

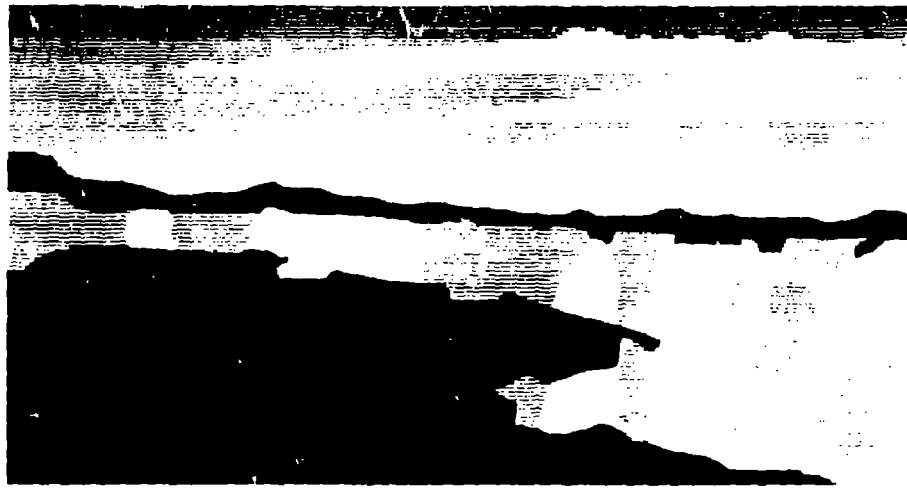
Title: FABRICATION OF A NON-FERTILE FUEL FOR THE DISPOSITION OF WEAPONS PLUTONIUM IN WATER REACTORS

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Submitted to: 4th International Conference on Nuclear Engineering
New Orleans, LA
March 10-14, 1996

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MASTER

FABRICATION OF A NON-FERTILE FUEL FOR THE DISPOSITION OF WEAPONS PLUTONIUM IN WATER REACTORS

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ABSTRACT

The feasibility of fabricating a non-fertile fuel containing weapons plutonium was evaluated. A surrogate fuel, specifically a $\text{CeO}_2\text{-ZrO}_2\text{-CaO}$ fuel pellet, was fabricated using the solid-state reaction method to determine the effect of powder comminution, pellet formation, and sintering conditions on the microstructural development of the fuel. Dry ball milling of the precursor powders (CeO_2 , ZrO_2 , and CaO) proved to be an ineffective method for producing reactive powders for pellet pressing and sintering. However, results indicate that formation of the calcia-stabilized diluent and solid solution between the diluent and the actinide surrogate (CeO_2) occurred as a result of sintering the fuel pellet at a temperature of 1200°C to 1700°C .

INTRODUCTION

The disposition of plutonium is an area of significant importance to the national security of the United States. A number of recent publications by eminent organizations have addressed the issue of fissile material management and protection [1-4]. Most notably, the Committee for International Security and Arms Control (CISAC), a standing committee of the National Academy of Sciences, conducted a study on the management and disposition of excess weapons plutonium [1]. The committee concluded that the use of plutonium as fuel in existing or modified reactors without fuel reprocessing is the leading contender for the long-term disposition of weapons plutonium.

Approximately two years ago, the Department of Energy (DOE) formed the Office of Fissile Material Disposition (FMD), whose charter was to develop plans and technologies for the disposition of excess fissile material from the US nuclear weapons program. The FMD is considering the option of converting weapons plutonium into mixed uranium-plutonium oxide (MOX) fuel for use in domestic or Canadian water reactors. As part of a once-through fuel cycle, the MOX fuel is converted into spent reactor fuel. This process burns only about 20

percent of the plutonium, but after insertion and burnup in the reactor, the fuel assemblies are highly radioactive and difficult to transport due to obvious size and weight constraints. Therefore, this process converts the weapons plutonium into a form that is unattractive to a potential proliferator.

In comparison to MOX fuel, non-fertile fuel offers several key advantages for the dispositioning of weapons plutonium. The non-fertile fuel exceeds the "spent fuel standard" by destroying greater than 60 percent of the plutonium initially loaded in the fuel compared to approximately 20 percent for MOX fuel. The non-fertile fuel achieves this performance because it does not contain any uranium-238, which breeds plutonium-239, but instead uses an inert material as the fuel diluent. Therefore, if applied as a full core in a light water or heavy water reactor, a non-fertile fuel form could greatly accelerate the rate of disposition of weapons plutonium.

In addition to the inventory of excess weapons plutonium, the growing inventory of unseparated plutonium in spent nuclear fuel is a concern to maintaining peace and security on a global basis. Using chemical separation methods, the plutonium in spent fuel can be recovered and subsequently used in nuclear reactors and nuclear weapons. Non-fertile fuel has the potential for allowing new or existing water reactors to become net consumers of plutonium instead of net breeders. The use of the "deep burn" capability of non-fertile fuel can ultimately result in a reduction of the world's inventory of plutonium in spent nuclear fuel.

