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INFORMAL REPORT

Initial Development and Characterization of Plutonia-Iridium Cermets (PIC)

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by

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INITIAL DEVELOPMENT AND CHARACTERIZATION OF PLUTONIA-IRIDIUM CERMETS (PIC)

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ABSTRACT

An investigation of a Plutonia-Iridium Cermet (PIC) as a candidate radio-isotopic fuel has been initiated at the Los Alamos Scientific Laboratory. Specimens containing 11 to 15 vol% iridium as a continuous phase have been prepared by a multi-step process which includes (1) granulation and prefiring of $^{238}\text{Pu}^{16}\text{O}_2$ to provide a ceramic phase having a selected size distribution usually ranging from 61 to 297μ , (2) comminution of -325 mesh Ir powder to $\leq 5\mu$ particles, (3) coating or mixing the ceramic granules with the metallic particles, (4) hot pressing the mixture in vacuum, and (5) adjustment of the stoichiometry of the oxide by heat treatment in a suitable atmosphere. The resultant microstructures consist of islands of $^{238}\text{Pu}^{16}\text{O}_2$ surrounded by a continuous Ir coating approximately 2 to 5μ thick. Several small pellets, nominally 0.3 in. diameter, have been prepared as well as a 1.5 in. diameter sphere with a ^{238}Pu thermal inventory of 100 watts. The pellets were used for process development, fractography, chemical analyses, metallography, strength measurements, etc. The sphere was fabricated to verify process up-scaling from the pellet development. It was subjected to some thermal testing.

I. INTRODUCTION

The purpose of any radioisotopic heat source is to produce heat for eventual conversion into electrical power. Usable power is then employed in various devices which operate in locations on the earth's surface or in space where more conventional power sources are not effective over long periods of time. The compound $^{238}\text{PuO}_2$ has been frequently used as a source of heat for these purposes. Taking into account the amount of ^{238}Pu actually present in the compound, coupled with the 87.8 year half-life and the determined alpha energies, there is available ~ 0.4 watt/g $^{238}\text{PuO}_2$.

This material is currently employed in two forms by the Space Nuclear Systems Division of the USAEC. One form is a plutonia molybdenum cermet (PMC) disk approximately 2 in. diameter and 0.2 in. thick. From the specified ^{238}Pu content, each disk carries a 40 watt (t) inventory. Stacks of these disks are encapsulated in suitable materials to form the working heat source. The second fuel form currently in use is spherical in shape, 1.465 in. diam, and consists only of $^{238}\text{PuO}_2$. This fuel form is called pure plutonium oxide (PPO). Each fuel sphere is separately encapsulated and arrays of encapsulated spheres are then combined to form the heat source.

Each of the above forms has inherent advantages and disadvantages. The PMC disks have higher thermal conductivity and thermal shock resistance due to the metallic phase. However, disk fabrication requires more elaborate processing and controls because of the multiphase system. Molybdenum is somewhat susceptible to oxidation. The PPO spheres, although lower in conductivity and thermal shock resistance, are fabricated by a much more simple process. Since they are separately encapsulated in Ir, manipulative techniques are not as demanding as with stacks of disks.

The Los Alamos Scientific Laboratory has been assigned the role of advanced fuel form development by the Space Nuclear Systems Division of the USAEC. Therefore, a program was initiated to explore the formation and preliminary characterization of a plutonium iridium cermet. Such a form could combine the best features of PMC and PPO; that is, maintaining the high thermal conductivity and thermal shock resistant qualities of a cermet while substituting the more chemically inert iridium for molybdenum in the metallic phase.

This report describes the conceptual phases of that developmental study. Enough data have been accrued to demonstrate fabrication feasibility and initial characterization. Future studies will augment the properties evaluations so that prudent choices can be made for more advanced heat sources.

II. METHOD OF APPROACH

The preliminary fabrication procedures were dictated by the resultant microstructure of the cermets. A homogeneous dispersion of iridium particles in a $^{238}\text{Pu}^{16}\text{O}_2$ ceramic matrix was not desired. Instead, the microstructure was to consist of relatively large granules of ceramic surrounded by a continuous network of iridium. This microstructure was considered to have several advantages: (1) It provides a path for the release of helium generated from the decay of the plutonium. (2) A continuous metallic phase would have improved thermal properties compared to one consisting of isolated metal particles in a ceramic matrix. (3) The

envelopment of the PuO_2 by oxidation and corrosion-resistant Ir would have beneficial aspects in a re-entry situation.

To achieve the desired microstructure, it was necessary to prepare ceramic granules in an appropriate size range by prefiring cold-pressed agglomerates of PuO_2 powder, to coat the fired PuO_2 granules with Ir powder, and finally to hot press the mixture. A direct cold press and sinter approach was considered but the many unknown variables made hot pressing the favored choice for the initial study. By simultaneously pressing 3 small pellets there was sufficient material to permit adequate product characterization and process variable evaluation. After establishing the desired conditions, the process was scaled-up to produce a 100-watt sphere. The following section describes in detail the procedure used to prepare the plutonia iridium cermets.

III. MATERIALS ACQUISITION AND PREPARATION

A. Iridium Preparation and Characterization

The iridium was received* as 99.5% purity, -325 mesh powder. Spectrochemical data on this powder in the as-received condition are provided in Table I. Small batches of powder (~15 g) were slurried with ethyl alcohol in a tungsten carbide-lined oscillatory mill** and were ground with tungsten carbide balls. The proportions used were 15 g Ir, 15 ml $\text{C}_2\text{H}_5\text{OH}$, and 200 WC balls, each 0.5 cm diam. Milling time was approximately 2 hours per batch.

After the milling, the powder was dried and screened in a Sonic Sifter***. The material > 5 μm in size was recycled, whereas the smaller particles were used in the cermet preparation. Spectrochemical analysis of the comminuted powder indicated some tungsten pick-up occurred. Other milling materials (such as UO_2) are being considered to eliminate this problem.

