder is loaded from the transfer vial into a die (Figure 3) which has been cleaned and lubricated with a slurry of 0.8 g *Sterotex** in 50 ml of carbon tetrachloride (CCl_4). The die is made of hardened tool steel and has an inside diameter chosen to produce a pellet with a length-to-diameter ratio of 1 to 2 at 50% theoretical density. The powder is poured into the die through a stainless steel funnel, which is then vibrated with a vibratory engraving tool to transfer all of the cermet powder into the die. The top ram is inserted, and the loaded die is placed in the press.

A pressure of 15 kpsi will produce a compact with sufficient strength to be handled. Higher pressures cause laminations which may lead to cracking during subsequent fabrication. The compact is ejected from the die by removing the base plate and bottom ram, setting the die on a split ring, and pushing the compact down with the top ram.

The as-pressed compacts have 40-50% of theoretical density. They should be handled carefully with tweezers to avoid breakage. Glass vials should be used for transfer and storage. Compacts should be stored in a dry atmosphere or at ∿100°C in a nonoxidizing atmosphere to prevent absorption of moisture, which can cause surface cracking and swelling.

---

* Tradename of powdered vegetable oil used as a mold release agent. Supplied by Capital City Products Co., Columbus, Ohio.

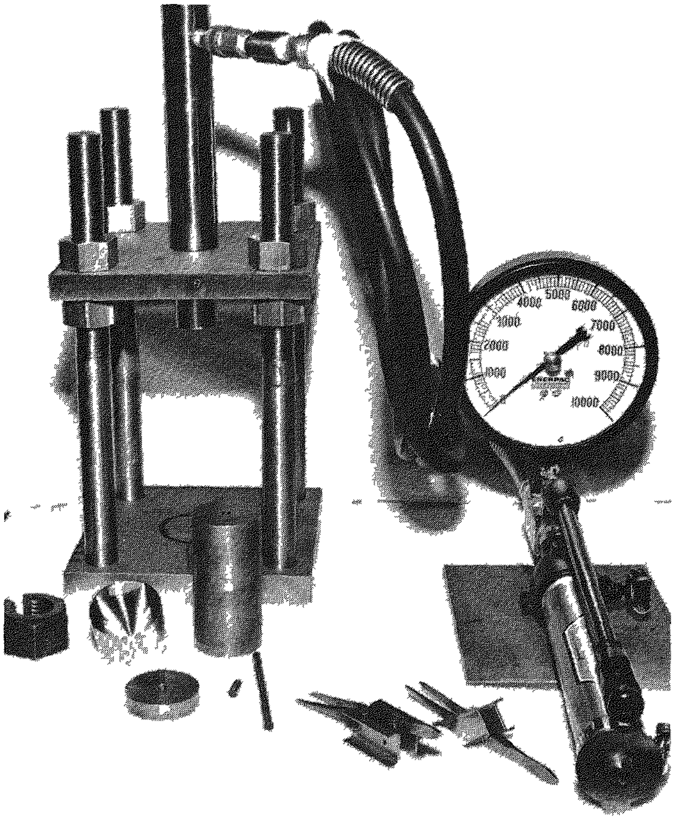


Figure 3. PRESS AND DIE ACCESSORIES. A. Press, B. Die, C. Rams, D. Base Plate, E. Funnel, F. Split Ring

The as-pressed compact is sintered in flowing argon (99.995% purity) at 1300°C for $\geqslant 2$ hours to produce an 80-90% dense pellet that can be easily handled and formed into a wire. The compact is set on an alumina substrate (Figure 4) that is dusted with palladium powder to prevent contact between the compact and the alumina and to reduce drag during shrinkage that could lead to a flared billet. The compact is heated slowly (at least 2 hours) to 1000°C in 4% H_2 - He flowing at 1 cfh, then heated in flowing argon to 1300°C, and held at 1300°C for at least two more hours. The hydrogen ensures conversion of any remaining salts to oxide and prevents formation of palladium oxide, which is unstable above 800°C. Argon ensures no reoxidation of palladium or hydrogen uptake in palladium on cooling. If the compact is heated too rapidly, the porosity will be closed on the surface, and the center will contain trapped gas that could cause cracking during wire forming. After cooling the sintered compact below 200°C in flowing argon, it is ready for the wire forming operations.

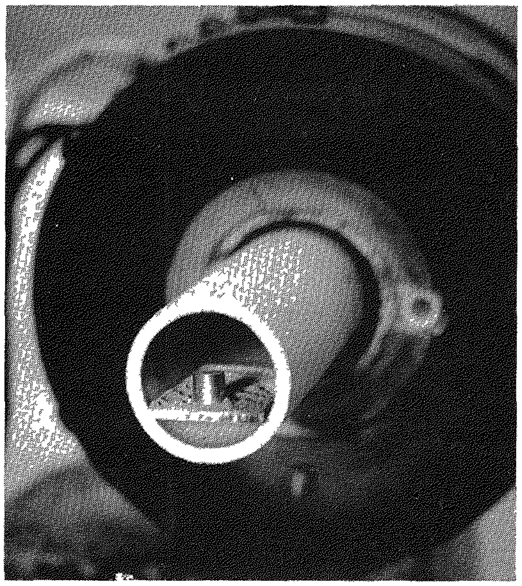


Figure 4. LOADING OF COMPACT INTO SINTERING FURNACE

Rolling

A sintered compact or billet is formed into a 0.040-in. square wire by rolling it in a Model 27B *New Town** wire rolling mill (Figure 5). The mill features a high-torque, reversible, slow-speed drive and is mounted on casters to allow rotation to feed the wire into the grooves from either side. A gear on top of the mill adjusts the separation of the two rolls. Grooved aluminum trays position the billet and wire for entry into the grooves in the mill. The square cross section, rather than round, facilitates control of flashing, and the wire is rotated 90° after each pass to compact the flashing.

Each groove produces a 30-40% reduction in area. Six passes of approximately 5% reductions are made through each groove starting with groove #3 for a 0.2-in.-diameter billet through groove #11 (0.042 in.) with the wire being turned 90° and the ends reversed after each pass to keep the wire square. The wire is annealed in flowing argon (to minimize oxidation) at ∿850°C for 10 minutes after rolling through each groove to relieve induced mechanical strain. Wire sizes down to 0.030 inch may be made as shown in Table VI. The most-precise method of rolling to a specified cross section is to precalculate the length of wire necessary (proportional to the desired cross section and the amount of palladium invested in the feed) and then roll to that length.

---

* Product of New Town Machine and Tool Co., Inc., Brooklyn, N. Y.