At the request of the CISAC, Sterbentz et. al. [5] conducted a study to investigate the feasibility of using a non-fertile fuel form for near-total destruction of weapons plutonium in existing or advanced light water reactors. Neutronic performance results show the non-fertile fuel containing weapons plutonium to be a potential fuel for use in a pressurized water reactor (PWR). As part of a INEL Laboratory Directed Research and Development (LDRD) study, Sterbentz, et al. [6] evaluated the neutronic performance of a $\text{PuO}_2\text{-ZrO}_2\text{-CaO-Er}_2\text{O}_3$ fuel form suitable for use in a commercial boiling water reactor (BWR). Plutonium oxide derived from weapons plutonium, calcia-stabilized zirconium oxide, and erbium oxide serve as the fuel, fuel diluent, and depletable neutron absorber, respectively. The results of the study show the $\text{PuO}_2\text{-ZrO}_2\text{-CaO-Er}_2\text{O}_3$ fuel form to be a potential fuel for use in a BWR.

One goal of this Los Alamos National Laboratory LDRD study is to develop a method for the fabrication of a non-fertile fuel for the disposition of weapons plutonium in water reactors. Specifically, we have chosen the $\text{PuO}_2\text{-ZrO}_2\text{-CaO-Er}_2\text{O}_3$ fuel composition for our initial fuel fabrication study. The objective of our study supports LANL's mission to support national security and reduce the nuclear danger by solving issues in plutonium disposition.

The initial phase of our research and development program consisted of fabricating a surrogate $\text{CeO}_2\text{-ZrO}_2\text{-CaO}$ fuel. The purpose of the surrogate study was to: 1) evaluate the feasibility of preparing the fuel by the solid-state reaction method using reagent-grade calcia (CaO), zirconia (ZrO_2), and ceria (CeO_2) as oxide precursors, 2) develop a powder comminution method acceptable to glovebox operations, 3) evaluate the behavior of PuO_2 in the fuel diluent using CeO_2 as the actinide surrogate, and 4) determine the specifications for a sintering furnace design and operation. Specifically, this paper will discuss the effect of ball milling, green body

formation, and sintering conditions on the microstructural development of the surrogate fuel pellet.

EXPERIMENTAL PROCEDURE

Powder Characterization

The equivalent spherical diameter of the precursor powders was determined using laser diffraction analysis. The particle size and morphology of the precursor powders was characterized using scanning electron microscopy (SEM). Sintered pellets were ground in an agate mortar and subsequently analyzed for crystalline phase content using x-ray diffractometry (XRD).

Pellet Fabrication

The flow diagram for the pellet fabrication process is shown in Figure 1. Reagent-grade ZrO_2 (87.19 wt%), CaO (10.12 wt%), CeO_2 (2.69 wt%), stearic acid (1 wt%), and polyethylene glycol (1 wt%) were dry ball milled for 24 hours. The milled powder was uniaxially pressed into pellets (6.5 mm x 6.0 mm) at 310 MPa. The green pellets were sintered for 5 hours at 1200°C, 1400°C, and 1700°C in an atmosphere consisting of 80% N_2 and 20% O_2 . Pellet samples were cooled from the sintering temperature at an average rate of 10°C/min.

Pellet Density and Microstructural Analysis

The bulk density and volume percent of open porosity were determined using the immersion density technique. Grain and pore structure including average size and size distribution were determined using optical microscopy (OM) and SEM analysis.

RESULTS AND DISCUSSION

Characteristics of Precursor Powders

Scanning electron micrographs of the ZrO_2 , CaO, and CeO_2 precursor powders are shown in Figures 2, 3, and 4, respectively. The ZrO_2 powder consisted of granules formed by the spray drying method. The granules ranged in size from ~ 25 μm to ~ 100 μm . Sub-micron particles of zirconia are visible on the surface of the individual granules. The CaO powder consisted of aggregates ranging in size from ~25 μm to ~ 100 μm . The CeO_2 powder consisted of aggregates ranging in size from ~ 25 μm to ~ 75 μm . Individual CeO_2 grains ranging in size from 3 to 5 μm are visible within the aggregates.

The results of the particle size analysis of the precursor powders are shown in Figure 5. The equivalent spherical diameter was determined to be 16.4 μm , 32.3 μm , and 21.7 μm for ZrO_2 , CaO, and CeO_2 , respectively.

Effect of Ball Milling on Precursor Powders

As shown in Figure 6, large (i.e., greater than 500 μm) agglomerates were formed as a result of ball milling the precursor powders for 24 hours. The scanning electron micrographs show a broad particle size distribution. Sub-micron particles are visible on the surface of the agglomerates. As shown in Figure 5, the equivalent spherical diameter of the ball milled powder was determined to be 87.3 μm .

Pellet Densification

As shown in Figure 7, a significant increase in the bulk density of the surrogate fuel pellet occurred between the sintering temperatures of 1200°C and 1400°C. This increase in density from 2.94 g/cm^3 to 4.24 g/cm^3 corresponds to a decrease in open porosity (vol%) from 47.3 % to 20.3 %. An additional increase in bulk density occurred between the sintering temperatures of 1400°C and 1700°C. This increase in density from 4.24 g/cm^3 to 4.67 g/cm^3 corresponds to a significant decrease in open porosity (vol%) from 20.3% to 0.281 %.