* Source: Englehard Industries, 429 Delaney Street, Newark, New Jersey 17105

** Pulverit Comminution Equipment (made in Germany by Alfred Fritsch Ohg Laborgeraeterbau 658 Idar-Oberstein 1).

*** Allen-Bradley Model L3P Pulse Type Sonic Sifter, Milwaukee, Wisconsin.

TABLE I
SPECTROCHEMICAL ANALYSIS OF
AS-RECEIVED IRIIDIUM POWDER
(ppm by weight)

Li	< 10	Ni	< 30
Be	< 3	Cu	< 4
B	< 10	Zn	< 300
Na	< 30	Sr	< 30
Mg	< 3	Zr	< 100
Al	< 100	Nb	----
Si	20	Mo	< 300
Ca	3	Cd	< 100
V	< 10	Sn	< 100
Cr	< 30	Ta	< 400
Mn	< 3	W	< 200
Fe	100	Pb	100
Co	< 30	Bi	< 30

TABLE II
TYPICAL CHEMICAL AND SPECTROCHEMICAL
ANALYSES OF MILLED AND O¹⁶-EXCHANGED
PLUTONIA POWDER

Pu	87.8 (wt. %)	Mn	< 2 (ppm)
Th	0.10 (wt. %)	Fe	70 (ppm)
O	11.85 (wt. %)	Co	< 5 (ppm)
Am	0.127 (wt. %)	Ni	10 (ppm)
Np	0.226 (wt. %)	Cu	< 2 (ppm)
²³⁴ U	1.165 (wt. %)	Zn	< 10 (ppm)
C	45 (ppm)	Sr	< 10 (ppm)
²³⁶ Pu	0.63 (ppm)	Mo	< 100 (ppm)
Li	< 4 (ppm)	Cd	< 20 (ppm)
Be	< 1 (ppm)	Sn	< 5 (ppm)
B	< 2 (ppm)	Pb	15 (ppm)
Na	< 50 (ppm)	Bi	< 1 (ppm)
Mg	15 (ppm)	K	15 (ppm)
Al	< 10 (ppm)	Ti	< 50 (ppm)
Si	30 (ppm)	Rb	< 4 (ppm)
Ca	150 (ppm)	Y	< 4 (ppm)
Cr	15 (ppm)	Ba	20 (ppm)

B. Plutonia Powder Preparation and Characterization

The plutonia was received from the Savannah River Laboratory. The as-received material, nominally 7 to 8 μ , was ¹⁶O exchanged by heating to 750°C for 96 hours in an H₂¹⁶O-Ar atmosphere. The ¹⁶O exchanged material was outgassed at 1000°C for 1 hour in the same atmosphere. The ¹⁶O exchanged and outgassed powder was ball-milled for 16 hours in 80 g batches. The material was milled dry at 20 RPM in stainless steel mills. Particle size analysis of the milled powder yielded a mass median diameter granule of 2⁺¹_{-0.6} μ . A typical chemical analysis of the milled powder is provided in Table II.

Recycled oxide provided a second source of PuO₂ feed. This recycled feed was obtained from various PPO spheres which had been originally hot-pressed at 1480°C and had been fabricated during the PPO development program. They were broken, crushed in the oscillatory mill, outgassed and ball-milled for 42 hrs rather than 16 hrs. With this exception, the feed treatments were identical. The particle sizes and chemical analyses of this material were not significantly different from the fresh oxide.

C. Preparation of Plutonia Granules

The exchanged and milled PuO₂ powder was ready for granulation to a selected size range. The PuO₂ powder was dry pressed in hardened steel dies at 50 tsi. The resultant pellets were broken manually and passed through a stack of screens to provide granules in the desired size range (for example, 105 to 295 μ). Material passing through the fine mesh screen was recycled.

The cold pressed, green granules were fired at temperatures from 1075 to 1350°C in CO₂ for 2 hours. This fired granular material was again screened. Table III shows a spectrochemical analysis of a typical lot of prefired granules.

Various size ranges of granules were used as feed material for the hot pressed pellets, but the recommended range from these studies is 61 - 295 μ . Some actual size distributions are provided in Table IV. A slightly higher percentage of fines was obtained from the recycled feed powder due to its previous thermal history and more friable nature.

TABLE III
SPECTROCHEMICAL ANALYSIS OF A TYPICAL
BATCH OF PLUTONIA GRANULES
AFTER PREFIRING

Element	ppm	Element	ppm
Al	70	Mn	8
B	< 1	Mo	2
Ba	4	Na	< 50
Be	< 1	Ni	60
Bi	< 4	Pb	< 4
Ca	100	Rb	< 4
Cd	< 10	Re	< 4
Co	< 4	Si	250
Cr	120	Sn	< 4
Cs	< 20	Sr	5
Cu	< 2	Ta	< 1000
Fe	400	Ti	15
Hf	< 4	V	< 2
K	20	W	< 50
La	< 4	Y	< 4
Li	< 4	Zn	20
Mg	25	Zr	< 4

TABLE IV
SIZE DISTRIBUTION OF PREFIRED
PLUTONIA GRANULES*

Size (μ)	Percent in Final Batch No.		
	PGT-3C	PGT-4A	PGT-5
246 - 295	8.56	19.12	18.3
208 - 246	18.29	22.63	21.3
175 - 208	13.23	14.45	16.1
149 - 175	15.18	11.68	12.2
125 - 149	14.40	9.93	10.6
104 - 125	12.06	8.76	8.4
74 - 104	16.34	13.28	12.7
61 - 74	<u>1.94</u>	<u>0.15</u>	<u>0.4</u>
Reject (-61 μ) Fines	19.84%	2.14%	2.50%

PGT-3C = Recycle oxide, fired at 1075°C in CO₂ for 2 hrs

PGT-4A = Fresh oxide, fired at 1075°C in CO₂ for 2 hrs

PGT-5 = Fresh oxide, fired at 1075°C in CO₂ for 2 hrs

*As determined by screening.

D. Cam-Coating

Earlier work on ThO₂-Mo cermets at the Evendale, Ohio⁽¹⁾ facility of the General Electric Company established that the desired microstructure could be achieved by creating an initial electrostatic attraction between the metal and ceramic particles. The metallic particles, having a different surface charge than the ceramic granules, would tend to coat the ceramic, and on subsequent pressing, the desired microstructure would be "locked in". Investigators at G. E. believed that this could be attained by a process called "cam-coating" wherein a thin coating of camphor was applied to the metallic powder. Metal powder particles were slurried with a 3.4 w/% solution of camphor in acetone in the proportion of 10 g powder to 2.8 ml of solution. These proportions were reported fairly critical.

