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HOT PRESSING TECHNIQUES FOR FABRICATING Cm_2O_3 FOR RADIOISOTOPIC FUEL FORMS

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ABSTRACT

Hot pressing techniques were developed for fabricating bulk oxide and oxide-refractory metal cermet fuel forms, using Gd_2O_3 as a stand-in for $^{244}Cm_2O_3$. High-density (95% theoretical) B-type oxide compacts were produced by pressing C-type oxide at 1200°C and then heating under pressure to 1300°C where the B-type oxide forms, or by direct pressing at higher temperatures (1500°C) in the B-type oxide range. High-density (>90%) cermet compacts containing 50-70 vol % oxide in tungsten or molybdenum matrices were also made by hot pressing. Most of the residual porosity for these structures was open and available for release of decay helium.

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INTRODUCTION

Hot pressing techniques for fabricating radioisotopic fuel forms were developed at Savannah River Laboratory as part of a program to acquire technology for producing heat source capsules containing ^{244}Cm. The development centered around ^{244}Cm fuel forms that would meet operating and safety requirements for both high-temperature (1600-1800°C) thermionic generators and lower temperature (<1000°C) thermoelectric or dynamic conversion systems.[1] B-type curium sesquioxide (Cm_2O_3) was the favored fuel material for such applications,[2] because of its high melting point,[3] low vapor pressure,[4] and good compatibility with potential container materials.[5] For development of the hot pressing fabrication techniques, gadolinum sesquioxide (Gd_2O_3) was used as a nonradioactive stand-in for the Cm_2O_3.

Both bulk oxide and oxide-refractory metal cermet compacts represented candidate fuel forms for these heat source applications. The bulk oxide compacts are being utilized in prototype thermionic module demonstration tests at Oak Ridge National Laboratory. Oxide compacts might also be needed to provide dense material for comminution into particles of appropriate minimum size (~100 μm) for use in cermet forms.

The cermet forms have better thermal conductivity and mechanical strength than the bulk oxide forms, and also potential for retaining radioactivity under accident conditions in which the primary fuel container ruptures. Because the advantages of the cermet fuel forms are fully realized, however, only if helium gas formed by radioactive decay of the isotopic fuel is released without excessive swelling of the fuel form, provision of open porosity in the cermet compacts was desired.

SUMMARY

Hot pressing techniques were demonstrated for making high-density compacts of either bulk oxide or oxide-refractory metal cermets, using Gd_2O_3 as stand-in for Cm_2O_3. Bulk oxide compacts with densities of 95% of theoretical were formed by pressing Gd_2O_3 at 1500°C, to form directly the monoclinic B-type oxide, or by pressing the bcc C-type Gd_2O_3 at 1200°C, and then converting under pressure to B-type Gd_2O_3 at 1300°C. The latter method greatly reduced carbon contamination and extended the life of the graphite die. Carbon contamination could also be eliminated by using a tungsten die liner. Annular washer compacts, a form which might be needed to avoid an unduly high central temperature in a bulk oxide fuel, were successfully fabricated.

Oxide-refractory metal cermets that contained 40 to 70 vol % Gd_2O_3 in tungsten or molybdenum matrices were pressed to densities of 90% of theoretical and higher. Uniform structure and a continuous metal phase, both desirable properties in a high temperature fuel form, were achieved within these compositional limits. The residual porosity of the cermets was shown to be principally open to the surface in compacts pressed to about 90% of theoretical density, but to be closed in a compact pressed to 97% theoretical density. Carburization at the hot pressing temperature of 1500°C was negligible for tungsten, but not for molybdenum.

DISCUSSION

EXPERIMENTAL PROCEDURE

Hot Press

An induction-heated vacuum hot press capable of operating at 1500°C was used to fabricate both the Gd_2O_3 oxide compacts and the Gd_2O_3-refractory metal cermets. The press is shown in Figure 1; the position of the die inside the press and the materials of construction used are shown schematically in Figure 2. The press design was adapted from one built by the Australian AEC.[6] Refractory ceramic (mullite) tubes were used for thermal insulation between the graphite die and the fused-silica housing tube to permit continuous operation at the maximum temperatures in the range 1300 to 1500°C. A Wilson seal was used in place of bellows to facilitate assembly of the press during operation. The operating pressure at temperature was limited by the strength of graphite die. ATJ-grade graphite furnished by Union Carbide Corporation was used in these experiments, and pressures up to 4000 psi were attained. A linear transducer mounted on the ram of the press was used to monitor the rate of compact densification. A mechanical pump was used to evacuate the chamber, producing pressures of 1 to 10 μm at pressing temperatures.