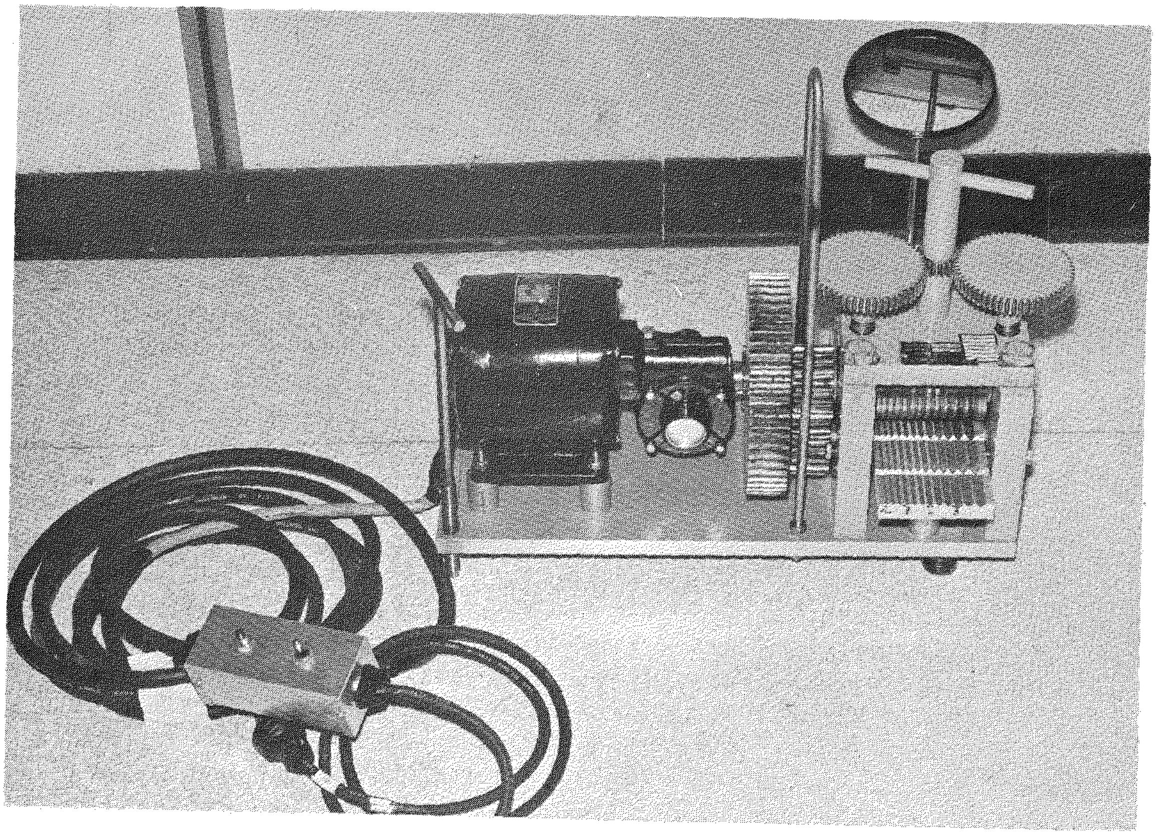


Figure 5. WIRE ROLLING MILL WITH GROOVED GUIDE PLATES

TABLE VI. SIZES OF ROLLING MILL GROOVES

Groove No.	Finished Wire Cross Section, in.	Area Reduction, % Cumulative	Area Reduction, % Groove-to-Groove
3	0.160	--	
4	0.134	29.9	29.9
5	0.114	49.2	27.6
6	0.094	65.5	32.0
7	0.082	73.7	23.9
8	0.068	81.9	31.2
9	0.060	85.9	22.1
10	0.048	91.0	36.0
11	0.042	93.1	23.4
12	0.030	96.5	49.0

Roll Cladding of Bare Cermet Wire

Bare cermet wires with high linear concentrations of ^{252}Cf can be roll clad in palladium tubing to reduce the concentrations to a desired lower loading without affecting linear uniformity. Round palladium tubing, typically, 0.180-in. O.D. x 0.040-in., is rolled in the wire rolling mill into a square configuration with an inside dimension large enough to receive the bare cermet wire. A measured length of bare wire is inserted into the square sheath, and the assembly is rolled through the mill to reduce the core to a precalculated desired cross section. The core can be reduced to 0.010 in. (89% area reduction). An even smaller core can be rolled if additional palladium sheathing is utilized.

Analyses of Cermet Sources

A gamma autoradiography technique was developed to evaluate the uniformity of the linear dispersion of ^{252}Cf in the wire. Sheathed wires are autoradiographed to determine the core location in the sheath. A piece of active core is put on one end of the wire and is then photographed, autoradiographed, and photographed again. The photograph and radiograph are then measured to determine the core location.

Autoradiographs are made with *Kodak*[a] Spectrum Analyses No. 1 plates that are sensitive to soft gamma rays. A 0.025-in.-thick stainless steel sheet is inserted between the wire and the plate for X-ray absorption to improve resolution. The plates are in a plastic bag and are pressed down on the wire for a predetermined time, for example, 2 seconds for a linear concentration of 500 μg/in.

Densitometer measurements are made on the exposed plate at 1/8 in. intervals. The measurements are converted to percent absorption, and the data are statistically reduced to determine average variation. The decrease in exposure within 1/8 in. of the end of the wire precludes analysis of uniformity for the last 1/8 in. on each end. This discernible end defect is equal to the core diameter and is not uniform and should be cut off prior to shipping. A typical roll clad product is shown in Figure 1 together with a typical autoradiograph and graph of densitometer measurements.

Pellets and wires are assayed within ±3% in a neutron counter to determine the total amount of ^{252}Cf in the sources.

---

[a] Tradename of Eastman Kodak Inc., Rochester, NY.

Recovery of ^{252}Cf from Cermet

A nitric acid anion exchange system is used to recover ^{252}Cf from californium oxide-palladium cermet. The powder, pellet, or wire is dissolved in hot concentrated nitric acid containing a trace of hydrochloric acid. The solution is adjusted to about a 20-ml volume with 0.1N nitric acid and passed at room temperature through a glass column containing 100 ml of *Dowex** 1-X8 (200-400 mesh) resin. The solution flow rate is 3 ml/minute. The column is washed with 6N nitric acid. All of the ^{252}Cf should be recovered in the first three bed volumes; the palladium content should be less than 1 μg/ml. After denitration, ^{248}Cm can be separated from the ^{252}Cf by pressurized elution development chromatography with alpha hydroxyisobutyrate.[1]

Expected Product Yields and Losses

A one gram californium oxide-palladium cermet wire with 0.040-in.-square cross section should be about 3-3/8 in. long. The wire should contain 80 to 90% of the ^{252}Cf in the shipping package. Losses of ^{252}Cf are expected to be as follows:

Type of Loss	^{252}Cf Loss	Recoverability
Shipping Package	1%	If sufficient quantity
Frit	0-7%	Yes
Filtrate	0-5%	If sufficient quantity
Press & Sinter	0-2%	No
Rolling	2-3%	No
Splintered ends	0-10%	Yes

Only losses in the shipping package and filtrate affect the Cf/Pd ratio so that the ratio can be fabricated within 95% of the desired composition. The other losses affect the californium and palladium recovery equally and affect only the length of the wire.