Phase Development

Figure 8 shows the x-ray powder diffraction pattern of the surrogate fuel sintered at 1200°C, 1400°C, and 1700°C. The cubic crystalline phase, $\text{Ca}_{0.15}\text{Zr}_{0.85}\text{O}_{1.85}$, is present in the surrogate fuel sintered at 1200°C, 1400°C, and 1700°C. This cubic phase is the calcia-stabilized form of zirconia corresponding to a CaO content of ~ 20 mole %. The orthorhombic crystalline phase, CaZrO_3 , is present in the surrogate fuel sintered at 1200°C and 1400°C. The CeO_2 precursor is present in the surrogate fuel sintered at 1200°C and 1400°C. The XRD data indicates that a sintering temperature of between 1400°C and 1700°C is required to form a solid solution of CeO_2 in calcia-stabilized zirconia.

Microstructural Development

As shown in Figures 9 and 10, porosity is clearly present in the microstructure of the sintered surrogate fuel pellet. The dark areas in the optical micrographs indicate the presence of pores (intergranular and intragranular) within the sintered pellet. As shown in Figure 10, pellet porosity decreased with an increase in sintering temperature from 1400°C to 1700°C. In addition to densification, grain growth occurred as a result of increasing the sintering temperature from 1400°C to 1700°C. As shown in Figure 9, the average grain size for the pellet sintered at 1400°C and 1700°C was 8 μm and 20 μm , respectively.

SUMMARY AND CONCLUSIONS

- (1) Dry ball milling of the precursor powders did not produce a highly reactive powder for pellet fabrication (i.e., pressing and sintering). Reactive powders typically have a particle size of 1 μm or less. Uniform particle size reduction of the precursor powders to less than 1 μm and subsequent granulation of the precursor powder mixture is necessary for pellet fabrication. Future work will examine the feasibility of

using vibratory and/or attrition milling methods to produce reactive precursor powders for the solid-state reaction synthesis.

- (2) A significant increase in bulk density of the surrogate fuel pellet occurred between the sintering temperatures of 1200°C and 1400°C.
- (3) A significant decrease in open porosity (vol%) of the surrogate fuel pellet occurred between the sintering temperatures of 1400°C and 1700°C.
- (4) Formation of the calcia-stabilized fuel diluent occurred as a result of sintering the fuel pellets at 1200°C.
- (5) Complete solid solution formation between the surrogate (CeO₂) and the fuel diluent occurred as a result of sintering the fuel pellets at 1700°C.
- (6) Significant grain growth occurred as a result of increasing the sintering temperature from 1400°C to 1700°C.

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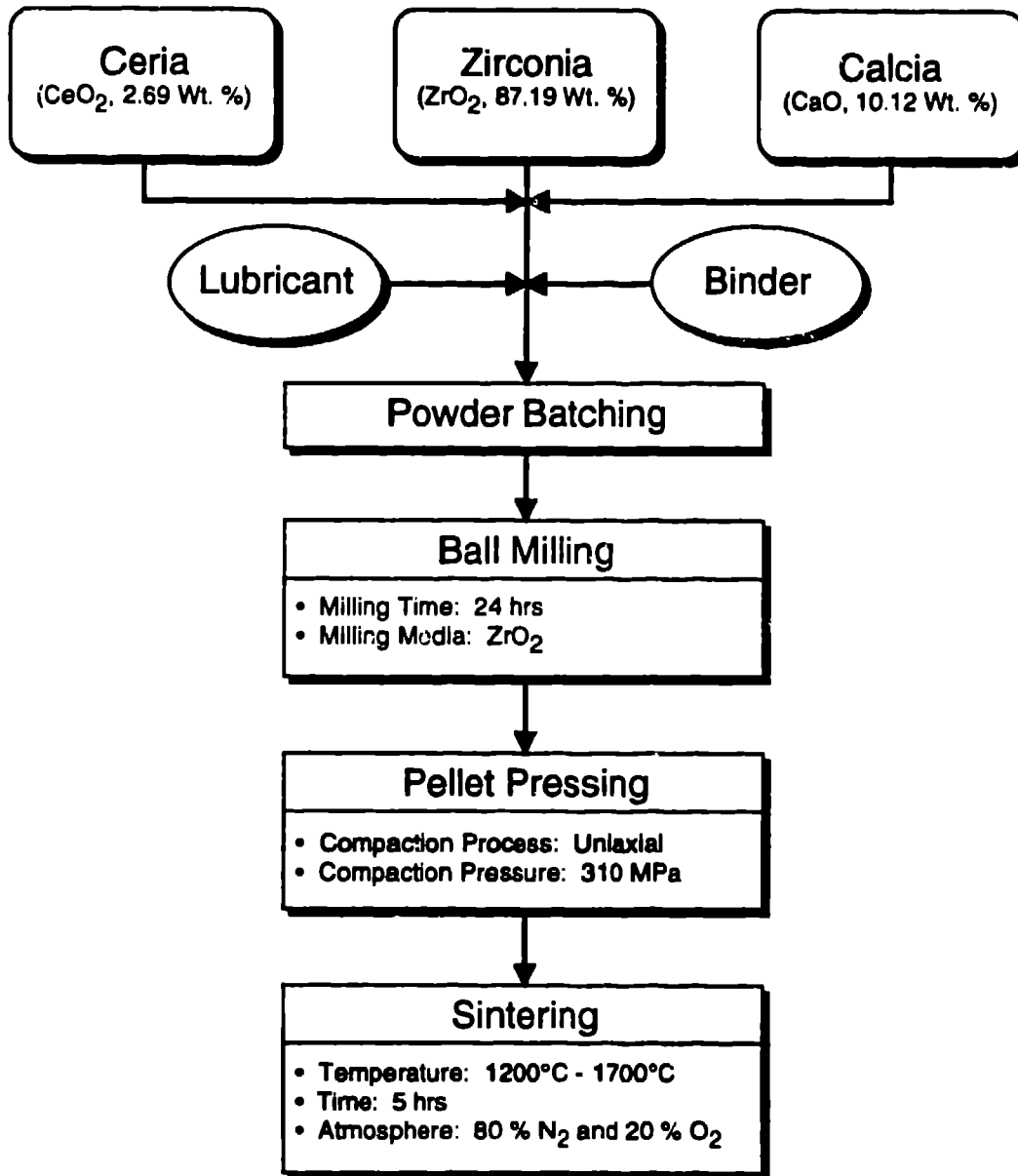