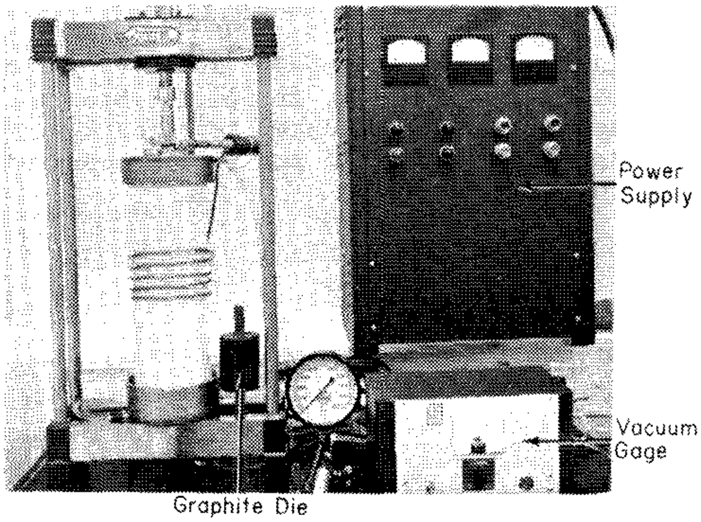


FIGURE 1. Induction-Heated Vacuum Hot Press

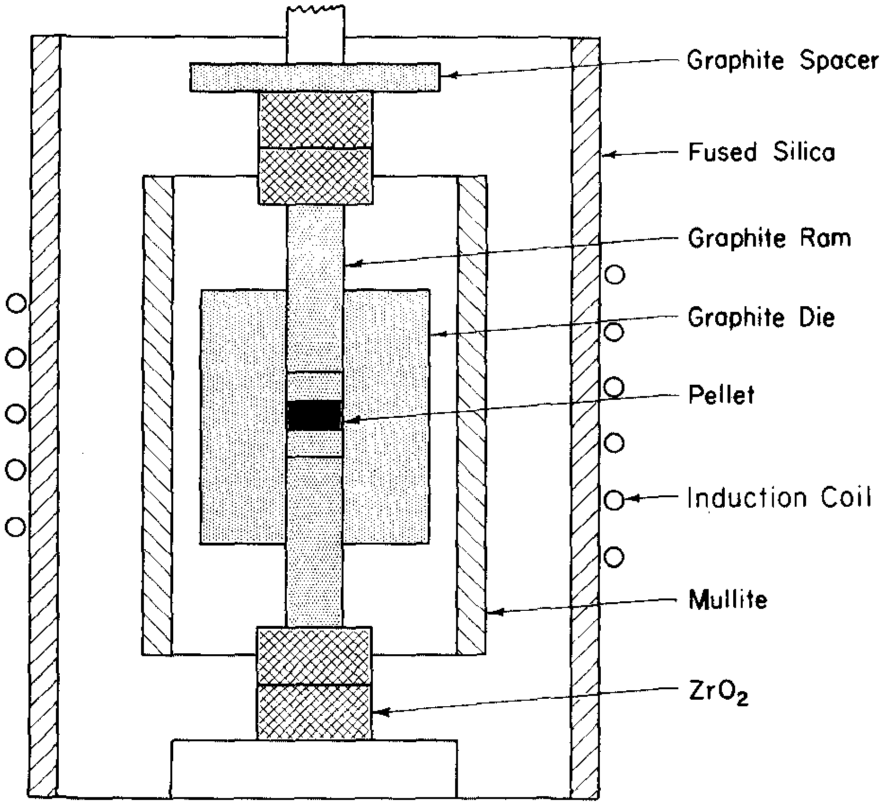


FIGURE 2. Hot Press Components and Materials

Materials

Gadolinium oxide (Gd_2O_3) powder of 99.9% purity was supplied by Research Chemicals, Phoenix, Ariz. Molybdenum power of 99.9% purity was supplied by Consolidated Astronautics, Inc., Haupage, N. Y. Tungsten powder of 99.9% purity was supplied by Fansteel Corporation, N. Chicago, Ill.