---

* Registered trademark of Dow Chemical Co., Midland, Michigan.

Process Scale-Up, Variations, and Limitations

The processes described above have been demonstrated for batch sizes from 40 µg to 1200 µg ^{252}Cf and about 1 g palladium to produce 1-1/2- to 6-in. lengths of bare and roll-clad wire. These wire sources contain 1 to 500 µg ^{252}Cf per inch of square wire, ranging from 0.030- to 0.100-in. in length on each edge. The processes can readily be scaled up to anticipated maximum batch sizes of 50 mg ^{252}Cf for large scale production of industrial sources, and scaled down to submicrogram quantities of ^{252}Cf per inch for medical sources. The process parameters most sensitive to the scale of operations are:

1. Nitric acid concentration above 0.5M in ^{252}Cf feed increases the solubility of the oxalate precipitate and hence increases the amount of ^{252}Cf lost to the filtrate.

2. Higher acidity than 2M in the ^{252}Cf feed will cause the palladium coating to form a sludge of palladium nitrate which is difficult to filter. A hard filter cake may also form.

3. Terbium carrier may not be needed for more than 2 mg batches of ^{252}Cf.

4. Loss of ^{252}Cf to the filtrate may occur if sufficient time (30 minutes) is not allowed for the oxalate to precipitate before plating.

5. Oxalic acid concentrations above 40 mg/mg of ^{252}Cf will cause palladium to precipitate as the oxalate rather than form a metallic coating on the suspended californium oxalate particles. This is the reason Pd^{2+} must be added to the oxalate-hydrazine slurry rather than adding hydrazine to the Pd^{2+}-oxalate slurry.

6. Concentrations of 85% hydrazine hydrate above 10 ml/g Pd will cause bubbling that interferes with settling of the powder and filtering of the palladium-coated particles.

7. Insufficient rinsing (with less than 300 ml of distilled water) of the filter cake will cause the particles to agglomerate during pulverization. Residual oxalic acid and hydrazine will cause blisters to appear on sintered pellets.

8. Calcining above 500°C will cause the borosilicate glass filter frit to deteriorate.

9. Pressing above 15 kpsi will cause pellet laminations which may induce cracking during rolling.

10. Rapid heatup during sintering (less than 2 hours to 1300°C) causes entrapment of gas in the palladium matrix and reduces the density of the sintered pellet.

11. Increasing the amount of impurities in ^{252}Cf feed will affect the maximum loading of ^{252}Cf in cermet (as shown in Figure 6) by contributing more to the 2.5 vol % total oxide limit.

12. Specific ^{252}Cf feed impurities, such as silicon, phosphorus, and sulfur, form low melting eutectics with palladium which may distort the cermet billet shape during sintering and annealing above 800°C.

Other forms than wire can readily be fabricated. The rolling mill can be used to supply bare (or sheathed) square configurations from nearly the diameter of the billet down to about 0.030-in. square. Core thicknesses down to 0.001 in. with good uniformity have been demonstrated. The maximum length of wire that can be conveniently fabricated in the rolling mill is about one foot. Swaging and drawing operations are being developed to make longer clad wires. Contamination-free pinch-cutting of clad wire has been demonstrated. Sheet might be rolled using a suitable rolling mill.

Cermet with heavier loadings than 2.5 vol % total oxide (1 mg ^{252}Cf/in.) should not be fabricated by rolling (Figure 6) unless the density of the billet is increased significantly above the present 90% level. Lighter loadings of ^{252}Cf than 1 μg/in., for example, down to nanograms/in. [10^3 n/(sec-in.)] or less, can be fabricated provided the concentration in the billet is sufficiently low and terbium carrier is added. Based on demonstrated technology with rare earth stand-in, loadings up to 25 mg ^{252}Cf per gram of palladium can probably be fabricated as sintered pellets of about 80% theoretical density. These pellets will be brittle and cannot be rolled into wires. The ^{252}Cf density in such a pellet is limited by the potential degradation of the cermet by pressure from helium decay gas.

A californium-palladium metal alloying technique has been demonstrated with 50 μg ^{252}Cf/in. of palladium wire as an alternative means to recycle scrap into usable wire.[1] Alloying is effected by carbothermic reduction of oxide cermet under an helium - 4% hydrogen atmosphere in the presence of molten palladium. The product globule can be rolled readily into wire.

Cermet forms containing 10-50 mg ^{252}Cf generate enough heat to cause some concern about surface temperatures. At 40 watts(th)/g for pure ^{252}Cf, 10-50 mg ^{252}Cf produces 0.4 to 2 watts(th). Similar experience with an equivalent amount of heat from ^{242}Cm [1.2 watts(th) from 10 mg] showed surface temperatures of about 100°C in air for 1 g pellets of curium oxide-palladium cermet. Wires formed from this material were at sufficiently high temperature to melt plastic bags containing film plates during radiographic analyses. Paper towels were scorched. There is no problem of oxidation; however, the pellets and wires should not be stored or handled in plastic containers or in an effective insulating medium.