Figure 1. Flow diagram for fabrication of surrogate fuel pellet.

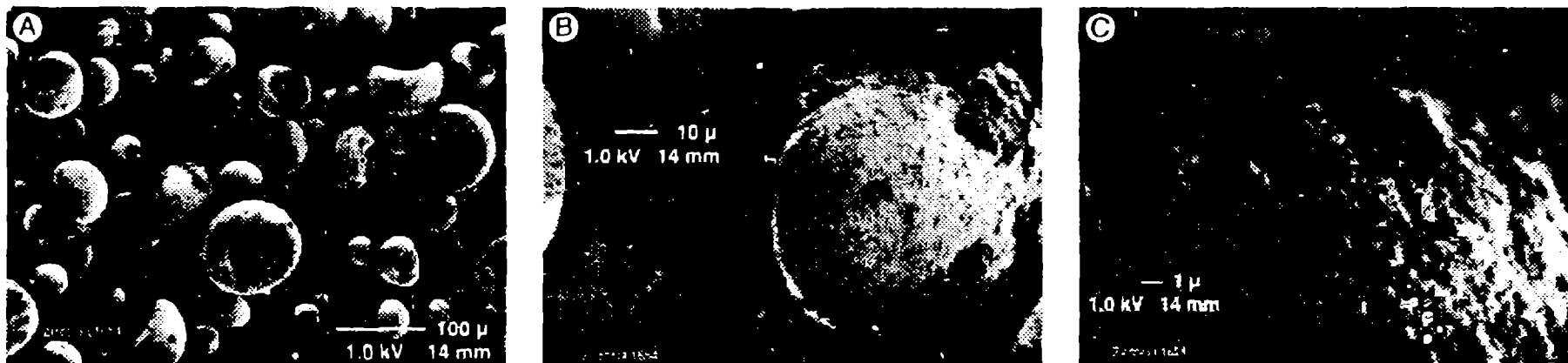


Figure 2. Scanning electron micrographs of ZrO_2 powder: (A, B) granules formed by the spray drying method, and (C) surface of a granule.

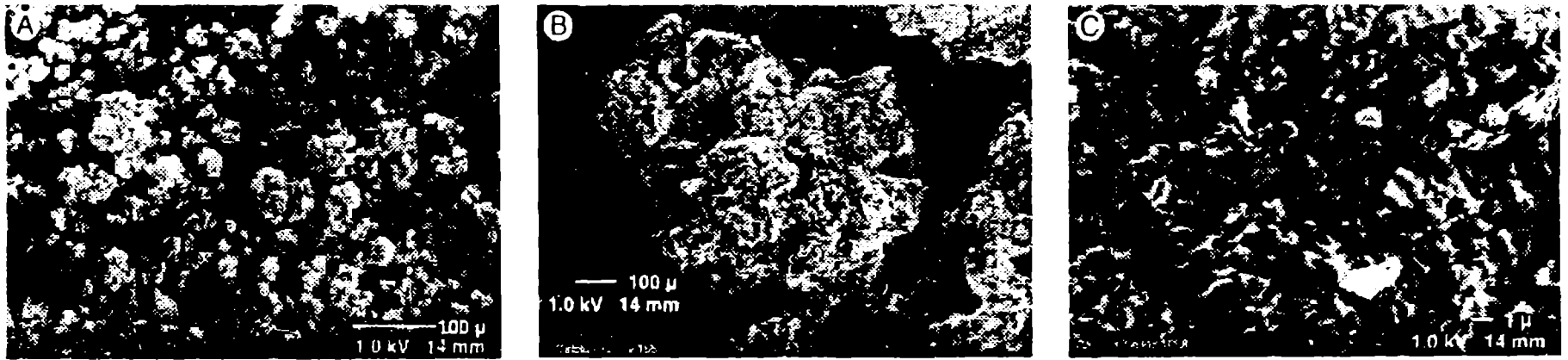


Figure 3. Scanning electron micrograph of CaO powder: (A, B) particle aggregates, and (C) surface of aggregate.