Blending

To prepare the cermet compacts for hot pressing, the oxide (300-500 Å Gd_2O_3) and refractory-metal powder (-325 mesh) were blended to achieve a uniform mixture. Two methods of blending, rod milling and a more efficient manual method, were used. The rod milling method consisted of rotating the constituent powders in a glass jar on a roller mill overnight. Small tungsten welding rods (~1/8 in. diameter) were placed inside the glass jar during blending to break up agglomerates. In the manual method, the oxide and refractory-metal powders were enclosed in a plastic bag and mixed manually by rubbing the powder between the fingers. Equivalent mixing could be generated mechanically for Cm_2O_3 powder.

Hot Pressing Procedure

To make bulk oxide compacts, the Gd_2O_3 was first cold pressed at the desired hot pressing pressure, to assure that the die would safely restrain the pressure when hot, since the strength of graphite either remains the same or increases slightly on heating to temperatures of interest. The pressure was reapplied after heating to the desired temperature until densification was complete as indicated by the transducer mounted on the ram of the press. One to two hours were generally sufficient to achieve maximum densification at the various hot pressing temperatures.

For the cermet compacts, the blended powders were cold pressed in the graphite die at 3000 psi. After heating to 1500°C, the pressure (3000 psi) was reapplied and held approximately one hour. All pressing was done under vacuum, varying from 1 to 50 μm pressure.

Determining Gd_2O_3 Structure

The amount of C-type and B-type Gd_2O_3 present in a hot-pressed compact was determined from X-ray diffraction measurements in the following manner. First the ratio of the area under the (402) peak of the B-type oxide to the area under the (222) peak of C-type oxide was computed. This value was then compared to a standard curve which was prepared with mixtures of known weight of the two oxides.

Density and Porosity Measurements

Bulk and apparent densities were determined by a method similar to that in Reference 7, in which the specimen is weighed successively dry, impregnated with a liquid, and submerged in a liquid (toluene). Densities and porosities were calculated using the following equations

$$\text{Bulk density } \rho_B = \frac{W_{dry}}{W_{imp} - W_{sub}} \cdot \rho_{liq}$$

$$\text{Apparent density } \rho_A = \frac{W_{dry}}{W_{dry} - W_{sub}} \cdot \rho_{liq}$$

$$\%\ \text{Theoretical density } (\rho_T) = \frac{\rho_B}{\rho_T} \times 100$$

$$\%\ \text{Total porosity } P_T = (1 - \frac{\rho_B}{\rho_T}) \times 100$$

$$\%\ \text{Closed porosity } P_C = (1 - \frac{\rho_A}{\rho_T}) \times 100$$

$$\%\ \text{Open porosity } P_O = P_T - P_C$$

where:

W_{dry} = weight dry

W_{imp} = weight impregnated

W_{sub} = weight submerged

ρ_{liq} = density of toluene

RESULTS

Bulk Oxide Compacts

Fabrication Conditions and Structure Type

Hot pressing of the rare-earth oxide stand-in Gd_2O_3, which has crystal structures analogous to Cm_2O_3, demonstrated marked differences in densification rates for the body-centered-cubic C-type and monoclinic B-type oxide. As shown in Figure 3, higher density (~90% of theoretical) compacts were obtained by pressing at temperatures where C-type Gd_2O_3 is stable (1150-1250°C) than at somewhat higher temperatures (1250-1450°C) in the B-type oxide range. High-density (95% of theoretical) compacts were again produced by pressing at high temperatures (1450-1500°C) in the B-type oxide range. Analogous behavior had previously been observed during sintering of cold pressed Gd_2O_3 compacts: the densification rate of the C-type oxide just below the C-type to B-type transformation temperature of 1250°C was a factor of 10^5 greater than that of the B-type oxide at a temperature slightly higher than the transformation.

