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EP 0249549 A1 EP 0218924 A2 EP 0026389 A1
US 4671904 A US 3872022 A

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(54) A sintered nuclear body and the production thereof

(57) Gadolinia-doped nuclear oxide material pellets have the gadolinia free and undissolved in the nuclear oxide material to improve the thermal conductivity of the body. The pellets may be made by mixing together gadolinia and nuclear oxide material, shaping the mixture, and subsequently heating the shaped mixture to a sintering temperature. The heating and duration at the sintering temperature and the environment in which the sintering is performed are selected to inhibit the dissolution of the gadolinia in the nuclear oxide material. Aluminium oxide may also be present in the pellets.

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A Sintered Nuclear Body and the Production thereof

This invention relates to a sintered nuclear body, and the production thereof, and more particularly to an oxide nuclear body containing gadolinia.

It is known to include gadolinia as a burnable poison dopant in uranium oxide or mixed uranium oxide, plutonium oxide fuel.

It is an object of the present invention to provide such a gadolinia-doped oxide nuclear fuel having an improved thermal conductivity.

According to one aspect, the invention provides a sintered body comprising nuclear oxide material having free gadolinia dispersed therein, thereby to improve the thermal conductivity of the body.

According to another aspect the invention provides a method of producing a sintered body comprising nuclear oxide material having free gadolinia dispersed therein, the method comprising mixing together gadolinia and nuclear oxide material, shaping the mixture, and subsequently heating the shaped mixture to a sintering temperature, the heating and the duration at said sintering temperature and the environment in which said sintering is performed being selected to inhibit the dissolution of the gadolinia in the oxide nuclear material.

The sintering may be performed by heating the shaped mixture to a sintering temperature of about 2100°C at a rate of about 200°C/min, holding said mixture at the sintering temperature for about 200 seconds, and cooling said mixture at a rate of about 300°C/min, said sintering being performed in an environment comprising moist hydrogen.

Alternatively, the sintering may be performed by heating the shaped mixture to a sintering temperature of about 1200°C, holding said mixture at the sintering temperature for about two hours, said sintering being performed in an environment comprising carbon dioxide, and subsequently heating said mixture in an environment comprising hydrogen at about 1150°C.

Preferably, between 4% and 12% by weight of gadolinia is included in the shaped mixture, at particle sizes of between 50 and 250 microns, for example between 50 and 100 microns, or between 100 and 150 microns, or between 150 and 250 microns.

The invention also includes a sintered body made by the method of the invention.

The invention further includes a method of testing sintered gadolinia-doped oxide nuclear material articles, the method comprising measuring the electrical resistance of the articles, thereby to determine the extent to which the gadolinia has dissolved in the oxide nuclear material.

The invention will now be further described in the following examples:

Example I

Gadolinia granules were prepared by adding binder to gadolinia powder together with a conventional binder solvent. The solvent was allowed to evaporate and the resulting paste was broken up into granules by stirring. when fully dry the granules were sieved into fractions between 100 and 250 microns. The sieved gadolinia granules

were mixed with granules (~1200 μm) of uranium dioxide and pressed into pellets. The binder in the gadolinia granules in the pellets was removed by "debonding" in carbon dioxide at about 800°C.

The pellets were divided into three batches and subsequently sintered by:

1. In hydrogen containing ½% carbon dioxide at 1700°C for 5 hours - (a conventional sintering process).
2. Heating to 2100°C at about 200°C/min, holding at this temperature for 200 seconds, followed by cooling at 300°C/min. The same hydrogen environment was used as in batch (1) above.
3. Heating to 1200°C for 2 hours in carbon dioxide, followed by reduction in hydrogen at 1150°C.

The sintered pellets were examined by scanning electron microscopy for the presence of free and dissolved gadolinia. The scanning revealed essentially free gadolinia with little or no dissolved gadolinia in the batches (2) and (3) but batch (1) had dissolved gadolinia.