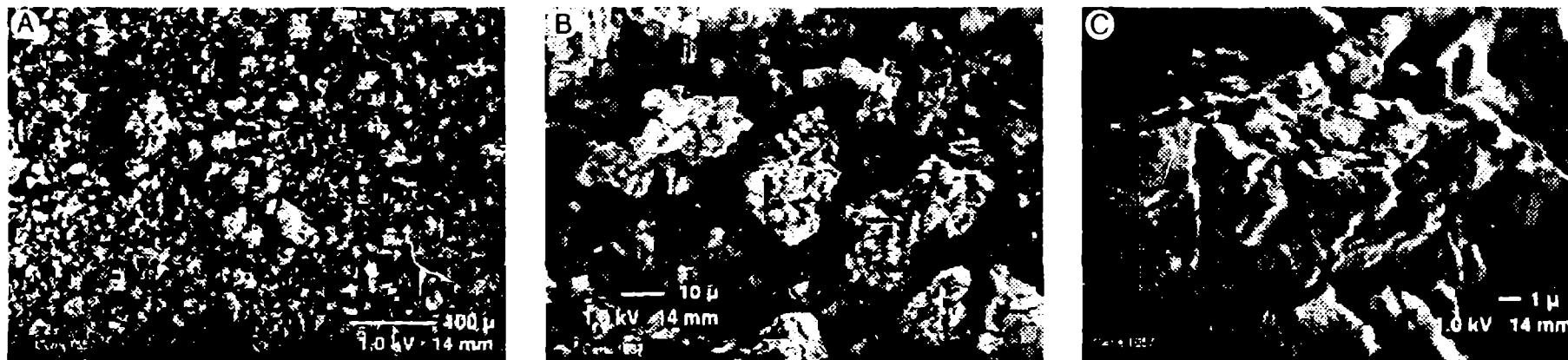


Figure 4. Scanning electron micrograph of CeO₂ powder: (A, B, C) particle aggregates.