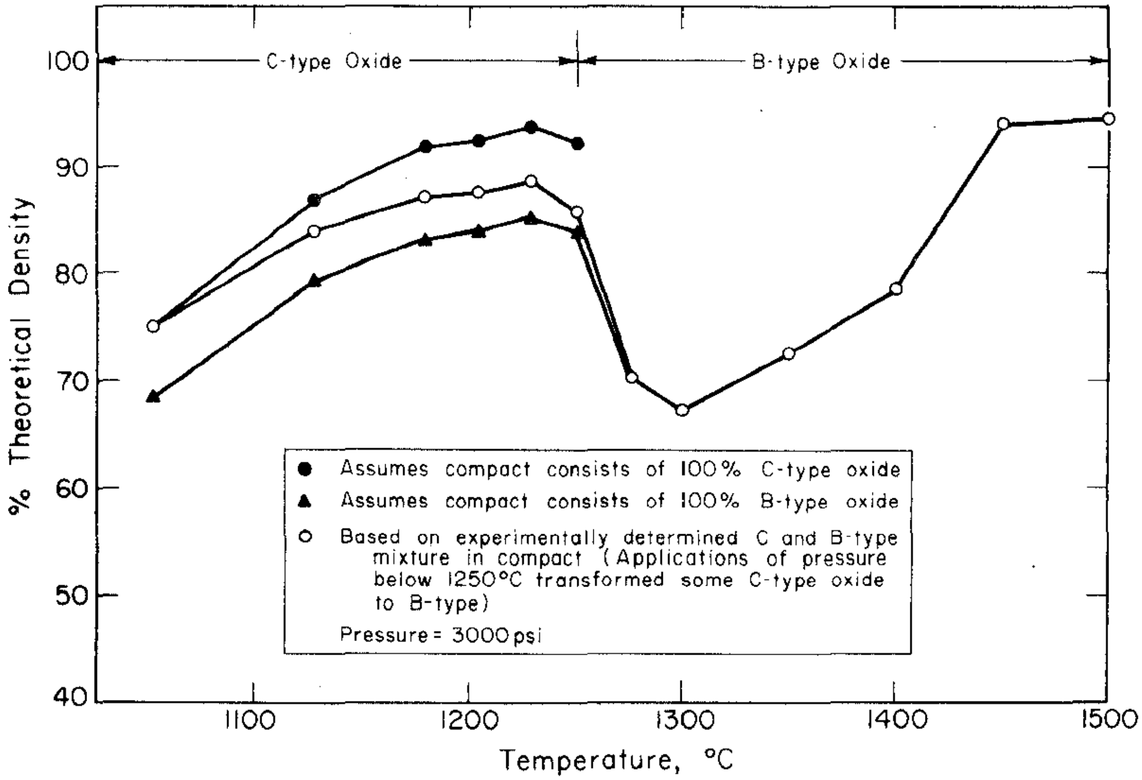


FIGURE 3. Effect of Pressing Temperature on Density of Gd_2O_3 Compacts

High density (>90% of theoretical) compacts of B-type Gd_2O_3 were produced at lower temperatures by taking advantage of the higher rate of densification in the C-type region. Pressing from 1/2 to 1 hour at 1200°C where C-type oxide was present, then heating rapidly under pressure to 1300°C to convert to B-type oxide, and holding at temperature for 15 to 30 minutes resulted in densities 93% of theoretical, equivalent to those produced by hot pressing at 1450-1500°C. The fabrication at lower temperatures reduced material interaction problems: contamination from the graphite die was greatly reduced, and the life-time of the die liner was substantially increased.

Effect of Heating Rate

Variations in the rate of heating to the temperature of hot pressing produced marked differences in the densities of oxide compacts. For example, density was ~90% of theoretical after heating to 1400°C in one hour, compared to a density ~70% of theoretical after heating to 1400°C in 1/2 hour using the same time and pressure of hot pressing. The higher densities may have been caused by two effects. First, the slower heating rate allowed more time for sintering in the C-type oxide region, where diffusion rates were greater. Second, the slower heating rate may also have enabled volatile constituents, which could cause residual porosity, to escape from the Gd_2O_3 before pressing.