Example II

Gadolinia granules prepared as in Example I were heated to 1500°C to 1800°C in hydrogen or air following binder removal at 800°C in air. The granules were then sieved into size fractions 100-150 μm and 150-250 μm. Material from each fraction was mixed with a respective

quantity of UO_2 powder at approximately 10% by weight, and the mixture pressed into pellets. The pellets were sintered as in batches (1) to (3) of Example 1. The sintered pellets were examined as in Example 1 and similar results were obtained, ie essentially undissolved gadolinia in a matrix of UO_2 resulted in the case of pellets sintered as in batches (2) and (3) of Example I with some dissolution of the gadolinia resulting after sintering as in batch (1) of Example I.

Example III

Gadolinia granules prepared as in Example I were pressed into pellets. The pellets were crushed through sieves and the fractions 50-100 μm, 100-150 μm, and 150-250 μm obtained. Material from each fraction was mixed with a respective quantity of UO_2 powder at approximately 10% by weight, pressed into pellets, and sintered as in Example I. On examination as in Example I, little gadolinia was found to have dissolved in the pellets sintered as in batches (2) and (3) of Example I, but some dissolution of gadolinia occurred from sintering as in batch (1) of Example I.

Example IV

Pellets of gadolinia as obtained in Example III, after binder removal, were sintered in hydrogen at 1800°C for 2 hours to a high density. The sintered pellets were crushed and the size fractions 50-100 μm, 100-150 μm and 150-250 μm obtained. Material from each fraction was mixed with a respective UO_2 powder at approximately 8% by

weight. The mixtures were pressed into pellets, and samples of each pellet were sintered in conditions selected as follows:

1. for 5 hours in hydrogen containing ½% carbon dioxide at 1700°C,

2. at 2100°C for 200 seconds in an atmosphere of moisturised hydrogen after heating to temperature in approximately 10 minutes, and

3. sintered in carbon dioxide at 1300°C for 1 hour prior to reduction in hydrogen at 1150°C for 1 hour.

Electron microscopy revealed that sintering of the pellets in condition (3) above resulted in little or no dissolution of gadolinia in the UO_2. This was less than that produced under condition (2) above but this in turn resulted in appreciably less dissolution of the gadolinia than in condition (1) which represents conventional sintering conditions.

The electrical resistance of each of the 9 sample types from Example IV was measured using a digital multimeter and the normalised resistances (per mm of thickness) were as follows:

size range (microns)	Normalised Resistance (k ohm) sintering condition (1)	sintering condition (2)	sintering condition (3)
50-100	.35	1.38	6.50
100-150	.57	2.42	10.90
150-250	1.04	5.43	24.91

It can be seen that the electrical resistance increases from condition (1) → (2) → (3) for all size ranges and that dissolved gadolinia decreases as

observed via microscopic examination as the resistance increases.

It is envisaged that other techniques such as plasma melting may be used to produce the gadolinia granules and that furthermore gadolinia may be added in combination with another material such as aluminium oxide. In this case gadolinium aluminate would be the material added to UO_2 powder.

Using proprietary data the thermal conductivity of UO_2 containing dispersed gadolinia has been calculated using an established formula (Kingery, Bowen and Uhlman, Introduction To Ceramics, 2nd edition, page 636, John Wiley & Sons 1976). Significant improvements in thermal conductivity were obtained for the compositions examined compared to the case where the gadolinia is dissolved in the UO_2, as shown below. Furthermore it can be shown that even if the gadolinia makes no contribution to the overall thermal conductivity there is still an improvement over the case of dissolved gadolinia.

Effect of Dispersed Gadolinia On The Thermal Conductivity of UO_2 At 1000°C:

Weight % Gadolinia	Ratio of Thermal Conductivities*	Improvement %
4	1.10	10
8	1.09	9
12	1.15	15

* Thermal conductivity of dispersed gadolinia doped nuclear fuel/thermal conductivity of dissolved gadolinia-doped nuclear fuel.

At temperatures lower than 1000°C it is envisaged that

the improvements in thermal conductivity will increase as the temperature decreases.

Claims

1. A sintered body comprising nuclear oxide material having free gadolinia dispersed therein, thereby to improve the thermal conductivity of the body.