In the present work, the Ir to be coated was placed in a 50 ml beaker with the camphor-acetone solution. The beaker was placed in an ultrasonic cleaner and agitated for 2 to 3 minutes until the contents were thoroughly mixed. The slurry was then dried to a cake at $\leq 40^\circ\text{C}$. The dried cake was broken in a blender (G. E. - Evendale stated this was an essential part of the procedure to produce an electrostatic charge on the metal particles). After removing the powder from the blender, the material was screened through a 20 μ screen in the Sonic Sifter and was stored.

Although this procedure was followed without deviation during the initial phases of this investigation, there was incentive to simplify this step. The presence of organic materials as camphor/acetone in combination with thermally warm PuO₂ is not a desirable situation. Therefore, cam-coating was eliminated in later runs, and comparison of the product microstructures indicated no significant differences. This will be discussed in more detail in a later section.

E. Mixing of PuO₂ and Ir

The desired quantity of ²³⁸Pu¹⁶O₂ granules was spread evenly over the bottom of a glass Petrie dish. After placing a 325 mesh screen over the dish, the iridium was sprinkled onto the screen and the entire system was vibrated to sift the Ir onto the PuO₂. The combined

powders were mixed by oscillation for 10 minutes in the glass dish.

Because of the self-heating of $^{238}\text{PuO}_2$, the Ir-PuO₂ mixtures were restricted to ~10 g batches. The reasons for this were two-fold: (1) To decrease the loss of camphor during the early studies, and (2) to maintain as homogeneous a mixture as possible.

F. Preparation and Loading of Graphite Dies

Stackpole A331 and POCO AXF graphite were used for the hot press dies and punches. The A331 dies were used for the early runs, but their relatively low strength limited pressures to 4000 - 6000 psi. POCO AXF die material allowed pressures up to 10,000 psi.

In the first fourteen runs the material was loaded into a bare die cavity. However, subsequent metallography indicated the plutonia had been slightly reduced indicating interaction with the die carbonaceous material. In subsequent pressings, the die cavities and inner punch faces were coated with Ir prior to loading by painting the graphite with a slurry of $\leq 5\mu$ Ir and alcohol and drying the parts at $\sim 100^\circ\text{C}$. During hot pressing, the painted Ir powder adhered to and became part of the hot pressed piece leaving the graphite surface Ir-free.

Except for PIC-20 and PIC-21 the Ir-PuO₂ charge was initially cold-pressed at a pressure equal to the subsequent hot press pressure.

G. Hot Pressing

The major portion of the process development involved the hot pressing of 0.3 in. diam x 0.3 in. long pellets. The final step in this phase of this investigation was the successful fabrication of a 1 1/2 in. diam sphere. The types of dies and punches used in hot pressing these shapes are shown in Fig. 1. Three pellets were pressed simultaneously in a small vacuum furnace powered by a 15 kw, 10 kHz MG. The 3-hole graphite die was the susceptor as well as the material container. The PIC sphere was hot pressed in a larger vacuum furnace powered by a 100 kw, 10 kHz MG. In both cases, the initial vacuum was $\sim 1 \times 10^{-6}$ Torr, the pressure rising to $\sim 1 \times 10^{-4}$ Torr as the temperature was raised.

Fig. 1a. Die and punch assembly for small PIC specimens.

Fig. 1b. Die and punch assembly for 100 watt PIC spheres.

Process Flow Chart for Fabrication of Plutonium-Iridium Cermets

Fig. 2. Flow chart for PIC specimen preparation.

Pressure was applied hydraulically. Except for PIC-20 and 21 (the PIC sphere) the pressure was applied prior to heat-up of the charge and was released before starting cool-down. With PIC-20 and 21, the pressure was applied at temperature. It was necessary that this latter procedure be used with the sphere fabrication because applying full pressure initially could have caused punch knife-edge fracture.

The hot-pressing parameters of interest included the pressure, maximum temperature, and soak time. Typically, the temperature was raised as quickly as possible so that the soak temperature (read optically

through a black-body hole in the susceptor) was reached in 3 to 4 minutes. The time interval from pressure release to motor-generator shut-down was approximately 1/2 hour.

A summary flow sheet for the materials preparation and fabrication processes is given in Fig. 2.

IV. PROCESSING RESULTS AND DISCUSSION

A. Relationship of Microstructure and Density to Process Parameters and Feed

1. General Comments - The cermet specimens were evaluated primarily by microstructure.

Microstructural variables of interest included:

(a) porosity; amount, shape, and distribution (b) Ir distribution; integrity and homogeneity around the PuO_2 granules (c) stoichiometry of the oxide. The assessment of the relative worth of a processing method and the selection of a particular value for a process parameter depended upon the effect of that parameter on one or more of these microstructural variables.

Density was the easiest microstructure-related property to measure since it could be determined either mechanically, by pycnometry, or ceramographically. The effects of PuO_2 granule prefire temperature, granule size distribution, hot pressing parameters, Ir content, and type of PuO_2 powder feed on the density were of special interest because of the desirability of achieving high ceramic densities with uniform composition. The major processing variables and their effect on density are summarized in Table V. As expected, the relative density (expressed as percent of theoretical) generally increased with increasing temperature, pressure, soak time and decreasing PuO_2 granule prefire temperature. For example, the PIC-2 pellets prepared from high-fired (1320°C) granules and pressed at a relatively low pressure (2000 psi) averaged $\sim 81\%$ T.D. compared to the PIC-19 pellets (hot pressed at 10,000 psi from 1075°C - fired PuO_2 granules) at 96% T.D. A more precise determination of single variables on resultant density must await further investigation. However, it seems well-established that the PuO_2 granule prefire temperature be approximately 1075° to 1150°C . Granules prefired at $\geq 1320^\circ\text{C}$ were quite resistant to further sintering as evidenced by the relatively low density of the PIC-2 and PIC-3 pellets.

2. Fresh Savannah River Oxide (SRO) vs. Recycle Feed - As discussed in section III of this report, two sources of PuO_2 powder were used as feed granules: (1) "fresh" Savannah River Oxide (SRO) which had been ^{16}O exchanged and ball milled 16 hours, and (2) "recycle" feed which was recovered from PPO specimens by crushing and ball milling for 42 hours. PIC pellets prepared from these powders, however, did not have equivalent microstructures, as demonstrated in Fig. 3. The

oxide granules (in the PIC-9 pellet) prepared from the "fresh" feed had less intragranular porosity. Moreover, the Ir coating for the pellet prepared from "recycle" feed (PIC-14 HT) contained a much greater proportion of PuO_2 "fines".