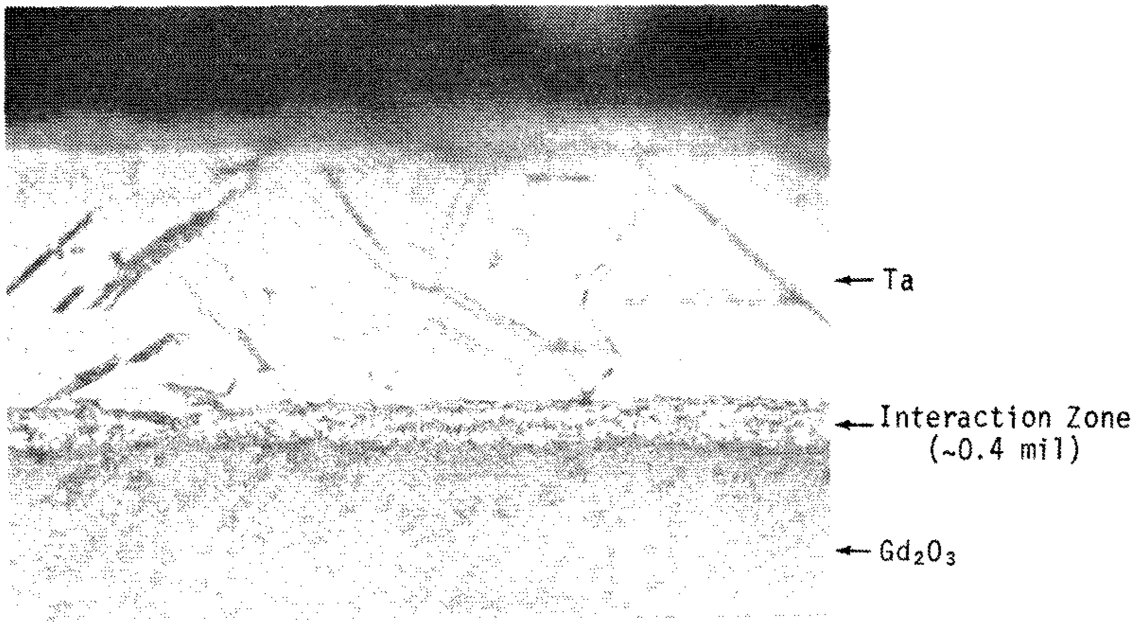
Oxide-Die Interactions

Oxide compacts pressed directly in graphite dies were dark grey to black in color due to the presence of carbon, and possibly to reduction of the oxide. Heating of the compact in air at 700 to 800°C for several hours generally restored the normal color. However, the carbon was difficult to remove from compacts pressed at high temperature (1450-1500°C). Heating in air to high temperatures (~1400°C) after pressing caused carbon-containing areas near the pellet edges to crack. This may have been due to mismatch in expansion between the normal oxide and carbon-rich oxide. Die liners that prevented contact between the Gd_2O_3 and the graphite die were used to eliminate this problem.

Die Liners

To evaluate candidate materials for die liners, thin disks (0.003-0.005 in.) of several refractory metals were placed between the graphite ram and the Gd_2O_3 pellets during hot pressing. The same materials are also potential capsule materials. Pellets pressed using tantalum spacers were firmly stuck to the tantalum, demonstrating a ceramic-metal bonding technique (Figure 4) that could prove useful. Wafers pressed using tungsten or TZM spacers were not stuck.

A tungsten tube with 0.020-in. wall was employed to line the graphite die. The tungsten tube performed satisfactorily and virtually eliminated the carbon deposit on the compact surface, thereby also reducing the amount of carbon which diffused into the compact. Graphite dies on which a layer of tungsten had been chemically vapor deposited could probably be used in place of the tube inserts. The work of Fries, et al.,[8] indicates that tungsten carburizes very slowly in the temperature range where Gd_2O_3 was hot pressed. This would extend the lifetime of the die, enabling it to be used many times.