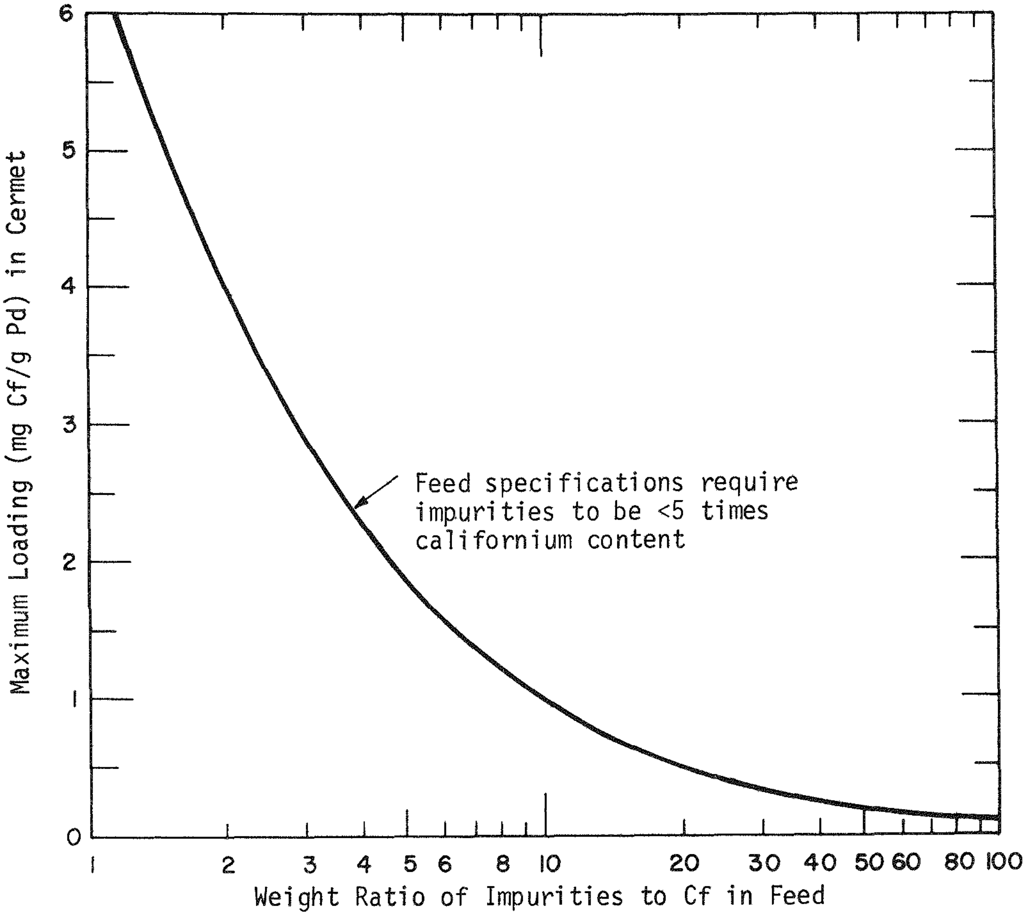


Figure 6. MAXIMUM LOADING OF CERMET (mg Cf/g Pd) THAT CAN BE ACHIEVED WITHOUT EXCEEDING FABRICABILITY LIMIT OF 2.5 vol % TOTAL OXIDE

Improvements to Process Equipment

The techniques used to demonstrate the chemical plating and wire rolling processes can be used for limited production. Some of the equipment should be redesigned or replaced for routine production in the interest of increased efficiency, yields, and safety. Two primary areas for improvement are better control of powder for pellet fabrication and an automated rolling mill. Listed below are the recommended alterations:

1. Develop a contained or shrouded powder transfer device from filter beaker into die to minimize dusting in the cell. Perhaps a Tesla coil (high-frequency oscillator) could be used to transport powder from the frit into the funnel rather than shaking the apparatus.

2. Use stainless steel rather than glass funnels that attach to the top of the die to provide a larger inside dimension and minimize breakage and loss of powder.

3. Redesign the die so that the base plate is attached to the die during handling. The die should also have a manipulator groove cut in the center of it for ease in handling.

4. Replace the present press with a model better suited for remote operation.

5. Eject the compact up rather than down to avoid dropping the compact.

6. Replace the platinum-rhodium sintering furnace (1400°C max.) with a model more convenient for remote use.

7. Replace the calcining furnace with a clam-shell type furnace (600°C max.) for ease of handling during drying and calcination of powder.

8. Replace the rolling mill with a model to facilitate positioning of wire in proper groove and retrieval after each pass through the rolls. This is presently the most tedious operation.

9. A device for inserting a bare wire into a cladding tube would facilitate remote production of clad wire in shielded cells. A method for locating the cermet core within the clad wire using fiducial marks on the autoradiograph is needed to ensure proper cutting.

PROCESS SAFETY

The primary safety concern in the production of cermet wire is containment of fine cermet powders during pellet fabrication. A total of 5.5 mg of ^{252}Cf was processed in the TFF in the cermet development program in a 300 ft^3 cell with an argon flow of 100 cfh, under conditions where powder was handled in the open and even spilled without detecting increased background activity on the cell exhaust filters. However, powder aerosols may form in containment cells with air atmospheres and large air flows, e.g., 250 cfm. Powder must be contained within the process equipment. A separately filtered off-gas system may be necessary to meet this requirement.

The chemically plated cermet powder consists of agglomerates of particles with average diameters as small as 0.1 μm. The texture of the filtered and dried cermet powder may be as fine as lamp black, if the friable cermet cake is broken up extensively to transfer it into a die. High Efficiency Particulate Air (HEPA) filters have efficiencies of 99.97% for >0.3 μm particles and 99.8% for >0.1 μm particles. It is possible that some small cermet particles could pass through the first filter; however, these would probably be retained on the second filter.

The process requires the use of high temperature, resistance-heated furnaces for drying, calcination, sintering, and annealing. The fire hazard associated with use of high temperature furnaces is higher in cells with an air atmosphere than in the present process development cells with inert gas atmosphere. Combustible material and manipulator boots should be removed from the vicinity of furnaces during heating. Fire extinguishing equipment should be available during heatings.

There are no flammable chemicals, gases, or materials in the process. The corrosive liquids (concentrated nitric acid used to dissolve cermet for recovery and hydrazine reductant used in admixing californium and palladium) should be put into the cells as needed and in limited quantities in capped polyethylene bottles. Mechanical hazards are minor and include pinch points in the press and the rolling mill and glass breakage.

PROPERTIES OF CALIFORNIUM OXIDE-PALLADIUM CERMET WIRE

The chemical and physical properties of californium oxide-palladium cermet wire are a combination of those of the palladium and californium mixed oxide components. The properties of palladium are listed in Table I. The properties of the refractory oxide phase in the cermet cannot be predicted exactly because of variations in impurity ion composition; californium oxide is often a minor constituent. However, the high-fired oxide is refractory and is similar to mixed oxides of lanthanide and actinide metals.

Palladium is resistant to oxidation and corrosion.[6] Superficial oxidation of cermet wire will occur at 400 to 800°C but not at higher temperatures, because palladium oxide is unstable above 800°C. Significant corrosion occurs only in strongly oxidizing chemicals such as nitric acid, hot sulfuric acid, ferric chloride and hypochlorite solutions, chlorine, bromine, iodine, and hydrogen sulfide (at greater than 600°C). No reactions are expected between palladium and stainless steels or zirconium up to 1000°C nor have any reactions been observed between the mixed oxide phase and palladium up to 1300°C.