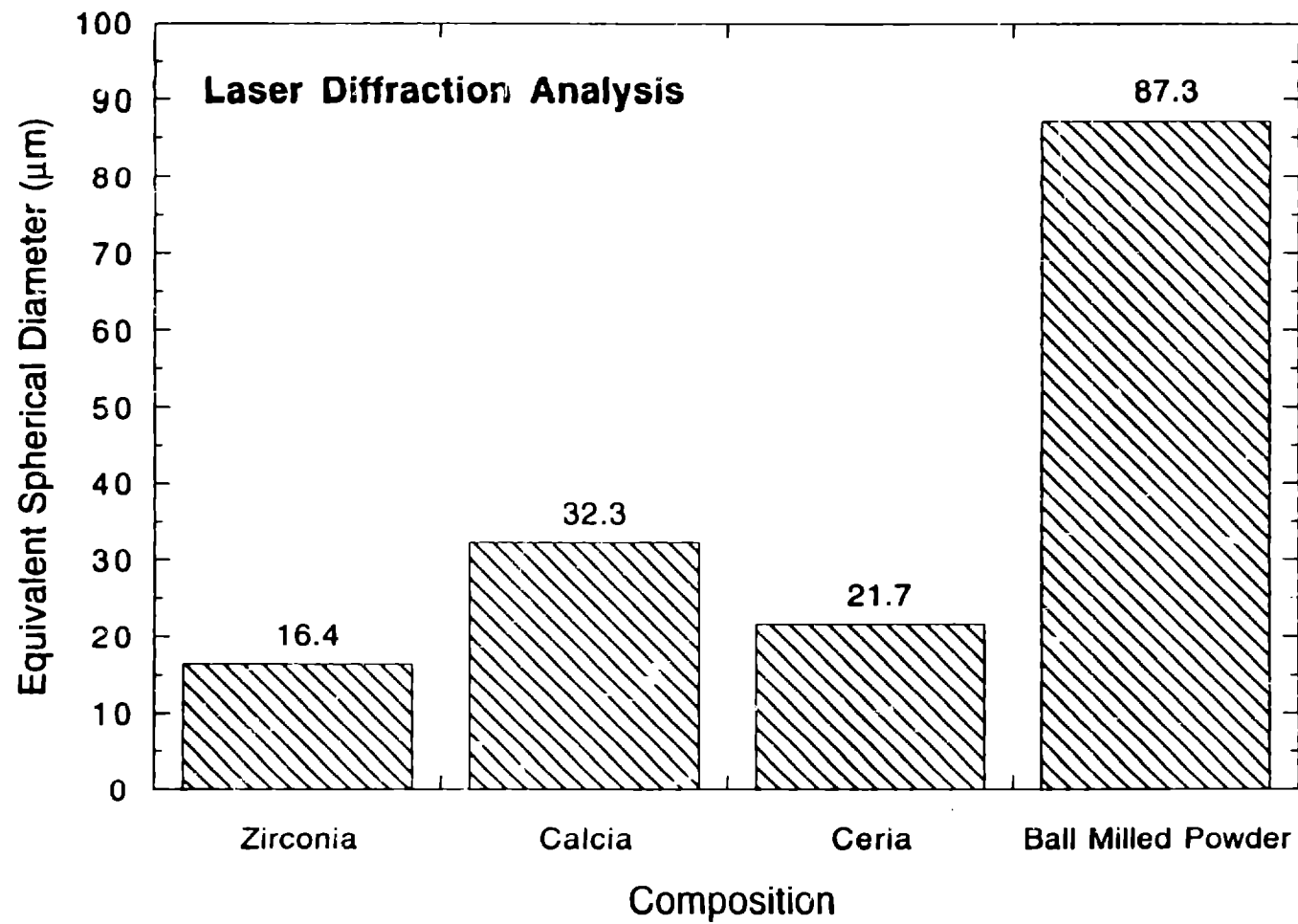


Figure 5. Particle size of precursor and ball milled powder.

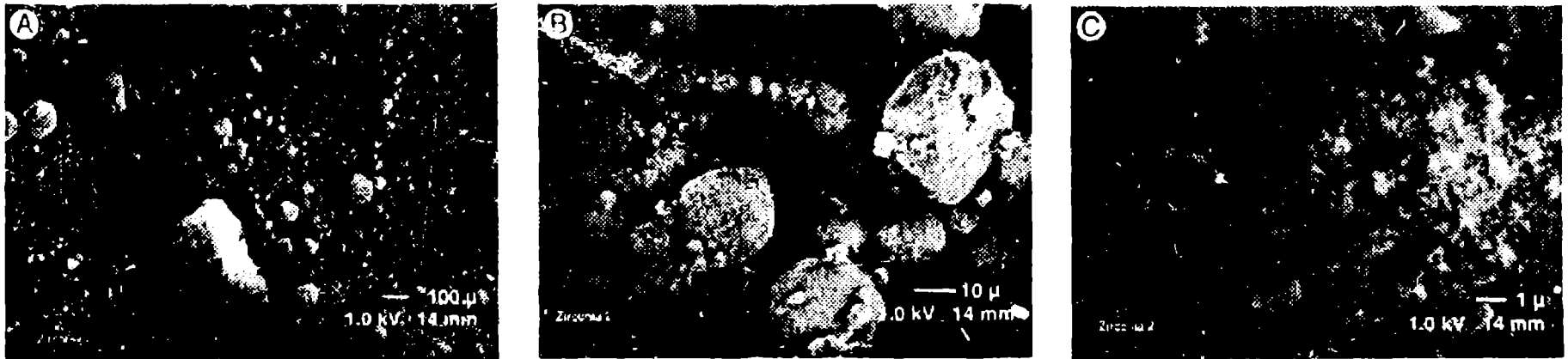


Figure 6. Scanning electron micrograph of ball milled powder: (A, B) particle agglomerates, and (C) surface of agglomerate.