Pressed at 1500°C for 1/2 hr at 3000 psi

FIGURE 4. Gd_2O_3 — Ta Interaction

Annular Oxide Washers

Annular washers of Gd_2O_3 were fabricated by hot pressing. The shape of annular washers might avoid excessive central temperatures that could lead to melting during service in a heat source. To prevent cracking of the washer during fabrication, the thermal expansion of the die material had to be less than that of Gd_2O_3, which in turn had to be less than that of the center plug. This combination enabled the washer to contract freely after hot pressing so that thermal stresses would not cause breakage. A washer of C-type Gd_2O_3 was fabricated at 1200°C to 82% of theoretical density using TD Nickel as the center plug. A washer fabricated with a tungsten plug, which had a lower thermal expansion than Gd_2O_3, cracked.

Attempts to fabricate annular washers of B-type Gd_2O_3 by pressing at 1200°C as the C-type oxide and then converting to B-type oxide under pressure at 1300°C were unsuccessful. The cobalt and TD Nickel used as center plugs because of their high expansion formed low melting eutectics with the carbon of the graphite die plugs. This difficulty might be avoided by a protective coating on the cobalt or nickel, or by using another high-expansion material as the center plug.

Cermet Compacts

Fabrication Conditions

Fabrication conditions and resultant cermet characteristics are given in Table I.

TABLE I

Hot Pressed Gd_2O_3 Cermets[a]

$\frac{\text{Oxide}}{\text{Metal}}$, vol %	Temp, °C	Time, hr	% Theo Density	Total Porosity, %	$\frac{P_{open}}{P_{total}}$, %
38/62 Mo	1500	1	97.2	2.8	7
50/50 Mo	1470	1	90.6	9.4	89
50/50 W	1500	½	90.0	10.0	79
70/30 W	1500	1	91.7	8.3	54

---

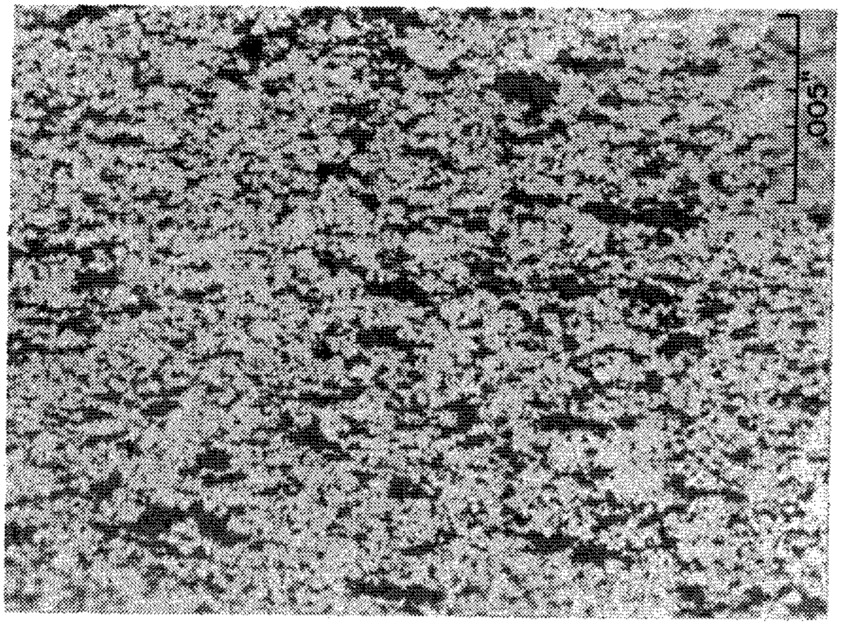
[a] All cermets were pressed at 3000 psi under vacuum.

The oxide content of the cermets ranged from ~40 to 70 vol %. Densities were at least 90% of theoretical at each composition. A high fraction of the total porosity was open to the surface in the cermets of about 90% theoretical density, but most of the porosity was closed to the surface in the highest density sample. This result is expected since porosity does not begin to close until the density approaches 95% of theoretical.

