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Zirconium carbonitride pellets by internal sol gel and spark plasma sintering as inert matrix fuel material

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HIGHLIGHTS

- Zirconium carbonitride pellets could be pressed by spark plasma sintering.
- Higher densities were reached by SPS compared to conventional sintering.
- Computer tomography could not detect any density gradients in the pellets.

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ABSTRACT

Inert matrix fuel is a fuel type where the fissile material is blended with a solid diluent material. In this work zirconium carbonitride microspheres have been produced by internal sol gel technique, followed by carbothermal reduction. Material nitride purities in the produced materials ranged from $Zr(N_{0.45}C_{0.55})$ to $Zr(N_{0.74}C_{0.26})$ as determined by X-ray diffraction and application of Vegard's law. The zirconium carbonitride microspheres have been pelletized by spark plasma sintering (SPS) and by conventional cold pressing and sintering. In all SPS experiments cohesive pellets were formed. Maximum final density reached by SPS at 1700 °C was 87% theoretical density (TD) compared to 53% TD in conventional sintering at 1700 °C. Pore sizes in all the produced pellets were in the μm scale and no density gradients could be observed by computer tomography.

1. Introduction

Nitride based materials are a category of materials that have been identified as a potential candidate in the sector of advanced nuclear fuels. Actinide nitrides, such as UN, or mixed nitrides, such as (U,Pu)N and (Zr,Pu)N, are considered to be interesting fuel materials compared to their oxide counterparts. This interest can be attributed to higher fissile material density, higher heat conductivity and better compatibility with liquid metal coolants, such as sodium or lead. An inert matrix is a material added to the nuclear fuel in order to reduce and control the fissile material density in the fuel. ZrN has been suggested as an inert matrix for actinide nitride fuel [1]. ZrN nitride has several advantages that make it a suitable inert matrix candidate, such as thermal conductivity that is comparably as high as that of UN and PuN [1–4]. ZrN also possess a similar melt temperature as UN and PuN [1,5,6], thus preserving a key property of the nuclear fuel. ZrN is a suitable diluent for nitride fuel in the respect that it also forms solid solution with UN and PuN instead of a two phase crystal system [1,7,8].

There are several viable ways of producing nitrides for nuclear fuel applications. Some of the studied production routes include cyclic hydriding/nitriding where metal is used as starting material and converted into hydride and subsequently nitride by heating in hydrogen and nitrogen atmospheres [9]. A different process that utilizes metallic material as a starting point is reactive ball milling. In reactive ball milling metal is milled in an N_2 atmosphere. The metal is nitrided by the N_2 and by exposing new metal surface to the atmosphere by the milling process the material can be converted into nitride, although long milling times are required [10]. Another production processes is nitride formation by carbothermal reduction. This is a process where metal oxide is blended with elemental carbon and heated in an N_2 environment. The

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carbothermal reduction process can be applied to materials where oxide powders have been blended with carbon powder, but it is also possible to produce nitrides from materials produced by internal or external gelation processes where carbon has been blended into an aqueous metal solution. The carbothermal reduction process has been identified as being a process suitable for nitride production with regard to the possibility for production of material in large scale [11].

The internal gelation process was originally developed in the KEMA (Keuring Electrotechnische Materialen Arnkem) laboratories in the Netherlands [12,13]. One of the main benefits connected to fuel production using microspheres formed by internal gelation techniques is minimization of fines formation throughout the production process, which is an advantage during reprocessing and refabrication of highly radioactive materials such as Pu. Microspheres formed using internal sol gel procedures tend to be more difficult to compact into fuel pellets compared to powders, often yielding lower green/sintered densities when applying conventional cold pressing techniques. In this work pellet production from microspheres produced by the internal gelation method has been pelletized using spark plasma sintering (SPS). The SPS produced pellets have been compared with the traditional cold pressing and high temperature sintering techniques. X-ray tomography was used to investigate density gradients in pellets produced by the different methods.