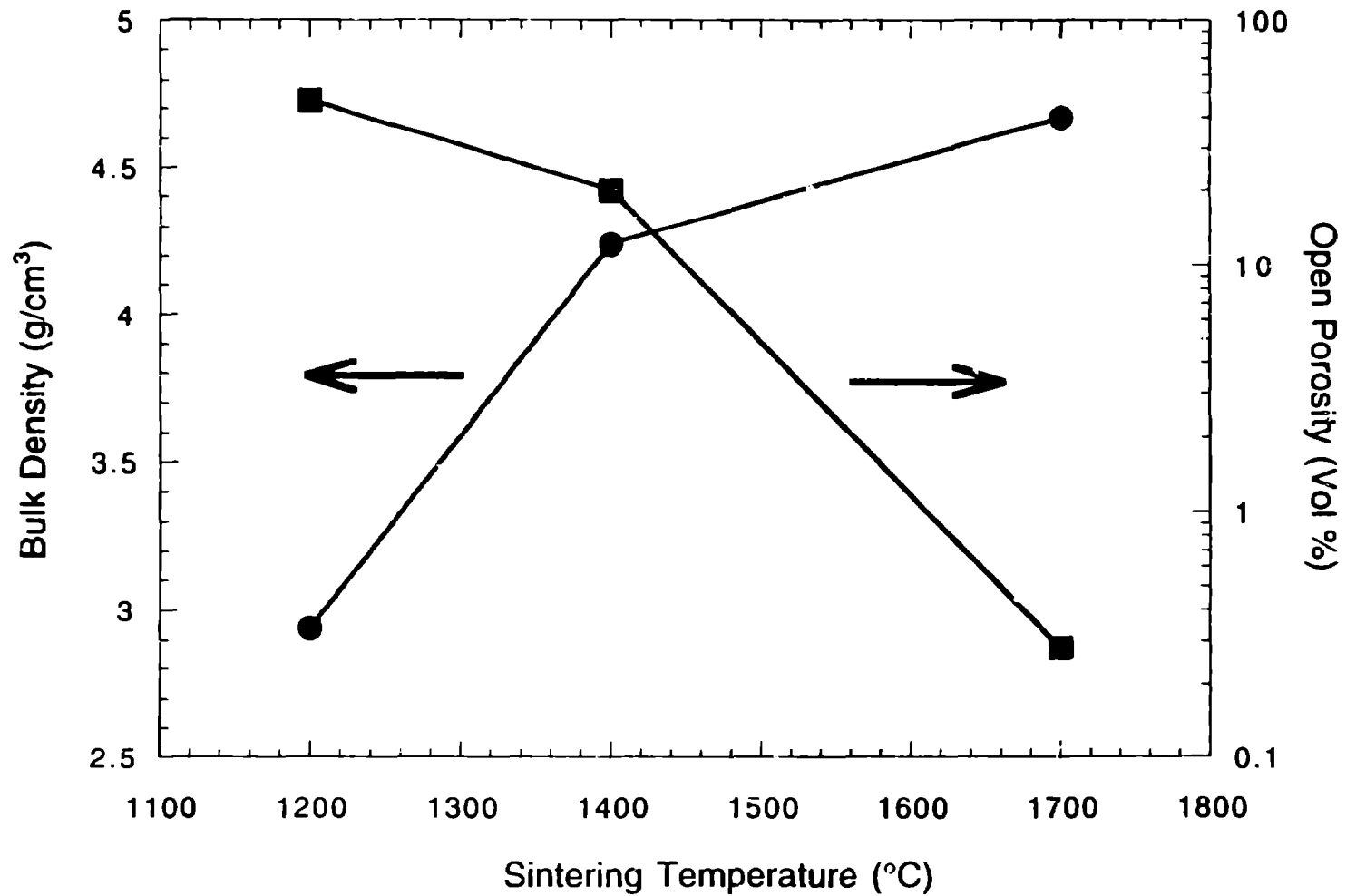


Figure 7. Densification behavior of surrogate fuel pellets.