Both the PIC-9 pellet and the PIC-14 HT pellet were prepared from granules prefired at 1075°C . The recycle feed powder, however, is apparently much less reactive (sinterable) than the fresh feed powder even though they are nominally the same size. The individual grains which comprise large granules are probably not well-bonded in the case of recycled material prefired at 1075°C . When PuO_2 and Ir are mixed together, the friable granules tend to disintegrate along the edges and PuO_2 "fines" are interspersed with the Ir coating. Raising the prefire temperature produces a more unsinterable particle, and thus is more difficult to press to desirable density levels. That approach to minimize interspersed fines appears unfruitful.

It should be pointed out that the microstructure shown in Fig. 3b, while not as esthetically pleasing as that produced from fresh oxide, has not been demonstrated definitely undesirable from the standpoint of strength, He release, thermal shock resistance, etc. The interspersed PuO_2 fines in the Ir could act as a strengthening agent at high temperatures. The greater number of intragranular pores could act as crack-propagation arresters and these effects could result in bodies having greater thermal shock resistance than those prepared from fresh material.

The difference in hot pressing behavior of the two feed materials is illustrated in Fig. 4, which shows slump gauge readings as a function of time for PIC-19 (fresh feed) and PIC-17 (recycle) under identical conditions; e.g. same pressing temperature and pressure, feed granule size distribution, prefire temperature, and Ir content (see Table V). The PIC-19 pellets averaged about 96% T.D., however, while the PIC-17 pellets were only 91% dense. The data show that the PIC-19 charge started to slump rapidly at about 1.25 min. (coinciding with a temperature of $\sim 1185^\circ\text{C}$) with most of the slump (> 0.10 in.) occurring in about one more minute. Total

| 20 μ | As Polished
 a) PIC-9 hot pressed from "fresh" Savannah River Oxide.

| 20 μ | As Polished
 b) PIC-14HT hot pressed from recycled oxide.

Fig. 3 Effect of oxide feed on microstructure

slump was ~ 0.115 in. The PIC-17 charge started to slump at ~ 1.75 min. (at approximately the same temperature) but the slumping rate was lower, and the total slump was 0.054 in. The difference in sinterability of the granules produced from the two feeds cannot at this time be ascribed to a single cause. Better characterization of the powders by electron microscopy and surface area measurements should yield more quantitative information.

3. PuO_2 Granule Size Distribution and Ir Content—As stated in section III-D, the amount of iridium required to achieve a desired microstructure is directly related to the PuO_2 granule size distribution because of surface area relationships. The specific surface or surface area per unit of mass would be valuable data for calculating the quantity of Ir required to coat a given mass of PuO_2 granules. The specific surface could have been computed if the granules were in the shape of regular solids, but since

they were irregular, the Ir content and granule size distribution were varied on a trial and error basis and were evaluated by ceramography.

Except for PIC-12 the cermets contained either 12 or 15 vol% Ir. Typical PuO_2 granule size distributions used with 12 vol% are provided in Table IV. Batch number PGT-4A, for example, was used to prepare the PIC-19 pellets, and a photomacrograph and photomicrograph are shown in Fig. 5. The Ir was reasonably well distributed throughout the pellet. Using the processing procedure described previously (in section III-E) it was not possible to achieve an Ir coating completely uniform in thickness as shown in Fig. 5b. The adequacy of such a coating must await further testing.

It should be noted from Fig. 5 that the PuO_2 granules tended to be flattened with respect to the pressing direction. Evidence of substantial plastic flow can be seen in lower magnification photomacrograph Fig. 5a).

TABLE V

PIC PROCESSING DATA

PIC Run No.	PuO ₂ Granule Size	Granule Prefire Temp.	Cam- coat?	Hot Pressing Parameters			Ir, vol %	Comments
				Time* min	Temp, °C	Pressure, psi		
1	104 - 295 μ ^(a)	1350 °C	Yes	30	1835	5000	15	Severe die reaction
2	104 - 295 μ ^(a)	1320	Yes	5	1500	2000	15	81% T. D.
3	104 - 295 μ ^(a)	1320	Yes	5	1600	4000	15	87% T. D.
4	104 - 295 μ ^(a)	1150	Yes	5	1520	4000	15	93% T. D.
5	104 - 295 μ ^(a)	1150	Yes	3	1500	5000	15	93% T. D.
6	104 - 295 μ ^(a)	1150	Yes	4	1600	5000	15	95% T. D.
7	104 - 295 μ ^(a)	-----	Yes	--	-----	-----	15	Aborted Run
8	104 - 295 μ ^(a)	-----	Yes	--	-----	-----	15	Aborted Run
9	104 - 295 μ ^(a)	1075	Yes	5	1500	4000	15	93% T. D.
11	104 - 295 μ ^(b)	1150	Yes	20	1475	6000	12	89% T. D.
12	104 - 295 μ ^(b)	1150	Yes	3	1600	5000	10.8	89% T. D.
13	104 - 295 μ ^(b)	1150	No	6	1500	4000	12	84% T. D.
14	175 - 295 μ ^(b)	1075	Yes	6	1500	6000	12	88% T. D.
15	175 - 295 μ ^(b)	1075	Yes	15	1500	10000	12	93% T. D.
16	175 - 295 μ ^(b)	1075	Yes	9	1600	10000	12	92% T. D.
17	61 - 295 μ ^(b)	1075	Yes	11	1475	10000	12	91% T. D.
18	61 - 295 μ ^(b)	1075	Yes	12	1500	6000	12	88% T. D.
19	61 - 295 μ ^(a)	1075	Yes	13	1475	10000	12	96% T. D.
20	61 - 295 μ ^(a)	1075	No	14	1500	4000 ^(c)	12	90% T. D.
21	61 - 295 μ ^(a)	1075	No	25	1535	4000 ^(c)	12	92% T. D. Sphere
22	61 - 295 μ ^(a)	1075	No	9	1475	10000	12	96% T. D.

* Time at max. temp.

(a) Fresh Savannah River Oxide

(b) Recycled Oxide

(c) Pressure applied at elevated temp., otherwise from ambient.

This is due to the 1075 °C prefiring temperature used for the PuO₂ granules and the high pressure (10,000 psi) used. These PIC-19 pellets had the highest relative density and the highest strength of all fabrications.