2. A body as claimed in Claim 1, wherein the gadolinia comprises between 4% and 12% by weight of said body.

3. A body as claimed in Claim 2, wherein the gadolinia comprises up to about 10% by weight.

4. A body as claimed in Claim 2 or Claim 3, wherein the gadolinia comprises up to about 8% by weight.

5. A body as claimed in any one of the preceding Claims, wherein the nuclear oxide material comprises a uranium oxide.

6. A body as claimed in any one of the preceding Claims, wherein the body includes a material comprising aluminium.

7. A method of producing a sintered body comprising nuclear oxide material having free gadolinia dispersed therein, the method comprising, mixing together gadolinia and nuclear oxide material, shaping the mixture, and subsequently heating the shaped mixture to a sintering temperature, the heating and the duration of said sintering temperature and the environment in which said sintering is performed being selected to inhibit the dissolution of the gadolinia in the oxide nuclear material.

8. A method as claimed in Claim 7, wherein the sintering is performed by heating the shaped mixture to a sintering temperature of about 2100°C at a rate of about 200°C/min, holding said mixture at the sintering temperature for about 200 seconds, and cooling said mixture at a rate of about

300°C/min, said sintering being performed in an environment comprising moist hydrogen.

9. A method as claimed in Claim 7, wherein the sintering is performed by heating the shaped mixture to a sintering temperature of about 1200°C, holding said mixture at the sintering temperature for about two hours, said sintering being performed in an environment comprising carbon dioxide, and subsequently heating said mixture in an environment comprising hydrogen at about 1150°C.

10. A method as claimed in any one of Claims 7 to 9 wherein the gadolinia comprises between 4% and 12% by weight in the shaped mixture.

11. A method as claimed in Claim 10, wherein gadolinia comprises up to about 10% by weight.

12. A method as claimed in Claims 10, or Claim 11, wherein the gadolinia comprises up to about 8% by weight.

13. A method as claimed in any one of Claims 7 to 12, wherein the gadolinia comprises particles having particle sizes between 50 and 250 microns.

14. A method as claimed in Claims 13, wherein the gadolinia has particle sizes between 50 and 100 microns.

15. A method as claimed in Claim 13, wherein the gadolinia has particle sizes between 100 and 150 microns.

16. A method as claimed in Claim 13, wherein the gadolinia has particle sizes between 150 and 250 microns.

17. A method as claimed in any one of Claims 7 to 16, wherein a material comprising aluminium is mixed with the gadolinia and the nuclear oxide material.

18. A method as claimed in any one of Claims 7 to 17, wherein the nuclear oxide material comprises a uranium oxide.

19. A method as claimed in Claims 18, wherein the uranium oxide comprises granules of about 1200 microns.

20. A method of producing a sintered body substantially as hereinbefore described with reference to:

Example I batch II or III,

or, Example II batch II or III,

or, Example III batch II or III,

or, Example IV batch II or III,

21. A sintered body made by the method as claimed in any one of Claims 7 to 20.

22. A method of testing sintered gadolinia-doped oxide nuclear material articles, the method comprising measuring the electrical resistance of the articles, thereby to determine the extent to which the gadolinia has dissolved in the oxide nuclear material.

23. A method of testing the sintered body as claimed in any one of Claims 1 to 6 or Claim 21, the method comprising measuring the electrical resistance of the body, thereby to determine the extent to which the gadolinia has dissolved in the oxide nuclear material.

Patents Act 1977
Examiner's report to the Comptroller under section 17 (The Search Report)

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Relevant Technical fields

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(ii) Int Cl (Edition 5) G21C

Search Examiner

T BERRY

Databases (see over)

(i) UK Patent Office

(ii)

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Documents considered relevant following a search in respect of claims 1 TO 21

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	EP A1 249549 (URANIUM PECHINEY) note Claim 6, Claim 8	1,7
X	EP A2 218924 (ASEA-ATOM) note inferred properties of prior art material, page 2 line 25 to page 3 line 24	1,7
X	EP A1 26389 (KRAFTWERK UNION) note Claim 1	1,7
X	US 4671904 (KRAFTWERK UNION) note column 2 lines 41 to 65	1,7
	US 3872022 (GENERAL ELECTRIC) note Claim 1, example 4	1,7

Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

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P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family, corresponding document.

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