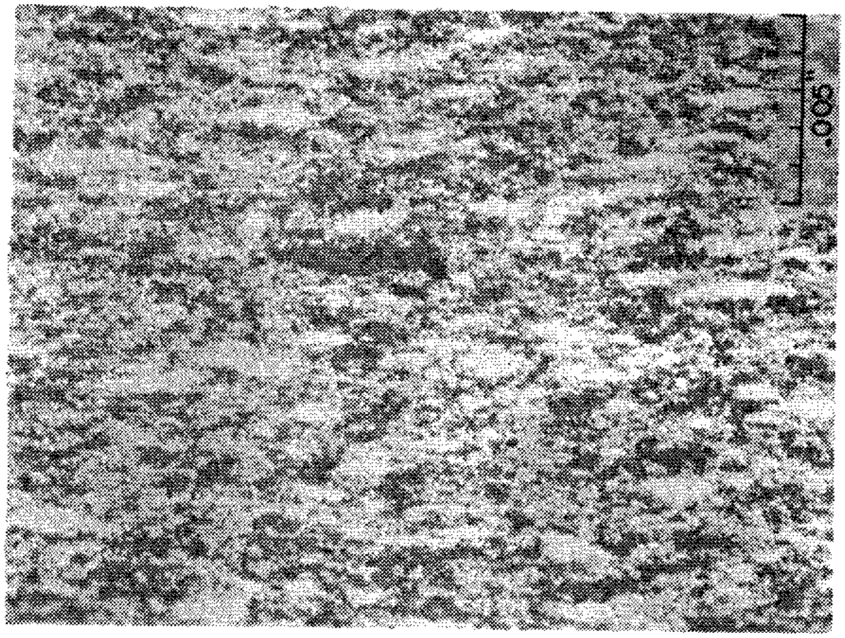
Constituent Distributions

Figure 5 shows representative areas of the microstructure of molybdenum and tungsten matrix cermets blended by the milling technique. The "layered" effect is produced by the unidirectional motion characteristic of hot pressing. The metal phase appeared to be continuous in both cermets. Although some dispersion of the oxide was attained in both cermets, segregated areas indicated that mixing was not complete.

Effects of increased oxide content, as well as the alternative hand-mixing technique, are illustrated for tungsten matrix compacts in Figure 6. The continuity of metal phase achieved in the 50 vol % oxide compact was lost in the 70 vol % because the oxide content was too high. Metal phase continuity was lost, although the 70 vol % oxide, mixed by the more efficient manual method, had a much greater dispersion of the constituent phases than the former, mixed by milling. The manual mixing technique (for example, with manipulation fingers) would probably not be directly applicable to an equivalent Cm_2O_3 form, but a fast wrist-action shaker might provide the same mixing effect. Mixing by mortar and pestle has also been used for small amounts of radioactive materials.