4. Ceramic Particle Coating - The cam coating process employed during the early stages of this investigation did not prove necessary to form cermetts of adequate microstructure. It appears, therefore, that the coating of the PuO₂ granules by the Ir occurs as a result of a combination of two factors. First, the Ir powder particles are attracted to the PuO₂ granules due to a surface static electric charge on the granules. Plutonium dioxide, as a ceramic insulator and dielectric will tend to acquire and retain a surface charge from the surround-

ings. The iridium powder particles will also become charged in a similar fashion. Metallic iridium is a relatively good conductor and would lose its charge more readily with a resultant net difference between the two phases. A second contributing factor to the coating phenomenon could be equally significant. The smaller Ir particles assume a packing distribution in the interstices of the larger PuO₂ granules thereby creating a microstructure of large PuO₂ islands surrounded by Ir.

B. Stoichiometry and Heat Treatment

The microstructure of the PIC pellets invariably contained some plutonium sesquioxide, PuO_{1.5}. This resulted from the hot pressing conditions of high temperature, pressure, and vacuum in graphite dies. Thus,

Fig. 4 Effect of feed history on slump gauge readings.

the pellets contained three phases: Ir metal, $\text{PuO}_{2.00}$, and $\text{PuO}_{1.6}$ in varying amounts depending on the processing conditions. Reduction of the dioxide to sesquioxide appeared to accelerate rapidly as the hot press temperature was raised above 1500°C . This can be illustrated by comparing Fig. 6a with Fig. 7a, which show the as-pressed microstructures of pellet PIC-4 (1520°C) and pellet PIC-3 (1600°C). It is evident that the pellet PIC-3 contained a substantially greater amount of sesquioxide. It is interesting to note the morphology of the sesquioxide in the pellet PIC-4 indicates a continuous interfacial layer of $\text{PuO}_{1.6}$ between the Ir and PuO_2 . Either the $\text{PuO}_{2.00}$ is reduced by the Ir (which seems unlikely), or there is an enhanced diffusion path between the Ir and the ceramic which leads to a reduction on the

surface of the ceramic granules. There might be a surface diffusion of oxygen atoms away from the metal-ceramic interface to the specimen surface. If this mechanism does exist, it could also be a positive factor in He release, since the He atoms could follow the same path.

To determine how the microstructure, stoichiometry, and density of the PIC specimens might change under various environments, a few pellets were subjected to varying heat treatments. The heat treatment conditions and results are summarized in Table VI.

According to the literature⁽²⁻⁴⁾, iridium may form a volatile oxide at temperatures above 1100°C . The first heat treatment, therefore, was performed on a PIC-3 and a PIC-4 pellet which were heated to 1100°C in air for 41 hours. The microstructure of the heat-treated PIC-4 pellet is shown in Fig. 6b. The sesquioxide was oxidized to PuO_2 whereas the Ir was relatively unaffected. A similar situation was encountered with the PIC-3 pellet (Fig. 7b). In the latter case, however, several microcracks are evident. These cracks probably result from stresses which are created in the structure by the change in volume as $\text{PuO}_{1.6}$ is reconverted to PuO_2 . The PIC-4 pellet had been pressed at 1520°C compared to 1600°C for PIC-3. It appears desirable, to limit the hot pressing temperature to some values near 1500°C to prevent excessive reduction of the plutonia.

As shown in Table VI, both the PIC-3HT and PIC-4HT pellets lost weight as a result of the heat treatment; they also underwent some shrinkage. Two factors enter into the weight changes caused by these heat treatments. If an oxidizing atmosphere is employed, some of the iridium may be oxidized and the weight of the body decreases. Countering this, however, is the weight gain caused by the reoxidation of the substoichiometric oxide to $\text{PuO}_{2.00}$. The net weight change is the resultant of these two effects. Changes in overall density involve both the weight change plus any dimensional changes due to sintering. For example, it is evident from Table VI that the density of the pellet PIC-3HT increased slightly whereas the pellet PIC-4HT underwent a slight density decrease. Pellet PIC-3HT however,

| 1000 μ |

As Polished

a) PIC-19 pellet cross-section.

| 100 μ |

As Polished

b) PIC-19 microstructure.

Fig. 5. Macrostructure and microstructure of a PIC-19 pellet. Pressing pressure was directed from top and bottom toward center of specimen.

| 20 μ |

As Etched

a) As pressed PIC-4

| 20 μ |

As Etched

b) Heat treated PIC-4 HT

Fig. 6. PIC-4 microstructure, (a) as-hot pressed at 1520°C, and (b) after heat treatment in air/1100°C/41hr.

20μ
a) As pressed PIC-3 .

20μ
b) Heat treated PIC-3 HT

Fig. 7. PIC-3 microstructures, (a) as pressed at 1600°C, and (b) after heat treatment in air/1100°C/41h.

TABLE VI

PIC PELLET HEAT TREATMENT DATA

PIC No.	Temp (°C)	Time (hr)	Atmosphere	Δ Weight (%)	Δ Length (%)	Δ Diam (%)	Δ Volume (%)	Δ Density (*)	Comments
3 HT	1100	41	Air	- 0.46	- 0.47	0	- 0.47	Increase	Substoichiometric oxide was reoxidized
4 HT	1100	41	Air	- 0.59	- 0.15	0	- 0.15	Decrease	Substoichiometric oxide was reoxidized
5 HT	1075	2	CO ₂	+ 0.14	+ 0.72	0	+ 0.72	Decrease	Substoichiometric oxide was reoxidized
12 HT	1370	6	Ar/H ₂ ¹⁶ O	+ 0.43	- 0.36	- 0.50	- 1.35	Increase	No change in surface appearance
13 HT	1200	36	Air	- 0.60	- 0.28	- 0.54	- 1.36	Increase	Light brown discoloration on surface
14 HT	1300	36	Air	- 1.16	- 0.45	- 0.66	- 1.77	Increase	Darker brown discoloration on surface
22 HT	1440	12	Ar/H ₂ ¹⁶ O	+ 1.81	+ 0.39	+ 0.60	+ 1.58	Decrease	Slightly dulled surface
22 HT	1440	12	Ar/H ₂ ¹⁶ O	+ 2.58	+ 4.19	+ 0.66	+ 2.19	Decrease	Slightly dulled surface
22 HT	1440	12	Ar/H ₂ ¹⁶ O	1.97	+ 1.17	+ 1.73	+ 2.95	Decrease	Slightly dulled surface

* Calculated from pellet dimensions and weights.