The melting point of californium oxide-palladium cermet is expected to be close to that of pure palladium (mp = 1552°C). Volatility of the californium oxide is expected to be insignificant up to 1000°C where the oxide vapor pressure is estimated to be $\sim 10^{-12}$ torr. No transport of ^{252}Cf from cermet has been observed during sintering at 1300°C in argon or in hydrogen-helium gas mixtures.

Neutron and gamma spectra from californium oxide-palladium cermet wire sources have been measured and have spectra similar to those for oxide sources in platinum-rhodium capsules. The gamma spectrum has considerably fewer interfering peaks than for oxide sources encapsulated in stainless steel capsules.

The mechanical properties of californium oxide-palladium cermet wires are expected to be the same as those measured for samarium sesquioxide-palladium cermet wires with equivalent total oxide contents. Elongations of 3-14% are to be expected (Figure 7). The ultimate tensile strength should vary between 20,000 and 40,000 psi depending on the total oxide content of cermet (Figure 8). Yield strengths between 9,000 and 17,000 psi are typical and are not affected significantly by oxide concentration (Figure 9). Hardness (DPH) will increase with oxide content from about 50 for pure palladium to about 80-100 for annealed cermet wire with up to 7.5 vol % oxide (Figure 10). Cold working can increase cermet hardness up to a DPH of 200.