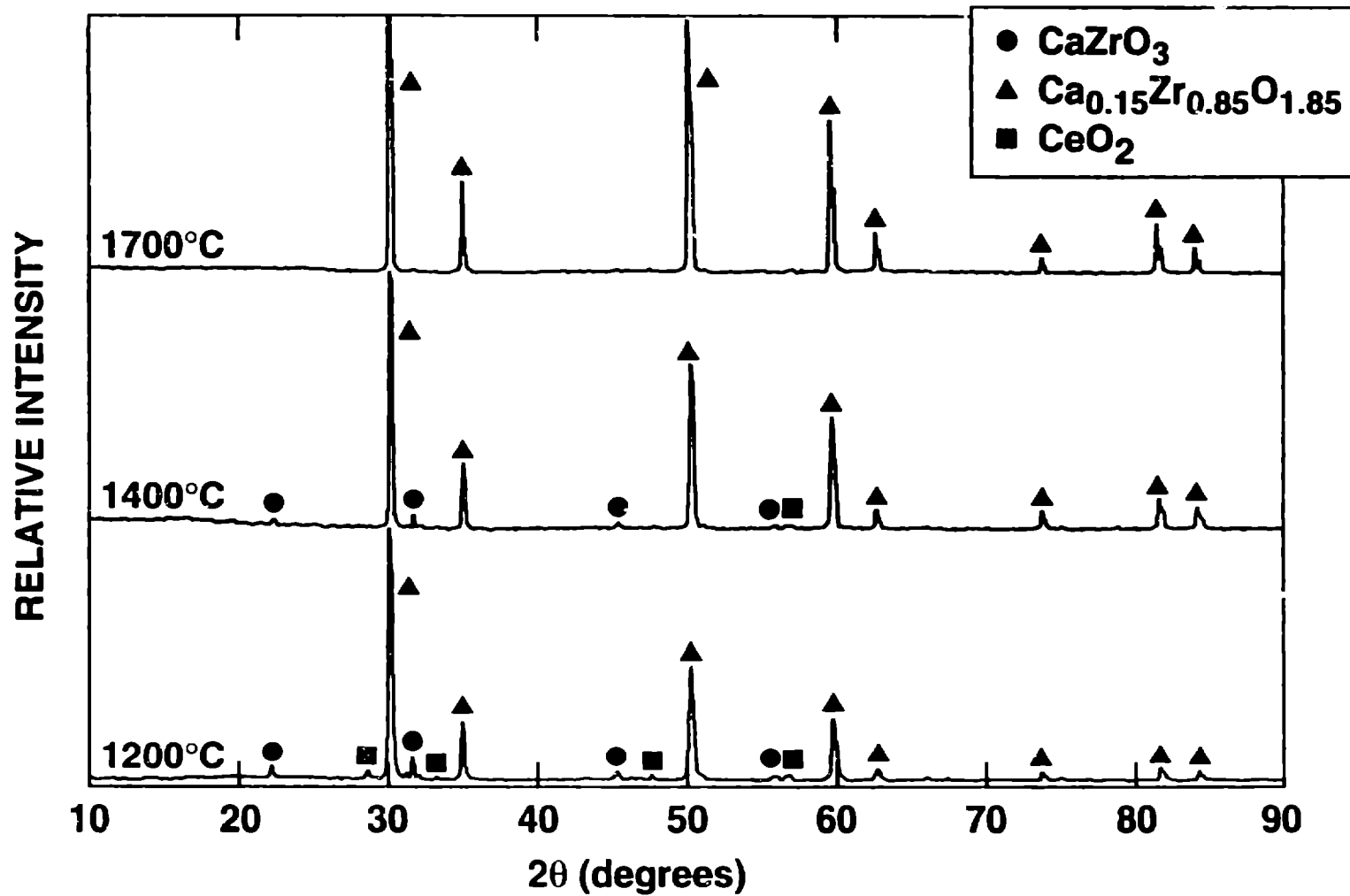


Figure 8. X-ray diffraction pattern of sintered surrogate fuel pellet.

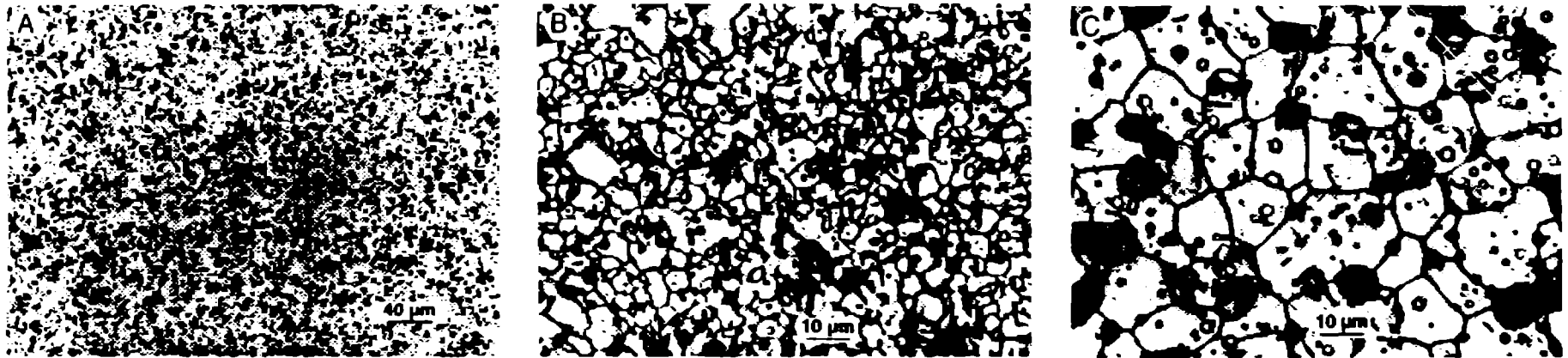


Figure 9. Optical micrograph of surrogate fuel pellet sintered at (A) 1700°C, (B) 1400°C, and (C) 1700°C.

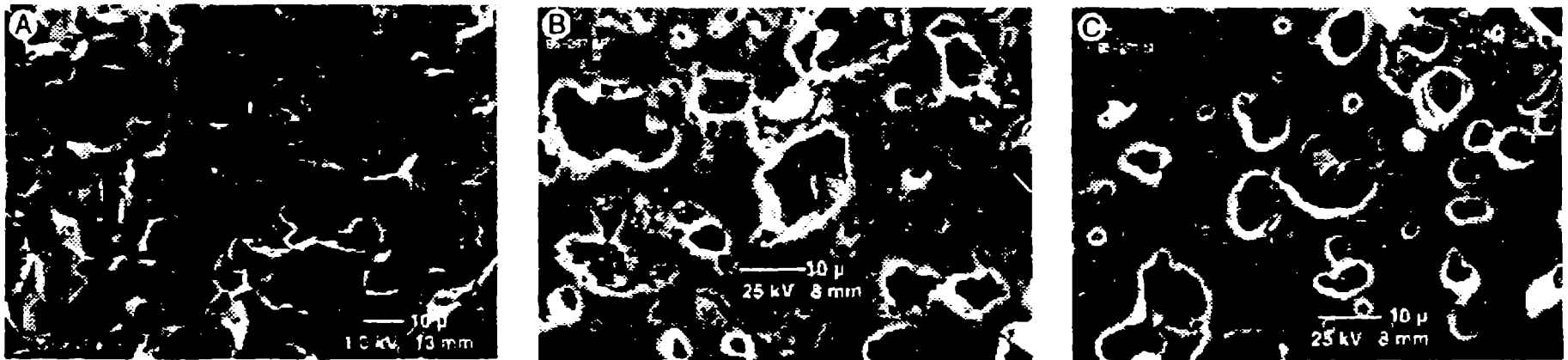


Figure 10. Scanning electron micrograph of sintered surrogate fuel pellet: (A) fracture surface of pellet sintered at 1700°C, (B) polished surface of pellet sintered at 1400°C, and (C) polished surface of pellet sintered at 1700°C.