2. Theory

2.1. The internal sol gel process

The internal sol gel process is based on heat induced gelation of metal nitrate solutions. The starting solution is cooled to about 0–4 °C [14] and urea is added as a metal ion complexation agent. Hexamethylenetetramine (HMTA) is then added to the sol gel broth as a gelation agent. When nitride materials are to be prepared elemental carbon is also added to the sol as fine dispersed powder. By introducing the sol as small droplets into an immiscible heat carrier, such as silicone oil, the droplets form a spherical shape during gelation. The oil is commonly heated to between 50 and 100 °C and the temperature elevation causes the HMTA in the sol to decompose and raise the pH of the sol droplet, thereby inducing the gelation reaction [15]. The internal sol gel process has been studied in closest detail for uranyl solutions. When performing internal sol gel on zirconium the decomposition of HMTA, and thus the driving force of the reaction, is still the same as when gelating uranium.

HMTA protonation

$$(CH_2)_6N_4 + H^+ \rightleftharpoons [(CH_2)_6N_4H]^+ \tag{1}$$

HMTA decomposition

$$[(CH_2)_6N_4H]^+ + 3H^+\ 4NO_3^- + 6H_2O \rightleftharpoons 4NH_4^+ + 4NO_3^- + 6CH_2O \tag{2}$$

and the zirconium has been suggested to form hydrated zirconium hydroxide tetramers during solidification [16–18].

$$[Zr_4(OH)_8(H_2O)_{16}]^{8+} + 8H_2O \rightleftharpoons [Zr_4(OH)_{16}\cdot 16H_2O] + 8H^+ \tag{3}$$

2.2. Carbothermal reduction

Nitride formation by carbothermal reduction is a method where metal oxide and elemental carbon is mixed and heated in an N_2 environment. The general reaction for the nitride formation is:

$$MeO_2 + 2C\,(s) + 0.5N_2 \rightleftharpoons MeN + 2CO\,(g) \tag{4}$$

In the case of nitridation of ZrO_2 several different temperature-dependent reaction paths have been suggested [19].

The initial step of the reaction proposed is the formation of oxynitride in the temperature range $1423 \leq T \leq 1883$ K by the reaction

$$ZrO_2 + xC + (y/2)N_2 \rightleftharpoons ZrO_{2-x}N_y + xCO \tag{5}$$

The reaction can then proceed by direct nitride formation in the temperature range $1673 \leq T \leq 1783$ K if graphite carbon is used as the carbon source by

$$ZrO_{2-x}N_y + (2-x)C + ((1-y)/2)N_2 \rightleftharpoons ZrN + (2-x)CO \tag{6}$$

If the temperature exceeds 1783 K there will instead be formation of carbonitride by

$$ZrO_{2-x}N_y + (2-x+z)C + ((1-y-z)/2)N_2 \rightleftharpoons ZrN_{1-z}C_z + (2-x)CO \tag{7}$$

In order to facilitate a high degree of oxygen removal during the reaction a hyperstoichiometric amount of carbon is needed during carbothermal reduction. It is therefore of necessity to remove residual carbon in a decarburization step. This is normally performed at 1873 K or above by heat treatment in either $N_2 + H_2$ or $Ar + H_2$ mixtures to remove the carbon as HCN and/or short chain hydrocarbons such as methane.

2.3. Sintering and spark plasma sintering (SPS)

Sintering is a heat-induced densification of a mechanical body. The driving force for sintering is minimization of surface free energy and the driving forces are caused by particle surface curvature, chemical reactions and externally applied pressure. When sintering without any external pressure applied to the green body the material normally has to be heated to about half of its melt temperature for atom mobility to be large enough to allow the sintering phenomena to occur.

When performing spark plasma sintering no green body is prepared prior to sintering but instead the powder is put into a graphite pressing die and pressed during sintering. In spark plasma sintering a current is run through the pressing die and material, heating both during the pressing. This technique allows sintering to be performed at lower bulk temperatures compared to conventional sintering but localized temperature at grain contact points may be higher than the average temperature measured for the entire system. If the sample sintered by spark plasma technique is a much worse electrical conductor than graphite there is a possibility that the major part of the current will pass through the die instead of the sample. In this case the spark plasma sintering will be similar to traditional hot pressing techniques.

2.4. Density gradient evaluation

When pressing solid compacts from free flowing entities it is possible that the green body produced is inhomogeneous in density. There is no guarantee that density gradients formed during pressing can be removed by sintering of a green pellet. During the sintering process it is also possible that density gradients in the green body can cause undesired shrinkage behavior and potential cracking in the pellet [20]. Any residual density gradients post-sintering may affect properties of the final product. Measurements of density gradients can be performed by various different techniques. One of which is X-ray tomography, which is a