20 μ

As Etched

a) As pressed PIC-5.

20 μ

As Etched

b) Heat treated PIC-5HT.

Fig. 8. PIC-5 microstructure (a) as-pressed at 1500°C, (b) after heat treatment in CO₂/1075°C/2h.

was not as dense initially as the pellet PIC-4HT (87% T. D. vs. 93% T. D., respectively).

Pellet PIC-5 was heat treated in CO₂ at 1075°C for 2 hours to determine the extent of reoxidation. As shown in Fig. 8, complete reoxidation took place even after this relatively mild heat treatment. Table VI shows the corresponding dimensional change. The specimen did undergo a weight gain and increased in length causing an overall volume increase and corresponding decrease in density. The volume increase may be due to cracking of the specimen as seen in Fig. 8b.

In addition to air and CO₂, an Ar/H₂¹⁶O atmosphere was used to heat treat a few pellets. This atmosphere should adjust the stoichiometry of the oxide with no Ir reaction. This treatment was successful as the photomicrographs displayed in Fig. 9 show. The microstructure following this heat treatment was free of sub-stoichiometric oxide and was similar in appearance to

the microstructures of pellets heated in air (at 1100°C) or CO₂ (Figs. 7b and 8b). As shown in Table VI, the PIC-12HT pellet increased in weight and apparent density. These pellets were highly dense (96% T. D.) as pressed, however, and any cracks formed in these pellets, which would tend to increase the dimensions, would not be compensated for by sintering shrinkage.

Although the pellets which had been heat treated in air at 1100°C did not show a visible iridium loss, they did exhibit some weight decrease. To explore this reaction further at higher temperatures, pellet PIC-13 was heated at 1200°C in air, and pellet PIC-14 was heat treated at 1300°C in air. The results are summarized in Table VI. The pellets lost weight with increasing temperature. The apparent density of each pellet increased due to volume shrinkage. The surfaces of the pellets were discolored. Ceramographic examination of the pellets revealed that the iridium was unaffected

| 20 μ | As Etched

a) As pressed PIC-12

| 20 μ | As Etched

b) Heat treated PIC-12 HT.

Fig. 9. PIC-12 microstructure, (a) as pressed at 1600°C, (b) after heat treatment in Ar-H₂O¹⁶/1370°C/6h.

| 100 μ | As Polished

Fig. 10. PIC-14HT heat treated in air/1300°C/36h -- note Ir loss near surface of pellet.

| 50 μ | As Polished

Fig. 11. PIC-20 microstructure as pressed -- fabrication analogous to PIC-21 sphere.

TABLE VII
DIMENSIONAL AND THERMAL DATA FOR
PIC-21, 100 WATT SPHERE

Treatment	Diam (in.) ^c	Weight (g)	Appearance
As Pressed	1.466 ± 0.002	318.0	No cracks.
Heated 32 h at ^a 1440°C	1.462 ± 0.004	319.0	Small crack on one pole.
Thermal Ramp ^b	1.470 ± 0.003	318.9	The one polar crack was slightly larger. Slight crack pattern in equatorial region

^a Isothermally heated in Ar - H₂¹⁶O atmosphere.

^b Asymmetrically heated in vacuum.

^c Diameters corrected to 65°F.

in the pellet interiors, there was an observable Ir loss near the surface. This is illustrated in Fig. 10, a photomicrograph of the PIC-14HT pellet.

C. PIC Sphere

The PIC sphere (PIC-21) weight and dimensions as pressed and after heat treatment are given in Table VII. The sphericity of the body was good as evidenced by the near identical diameter dimensions measured in the polar and equatorial directions. The sphere gained 1 g in weight after being heated to 1440°C in Ar-H₂¹⁶O for 12 hours. The dimensional stability of the sphere is obvious from the tabulated data.

The sphere contained approximately 252.5 g of ²³⁸PuO₂ or 100 watts (t). Since the sphere was nominally 92% T. D. and contained 12 vol.% Ir, the quantity of radioactive material per unit volume was essentially the same as that for PPO spheres which currently are pressed to 80 - 82% T. D. There is no reduction in power density of PIC compared to PPO. An approximation of the sphere microstructure is given in Fig. 11, which shows the microstructure of the PIC-20 pellet. This pellet had been fabricated under conditions similar to those used for the sphere (see section III-G).

The PIC sphere is shown in the as pressed condition in Fig. 12. The sphere was free of cracks. A surface irregularity near the equator "belly-band" was probably caused by partial break-down of the graphite punch knife edge during the hot press run. This irregularity was relatively minor. It will be possible to eliminate this problem in future runs by slightly reducing the maximum pressure and/or by applying the pressure

at a higher temperature; e. g. at 1440°C instead of 1155°C as followed in PIC-21. At the higher temperature the charged material should be more plastic and yielding.

Eleven days after being hot pressed, the PIC sphere was subjected to a re-oxidation heat treatment by heating to 1440°C in Ar-H₂¹⁶O for 12 hours. The sphere was heated over 4 hrs, held at 1440°C for 12 hrs, and subsequently cooled over 5 hours. The sphere had gained 1 g in weight in the 11 day interval between hot pressing and heat treatment, indicating it had undergone some self-adjustment in stoichiometry. This is not surprising because of the low (but finite) amounts of H₂O/O₂ (~ 100 ppm) in the inert gloveboxes. During the heat treatment one crack formed on one polar surface, hereafter referred to as the "south" pole. The remainder of the sphere was unaffected as shown in Fig. 13.

Fig. 12. PIC-sphere in as-pressed condition.

Fig. 13. PIC sphere after heat-treatment at 1440°C for 12 hr in $\text{Ar-H}_2^{16}\text{O}$.

(a). North pole.

(b). South pole

Fig. 14. Asymmetric ramp of PIC-21 sphere.

V. ASYMMETRICAL THERMAL RAMP OF PIC SPHERE

A. Ramp Experimental

As part of qualification of PPO spheres, they are subjected to an asymmetric thermal ramp over a short (~50 min) time. Temperature differentials are chosen to simulate "worst-case" re-entry conditions with the sphere leading edge at near 1750°C and the trailing edge $\sim 300^{\circ}\text{C}$ cooler. A more stringent parameter is

time since these conditions are attained within < 5 min.

To establish some basis for comparison, the PIC sphere was subjected to the same ramp.