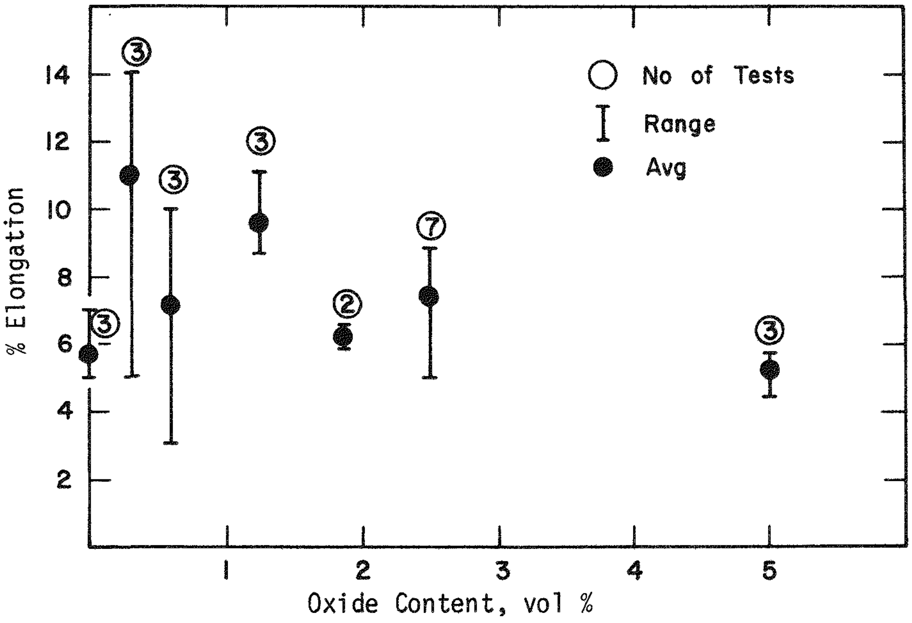


Figure 7. DUCTILITY OF Sm_2O_3-Pd CERMET

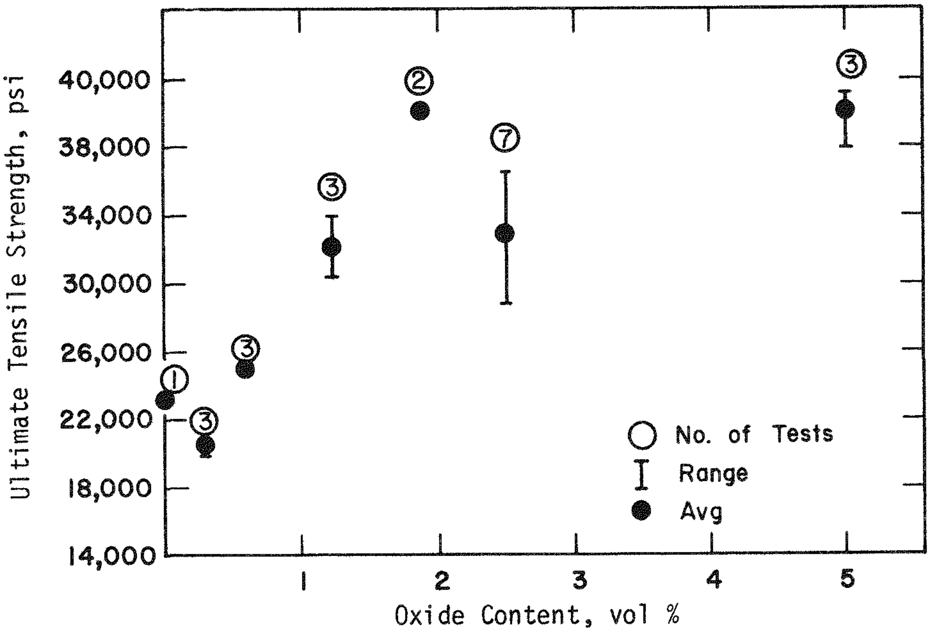


Figure 8. ULTIMATE STRENGTH OF Sm_2O_3-Pd CERMET

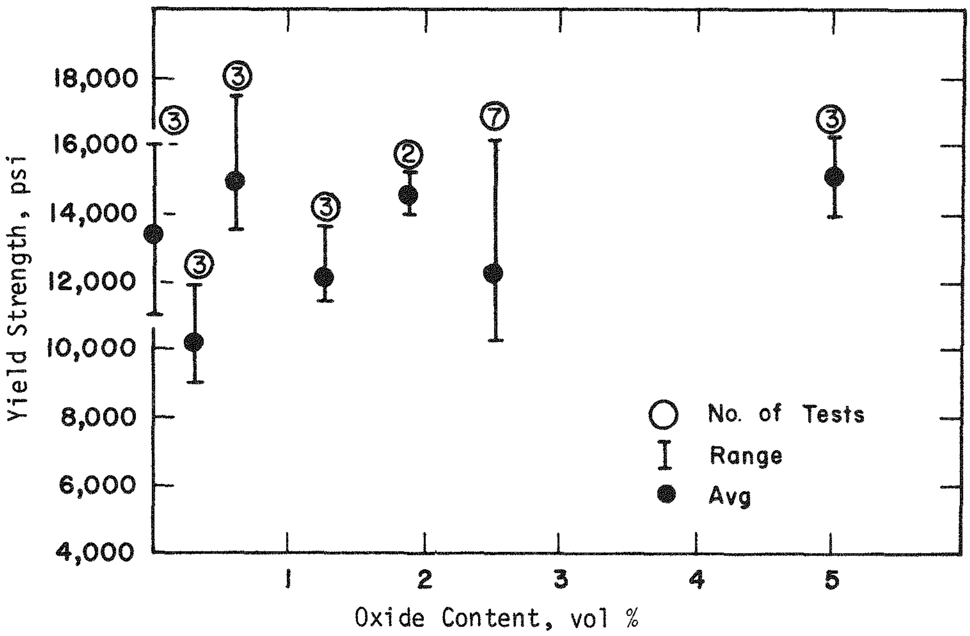


Figure 9. YIELD STRENGTH OF Sm_2O_3-Pd CERMET

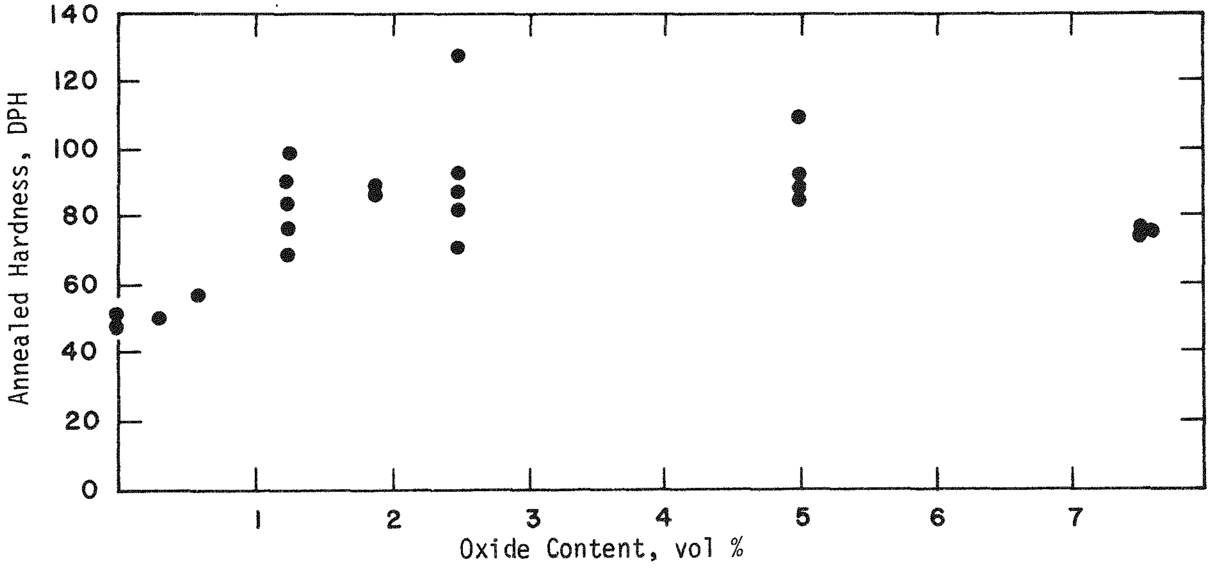


Figure 10. HARDNESS OF Sm_2O_3-Pd CERMET

Significant radiation embrittlement of californium oxide-palladium is not expected for fabricable concentrations (less than 0.1 vol % $^{252}Cf_2O_3$) for 10 year lifetimes. Wires containing about 0.1 vol % ^{252}Cf have been aged for nine months to produce a gas volume 0.5 times the solid volume without evidence of embrittling effects on rolling with or without annealing. Cermet wires made with ^{242}Cm became embrittled during aging at room temperature to produce a helium volume 1.6 times the solid volume. Annealing at 850°C and 1050°C restored the ductility of the cermet and produced no changes in the microstructure.

APPENDIX.

EARLY PRODUCTION EXPERIENCE FOR ^{252}Cf OXIDE – PALLADIUM CERMET

INTRODUCTION

Production of ^{252}Cf oxide-palladium cermet wire using the chemical plating process was demonstrated successfully during development in the Target Fabrication Facility (TFF). However, when production began with slightly modified equipment and procedures, some sintered cermet pellets stuck to the alumina tube during sintering at 1300°C, had an irregular configuration, exuded a glassy phase, and were too porous and brittle for successful wire fabrication. These problems, first attributed to impurities in the ^{252}Cf feed, also occurred with some pellets made in the containment cell with only terbium stand-in (Figure A.1), but not with pellets made in the laboratory with the same chemicals. While changes were being made to cell equipment, and procedures were modified to eliminate these problems, the causes of the problems were determined by analyses of the brittle pellets with terbium stand-in, and laboratory cell simulation of the cell procedures.

SUMMARY

The major cause of the ^{252}Cf oxide-palladium cermet fabrication problem was contamination by glass which was apparently introduced into the cermet by abrasion or chipping of the glass apparatus by the glass-covered stirring bar. The glass impurity resulted in slumping and exudation of a glassy phase during sintering of cermet compacts. Embrittlement of the cermet prevented successful coining and rolling of pellets. Use of a *Teflon**-covered stirring bar and a stir plate with better speed control (along with other changes to cell equipment and procedures) eliminated the glass contamination. A secondary problem of insufficient densification of cermet pellets sintered in the containment cell was attributed to a furnace malfunction that caused the thermocouple monitor to indicate a sintering temperature ∿200°C higher than the actual temperature of the compact. The data in Tables A.I and A.II represent the effect of variations in sintering temperature, pressing pressure, californium or terbium content, and process materials on the quality of manufactured cermet pellets.

---

* Tradename for polytetrafluoroethylene resins; assigned to E. I. du Pont de Nemours and Co., Wilmington, Delaware.

DISCUSSION

Changes to Cell Equipment and Procedures

Abrasion and chipping of the precipitator that occurred with a glass-covered stirring bar are thought to be the primary sources of glass contamination. A *Teflon*-covered stirring bar and a new stir plate with improved speed control were substituted. The fine filter was removed from the drying tube so that impurity particles trapped on the frit during filtering would not drop back into the cermet powder during drying or calcining. The chemically plated powder was rinsed with ∿300 ml of distilled water rather than with the ∿50 ml used in previous in-cell production. Contamination with glass did not occur after these changes were made, and subsequent pellets were acceptable for rolling to produce wire (Table A.I).

TABLE A.I.