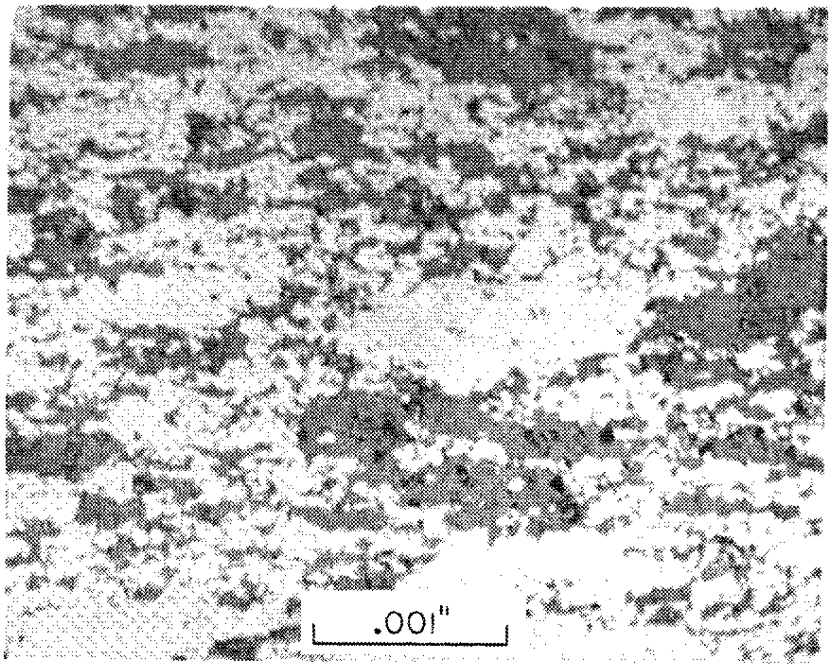
50 vol % W — 50 vol % Gd_2O_3



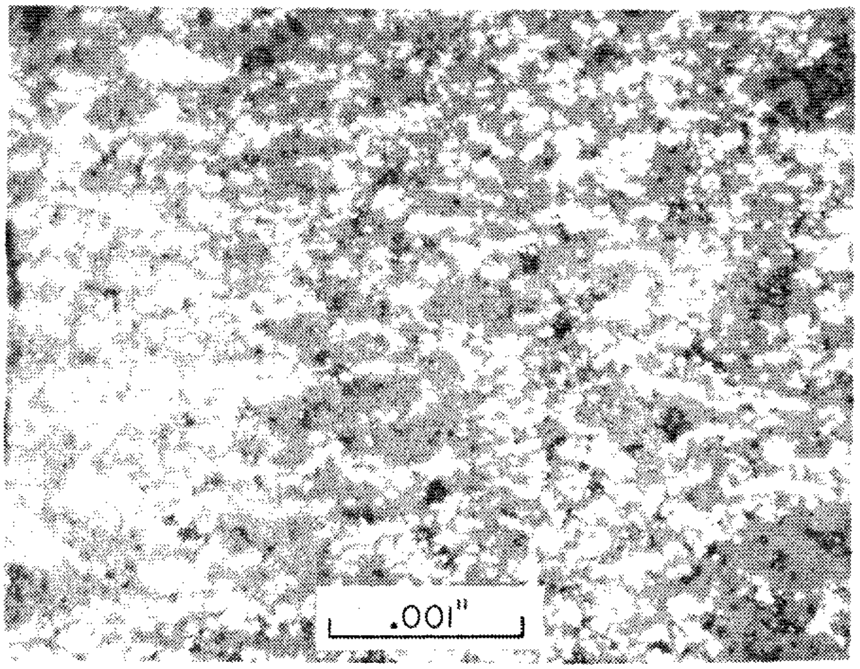
62 vol % Mo — 38 vol % Gd_2O_3

FIGURE 5. Refractory Metal — Gd_2O_3 Cermets

The dark oxide phase is surrounded by a continuous light metallic phase. Large oxide clumps indicate incomplete mixing by milling technique.



50 vol % W — 50 vol % Gd_2O_3



30 vol % W — 70 vol % Gd_2O_3

FIGURE 6. Tungsten — Gd_2O_3 Cermets

Interaction of Graphite Die and Refractory Metal

All cermet compacts were hot pressed directly in a graphite die; no die liners were used. In all cases, the compacts were easily removed from the die with almost no sticking. Edges of the compacts were sharp and well defined.

For the molybdenum cermets, molybdenum foil (0.002 in. thick) was placed between the graphite ram and the cermet. The foil was metallurgically bonded to the cermet after hot pressing, as shown by metallographic examination. Carbon was observed to have diffused through the molybdenum foil and into the cermet to a depth of approximately 0.002 in. The presence of Mo_2C in the diffusion layer was verified by microhardness measurements and X-ray diffraction. In contrast, no penetration of carbon into the tungsten cermet was detected by metallography or microhardness measurements, although X-ray diffraction indicated tungsten carbide (W_2C) on the surface of the pellet. Estimates based on the rates of carburization found by Fries et al.[8] indicate that a Mo_2C layer ~0.0035 in. thick might be expected in the hot-pressed molybdenum cermets; a thickness of 0.004 in. was observed. The depth of carbide formation in tungsten should be at least an order of magnitude less than in molybdenum under the same conditions; no penetration was observed in the tungsten cermets. The carbide layer in the molybdenum cermet compacts could be removed by grinding.

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