The most critical portion of the ramp schedule is shown in Fig. 14. The temperatures shown are on the hotter edge. The temperature increases almost 500°C degrees in 3 minutes. The experimental curve for the PIC sphere closely approximated the predicted re-entry values. Prior to the ramp, the sphere was heated to 1247°C in 2 1/2 hours, ramped, and cooled from 1728°C to about 700°C in approximately 35 minutes.

A schematic diagram of the susceptor used for the asymmetric ramp is shown in Fig. 15. This particular susceptor design was developed as a result of tests conducted on thoria simulant spheres. These tests were carried out in a cold apparatus in a separate facility with quite elaborate instrumentation to ensure that the proper temperature differential across the diameter was established. A similar susceptor, coil, and MG set were used for the actual PIC sphere ramp although the glove-box operation requirement prohibited installation of all analogous instrumentation. However, use of available temperature recording devices in addition to matching control settings allowed the ramp to be completed with acceptable accuracy.

Fig. 15 Schematic diagram of asymmetric ramp susceptor.

The post-ramped sphere is shown in Fig. 16. The north pole remained crack free. The thin crack on the south pole was extended to the equatorial belly-band and ran alongside the belly-band but did not cross it. Otherwise the sphere was unaffected by the ramp, as illustrated by the weight and dimensional data provided in Table VII.

B. Theoretical Considerations

A PIC sphere should have increased thermal shock resistance to PPO for two reasons: (1) the thermal conductivity of the body is higher as a result of the metal phase, (2) at elevated temperatures the metal should be relatively plastic and would tend to absorb the energy of a propagating crack, thereby arresting significant crack elongation and spreading. Hasselman⁵ showed that the optimum value of strength (for resistance to thermal shock) for a sphere is given by:

$$S_t = 1/2 \frac{7NE\gamma_{eff}}{2(1-\nu)b} \quad (1)$$

where S_t is the tensile strength, ν is Poissons' ratio, γ_{eff} is the effective surface energy, E is the modulus of elasticity, b is the sphere diameter, and N is the number of cracks. Incorporating a relatively ductile metallic phase in the ceramic PuO_2 matrix raises the γ_{eff} and hence raises the optimum strength value.

Alternatively, a measure of the thermal stress resistance of a sphere can be obtained by equating the total surface energy required for the propagation of the cracks to the elastic energy stored at fracture. For this case the mean area (A) over which (N) number of cracks will propagate in a sphere is given by:

$$A = \frac{2\pi S_t^2 (1-\nu) b^3}{7NE\gamma_{eff}} \quad (2)$$

If the calculated area (A) for a given material and sphere size is greater than the cross-sectional area of the sphere (πb^2), the cracks will completely traverse the body and lead to failure, but if (A) is smaller than the cross-sectional area of the sphere, the crack will be arrested and the sphere will remain intact.

Most of the parameters in equations 1 and 2 are readily measured by standard laboratory methods. The effective surface energy can be measured by the so-called work-of-fracture test which has recently^{6,7} seen increasing popularity because of the importance of fracture surface energy as a design parameter for ceramic materials. This parameter has been related to thermal shock resistance through strain-energy criteria^{5,8,9} and to strength via the Griffith-Orowan relation¹⁰⁻¹² and can be related to microstructural variations through electromicrography. When properties such as elastic modulus, tensile strength, etc. have been determined, it will be possible to use the SE data in the above equations to arrive at a valid "figure-of-merit" evaluation for all types of ceramic fuels.

VI. DIAMETRAL COMPRESSION TESTS

Some of the PIC specimens (recall that each "run" yielded three identical pellets) were used to obtain diametral compression data. This test has been

North Pole

Equator

South Pole

Fig. 16. PIC sphere appearance after asymmetric ramp.

used and described by Rankin,¹³ and Rudnick¹⁴ in studies on Al_2O_3 -Mo composites, a system reasonably analogous to PuO_2 -Ir. In this test, right cylindrical specimens are loaded laterally in compression, but according to elastic theory, a biaxial stress distribution is produced within the specimen so that a tensile stress is developed at right angles to the diameter (and to the compressive stress). The specimen actually fails in tension, with the maximum tensile stress easily computed from

$$\sigma = \frac{2P}{\pi Dt} \quad (3)$$

where σ is the maximum tensile stress P is the applied load, D is the specimen diameter and t is the specimen thickness.

Accordingly, a series of PIC pellet specimens nominally 0.3 in. long by 0.3 in. diameter were mechanically tested at room temperature. Specimens (with

TABLE VIII

PIC Pellet Strength Data

PIC Spec. No.	$\sigma_{\max}$ (psi)	E psi x 10^6	% T. D.	S_0 (psi)
2	5300	--	81	20,600
6	9300	3.0	92	16,000
9	6700	--	92	11,500
11 α	8900	5.4	89	19,100
11 β	9800	5.3	89	20,500
12	5900	6.6	90	11,900
13	--	8.0	84	--
14	3800	5.3	87	9,500
15 α	9300	3.0	93	15,300
15 β	9000	3.7	93	14,400
16 α	5400	--	93	8,200
16 β	9300	5.5	92	16,500
17	9100	7.6	91	16,600
19 α	16,900	--	97	21,400
19 β	15,200	--	96	20,400
22 α	--	7.0	95	--
22 β	3900	--	96	--
22 γ	2900	--	92	--

ends flat and parallel to within ± 0.005 in.) were first loaded axially in compression to obtain data for the determination of Young's modulus. The specimens were loaded in a device fitted with tungsten carbide platens and mounted in an Instron within a glovebox. The load was measured with an Instron compression load cell. The diametral compression test was performed using a cross-head speed of 0.05 in./min.

Compressive load-deflection data were obtained from eleven specimens. The deflection data were obtained with an LVDT deflectometer. It was necessary to correct these data for suppress deflection. Each specimen compression tested was loaded to 500 pounds twice to insure complete seating on the load platens. None of the specimens failed at this load, and by comparison with specimens which were tested in diametral compression only, the axial compression loading did not affect the subsequent diametral tests.

Diametral compression test data were obtained from 16 specimens. For these tests the specimens were each loosely wrapped in heavy aluminum foil. The foil

contained the pellet fragments after failure and provided a pad between the load platen and the specimen. This padding is required to avoid high shear stresses immediately under the points of loading. All the specimens failed in either the double or triple cleft modes. The double cleft is the normal tensile failure down the loaded diameter, whereas the triple cleft is a normal tensile failure in which the pellet breaks along the loaded diameter and opposite sides of and parallel to this cleavage. Double and triple cleft failures are evidence that the specimen definitely failed in tension rather than shear and that equation 3 is applicable.