RESULTS OF CERMET PELLET FABRICATION IN THE CONTAINMENT CELL WITH TERBIUM STAND-IN

Pellet	Loading, mg Tb	Compaction, kpsi	Diametral Shrinkage, %	Appearance
1	4.2	32	1	Acceptable
2	4.2	32	5	Glassy nodules
3	3.5	16	7.5	Glassy nodules, stuck to Al_2O_3 tube.
4[a]	7.0	15	20	Acceptable
5[b]	7.0	32	4	Acceptable
6	4.2	15[c]	5	Acceptable
7	4.2	14[c,d]	24	Acceptable
8	3.8	17[c,d]	22	Acceptable
9	3.8	16[c,d]	18	Acceptable
10	3.8	16[c,d]	5	Acceptable
11	3.9	14[c,d]	5	Acceptable
12	3.9	14[c,d]	7.5[e] 10[f] 18[g]	Acceptable Acceptable Acceptable

---

[a] Same as Pellet 16 (Table A.II).
[b] Same as Pellet 17 (Table A.II).
[c] Powder rinsed with ∿200 ml of distilled water.
[d] *Teflon* stirrer used. Filter frit not used in precipitator.
[e] Normal sintering cycle; 2 hr at 1300°C.
[f] 4 hr at 1300°C.
[g] Normal sintering cycle plus 2 hr at 1400°C.

Several of the 0.173-in.-diameter cermet compacts made with terbium stand-in were sintered insufficiently and could not be inserted into the 0.150-in.-diameter TFF coining die used for fabricating sized pellets. A malfunction of the furnace caused the compacts to be located outside the hot zone where the temperature was 100 to 300°C below the 1300°C required for proper sintering. Increasing the indicated temperature of the cell sintering furnace to 1400°C produced sufficient pellet densification. A second thermocouple was installed in the sintering tube to measure the temperature near the compact during sintering.

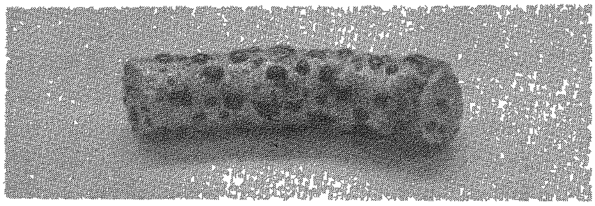
Analyses of Cermet Made in the Containment Cell

A distorted cermet pellet made only with terbium stand-in after sintering in the cell furnace is shown in Figure A.1. The pellet slumped during sintering in a vertical position causing the curvature. Nodules of exuded material covered the surface. Metallographic examination revealed that the pellet contained ∿30 vol % porosity and ∿15 vol % glassy phase throughout. Silicon content equal to the terbium content was detected by spark source mass spectroscopy in both the pellet and the unsintered powder from which it was made. The melting of the glass impurity apparently produced the surface nodules which in turn caused the observed sticking of the pellet to the alumina sintering tube. The large grains in the metal phase are not characteristic of a cermet but indicate that alloying of the palladium matrix with the impurity may have occurred during sintering.

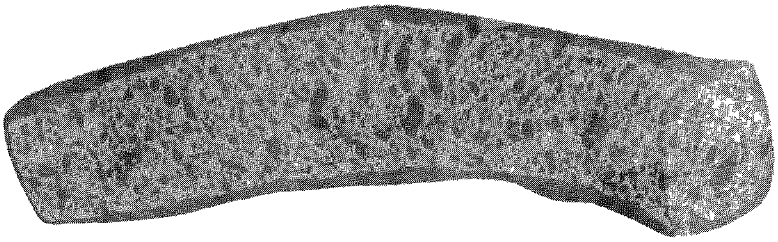
LABORATORY TESTS

Pellets have been made in the laboratory with a glassy phase and surface nodules similar to reject pellets by intentionally adding ∿0.1 g of crushed borosilicate glass per gram of cermet powder. Melting of the glass caused pellets to stick to the alumina sintering tube. A pellet containing ∿10 wt % glass cracked severely on initial rolling (similar to one observed during wire fabrication in the containment cell), while another pellet with ∿1 wt % glass was reduced 70% in cross-sectional area before cracking was detected.

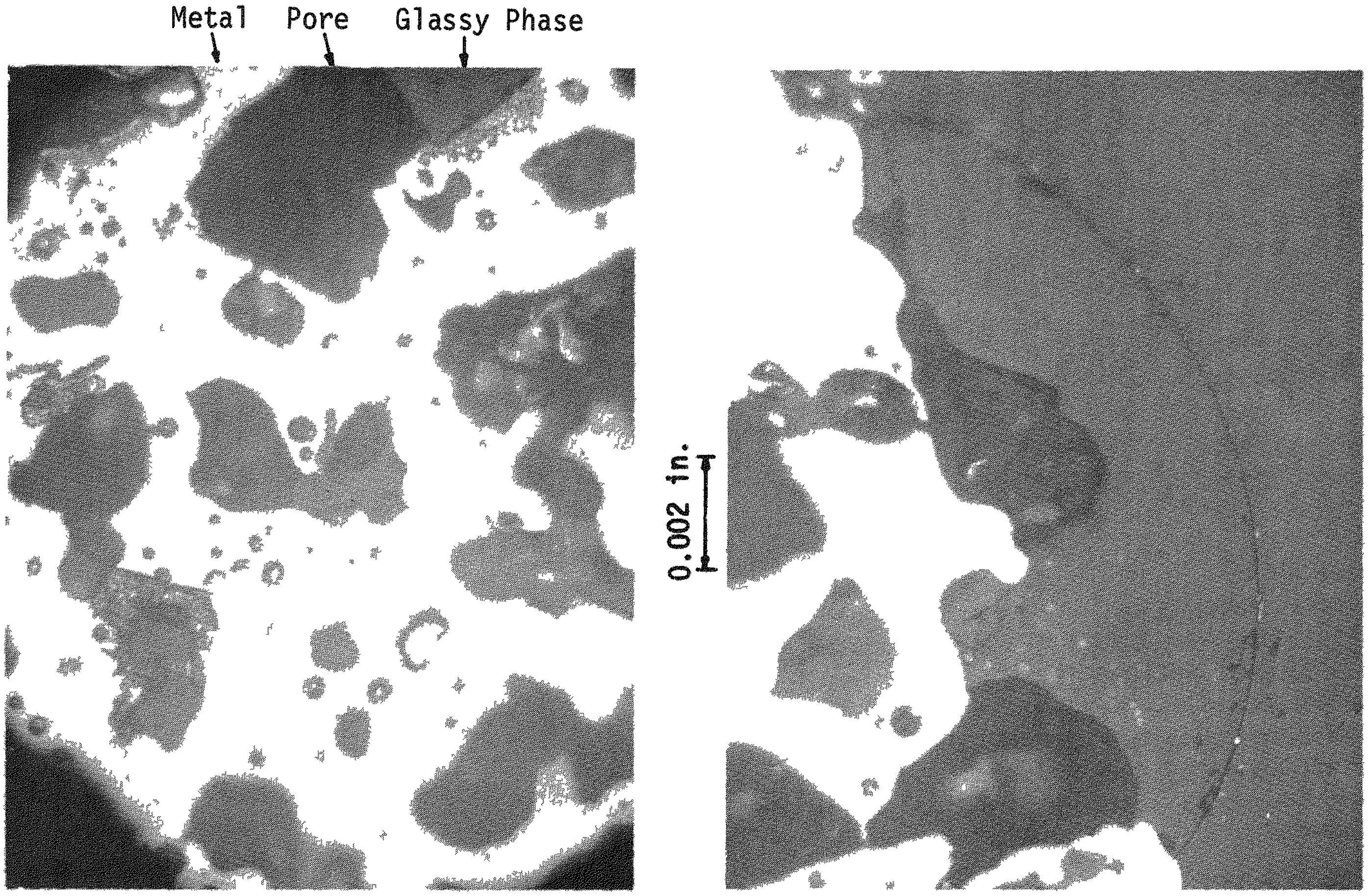
Insufficient densification (shrinkage) of cermet pellets is caused primarily by sintering at too low a temperature. Pellets sintered at less than ~1200°C did not undergo the ~13% diametral shrinkage needed to allow insertion into the TFF coining die for making medical sources. Results of other tests have indicated that impurities in simulated feed, insufficient rinsing of cermet powder, excess *Sterotex* die lubricant, high compaction pressures, initial outgassing of sintering tubes, and possible release of gas on reduction of terbium oxide ($TbO_{1.8}$) have only minor effects on densification of cermet compacts during sintering (Table A.II).