The strength data are tabulated in Table VIII.

The tensile strength at zero porosity, S_0 , was encapsulated from the Knudsen¹⁵ equation, $S = S_0 e^{-bP}$. To determine the constant, "b", S_0 ($\sigma_{\max}$) was plotted versus porosity (P) on a semi-logarithmic basis, and neglecting the lowest strength values (anomalies due to surface irregularities and internal flaws) a value of ~ 7 was determined. In an analogous way Young's modulus could be modified for porosity using an equation of the form $E = E_0 (1 - kP)$. The method used to determine the elastic modulus was too inexact, however, to warrant this treatment.

Some general observations can be drawn from these strength data. Although the tensile strength values varied from 2,900 to 16,900 psi, this is not surprising in view of the variation in Ir content, age, PuO_2 granule size distribution, firing temperature porosity, stoichiometry, and hot pressing parameters. There are not enough data to permit assignment of relative effects of all the processing variables on the mechanical properties. In fact, since the strength of brittle materials must be described statistically, the values listed in Table VIII should be regarded only as trends. It is apparent, however, that the pellets PIC-19 had significantly higher strengths than any of the others. These pellets had been prepared from fresh feed, pre-fired into granules at a relatively low temperature (1075°C) to retain as much sinterability as possible. They are pressed at high pressure (10,000 psi) to a high density (96% T. D.). From Fig. 5, the PuO_2 granules exhibit evidence of

plastic flow and distortion. Since none of the other pellet microstructures or strengths resembled PIC-19, the processing parameters should be re-examined more thoroughly. The PIC-22 pellets (prepared in a way similar to PIC-19) had very low strengths. These pellets, it should be remembered, were heat treated at 1440°C for 12 hours in Ar-H₂¹⁶O. It is possible that this post-press heat treatment produced cracks within the pellets which lowered their strength. The diametral compression strength test is well suited to quantify the effect of various post-press thermal equilibrations. When corrected for porosity, the strength values (S₀) approached 20,000 to 21,000 psi. The ultimate strength of a "refined" PIC material should be significantly higher.

VII. SUMMARY

Plutonia-iridium cermets were prepared by a multi-step method involving the formation of pre-fired PuO₂ granules, coating of these relatively large granules with iridium powder particles, and subsequent hot pressing of the mixture. While further studies are required, at present the optimum prefiring temperature for providing sinterable PuO₂ granules with sufficient strength and cohesiveness appears to be ~1075°C. The amount of plutonium dioxide reduction increased with increasing hot pressing temperature and time, becoming extensive at temperatures near 1600°C. The stoichiometry of the specimens could be adjusted by subsequent heat treatment without adversely affecting the iridium.

A 100-watt, ~1.470 in. diameter, PIC sphere was made. As hot pressed, the sphere was crack-free and was approximately 91.5% dense. Since the sphere contained 12 vol % iridium, the power density (watts/cm³) was essentially equal to that of the PPO spheres currently under study. The PIC sphere survived subsequent heat treatment and asymmetric ramp tests very satisfactorily.

Diametral compression tests performed on some of the PIC pellets indicated differences in strength which could be attributed to processing procedures. This type of measurement shows good promise as a process development tool.

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REFERENCES

1. M. W. Shupe, LASL, Informal Trip Report, General Electric Co., Evandale, Ohio, May 21, 1971.
2. C. B. Alcock and G. W. Hooper "Thermodynamics of the Gaseous Oxides of the Platinum-Group Metals," *Proc. Roy. Soc. A*, 254, 551-561 (1960).
3. H. Schafer and N. J. Heitland, "Equilibrium Measurements in the System Iridium-Oxygen: Gaseous Iridium Trioxide," *Zeitsch Anorg Chemie*, 304, 249 - 265 (1960).
4. W. L. Phillips, Jr., "Oxidation of the Platinum Metals in Air," *Trans. ASM*, 57, 33-57 (1964).
5. D. P. H. Hasselman, "Elastic Energy at Fracture and Surface Energy as Design Criteria for Thermal Shock," *J. Amer. Ceram. Soc.* 46 (11) 535-40 (1963).
6. J. A. Copolla and R. C. Brandt, "Measurement of Fracture Surface Energy of SiC," *J. Amer. Ceram. Soc.*, 55 (9) 455-560 (1972).
7. J. A. Copolla, R. C. Brandt, D. W. Richerson, and R. A. Alliegro, "Fracture Energy of Silicon Nitrides," *Ceram. Bull.*, 51 (11) 847-851 (1972).
8. F. J. P. Clarke, H. G. Tattersall, and G. Tappin, "Toughness of Ceramics and Their Work of Fracture," *Proc. Brit. Ceram. Soc.* (6) 163-172 (1966).
9. R. W. Davidge and G. Tappin, "Effective Surface Energy of Brittle Materials," *J. Mater. Sci.* 3 (2) 165-73 (1968).
10. J. A. Copolla and R. C. Brandt, "Fracture Energy of Silicon Carbide from -195.8°C to 1500°C," *Proc. Int. Conf. Mech. Behavior Matter*, Kyoto, Japan, Aug, 1971.
11. A. A. Griffith, "Phenomena of Fracture and Flow in Solids," *Phil Trans. Roy. Soc. London, Ser. A*, 221, 163-98 (1920).

12. F. F. Lange, "Fracture Energy and Strength Behavior of a Sodium Borosilicate Glass - Al_2O_3 Composite System," J. Amer. Ceram. Soc., 52 (2) 99-105 (1971).
13. D. T. Rankin, J. J. Stiglich, D. R. Petrik, and Robert Ruh, "Hot Pressing and Mechanical Properties of Al_2O_3 with an Mo-Dispersed Phase," J. Amer. Ceram. Soc., 54 (6) 277-281 (1971).
14. A. Rudnick, A. R. Hunter, and F. C. Holden, "Analysis of the Diametral-Compression Test," Mater. Res. Stand. 3 (4) 283-89 (1963).
15. F. P. Knudsen, "Dependence of Mechanical Strength of Brittle Polycrystalline Specimens on Porosity and Grain Size," J. Amer. Ceram. Soc., 42 (8) 376-87 (1959).