Glassy Nodules on Surface



Polished Cross Section



Interior as Etched

Surface Nodule

FIGURE A.1. PALLADIUM - TERBIUM OXIDE CERMET PELLET (0.543-in.-long)

TABLE A.II.

RESULTS OF OUT-OF-CELL CERMET PELLET FABRICATION

PELLET NUMBER	FABRICATION CONDITIONS	DIAMETRAL SHRINKAGE, %	APPEARANCE
1	1.5 mg Tb as synthetic feed + 3 mg Tb[a]	4	Top half porous
2	3.0 mg Tb as synthetic feed[a]	12	Top tenth porous
3	3.5 mg Tb[a]	7	Top eighth porous
4	1.5 mg Tb as purified synthetic feed[a]	16	Acceptable
5	3.0 mg Tb as purified synthetic feed[a]	11	Top eighth porous
6	3.5 vol % Sm_2O_3, sintered on Pd powder[b]	19	Acceptable
7	2 vol % Sm_2O_3, sintered on vitreous carbon[b]	16	Lamination near top
8a	2 vol % Sm_2O_3, sintered on Pd powder[b]	20	Acceptable
8b	2 vol % Sm_2O_3, sintered on bare Al_2O_3[b]	20	Acceptable
9	2 vol % Sm_2O_3, sintered on bare Al_2O_3[b]	15	Acceptable
10	6.6 mg Tb; 30,000 psi; 1250°C[c]	20	Acceptable, 88% TD[d]
11	6.6 mg Tb; 15,000 psi; 1250°C[c]	27	Acceptable, 84% TD[d]
12	6.6 mg Tb; 20,000 psi; 1150°C[c]	7	Acceptable, 69% TD[d]
13	6.6 mg Tb; 15,000 psi; 1150°C[c]	11	Acceptable, 59% TD[d]
14	6.6 mg Tb; 30,000 psi; 1350°C	15	Acceptable
15	7 mg Tb; not rinsed; 30,000 psi; 1350°C[e]	16	Acceptable
16	7 mg Tb; 15,000 psi; sintered in TFF	20	Acceptable
17	7 mg Tb; 32,000 psi pressed & sintered in TFF	3.5	Acceptable
18	7 mg Tb; not rinsed; 30,000 psi; 1 hr heatup, 2 hr at 1300°C	10	Acceptable
19	7 mg Tb; 12.6 mg ground glass; 30,000 psi; 1300°C	15	Very small glass inclusions, brittle
20	6.6 mg Tb; 0.1 g ground glass; 30,000 psi; 1300°C	10	Stuck to Al_2O_3; glassy nodules on surface
21	6.6 mg Tb; 0.1 g ground *Vycor*; 30,000 psi; 1300°C	12	No surface nodules
22	1 vol % Sm_2O_3; ~29 mg *Sterotex*; 0.09 g ground glass; 30,000 psi; 1300°C	8	Stuck to Al_2O_3
23	2 vol % Sm_2O_3; 0.1 g ground glass; 30,000 psi; 1300°C	5	Stuck to Al_2O_3; glassy nodules
24	2 vol % Sm_2O_3; 30,000 psi; 1300°C in new Al_2O_3 tube	20	Acceptable

---

a. Pellets pressed at 30,000 psi and sintered together in new Al_2O_3 tube at 1350°C.

b. Pellets pressed at 30,000 psi and sintered together at 1350°C.

c. Resintered at 1350°C to ~90% of theoretical density.

d. TD = Theoretical Density.

e. Powder tap density ~25% less than rinsed powder.

REFERENCES

1. *Californium-252 Progress.* No. 1-11. Issued quarterly. USAEC Savannah River Operations Office, Californium-252 Information Center, Savannah River Laboratory, Aiken, South Carolina 29801.

2. *Californium-252. Guide for Fabrication and Handling* ^{252}*Cf Sources.* USAEC Report SRO-153. Savannah River Operations Office, Aiken, South Carolina 29801 (1971).

3. W. C. Mosley, P. K. Smith, and P. E. McBeath. "An Improved Form for ^{252}Cf Neutron Sources: Palladium-^{252}Cf Oxide Cermet." *Trans. Amer. Nucl. Soc.* 15, 228 (1972).

4. W. C. Mosley, P. K. Smith, and P. E. McBeath. "Neutron Sources of Palladium - Californium-252 Oxide Cermet Wire." Presented at *ANS National Topical Meeting on Applications of Californium-252,* Austin, Texas, Sept. 11-13, 1972 (to be published).

5. N. Fuschillo and M. L. Gimpl. "Electrical and Tensile Properties of Cu - ThO_2, Au - ThO_2, Pt - ThO_2 and Au - Al_2O_3, Pt - Al_2O_3 Alloys." *J. Mater. Sci.* 5, 1078 (1970).

6. E. M. Wise and R. F. Vines, editors. *Palladium, The Metal, Its Properties and Applications.* The International Nickel Co., Inc., New York, N. Y. 10005 (1967).