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Journal of Nuclear Materials 319 (2003) 51–58

journal of nuclear materials

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Zirconium nitride as inert matrix for fast systems

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Abstract

Zirconium nitride has been proposed as inert matrix material to burn plutonium or to transmute long-lived actinides in accelerator-driven sub-critical systems or fast reactors. In combination with the possibility to fabricate specially shaped fuel pellets, e.g. barrel with a hole, an innovative fuel would be designed to reach higher burnup.The current project aims to use the direct coagulation casting process to shape mixed plutonium zirconium nitride annular pellets. As a backup option the conventional powder-pressing route is used to produce standard pellets. Gibbs energy calculations were used to optimise the thermal treatment of carborthermic reduction to yield mixed nitride powders. The status quo of the powder and pellet production as well as the first analytical results are presented in the following.

PACS: 28.41.Bm; 81.05.Je; 81.20.Fw; 81.20.Ev

1. Introduction

1.1. General

Zirconium nitride has been proposed by several authors [1–3] as inert matrix material to burn plutonium or to transmute long-lived actinides in accelerator-driven sub-critical systems (ADS) or fast reactors (FR). This material offers a relatively high thermal conductivity and a high melting point as well as a cubic lattice structure, which corresponds to the one of plutonium nitride.

Mixed nitride microspheres were produced using the PSI sol–gel route combined with a carboreduction. Additionally different mixed oxide powders were reduced by carbothermic reduction to synthesise the mixed nitrides. Before producing the plutonium containing fuel different plutonium free nitride solid solutions have been produced to investigate their chemical and physical behaviour. In addition, thermodynamic calculations of the Gibbs energy were carried out to predict the behaviour of the material.

Complex shapes of fuel elements could lead to higher burnup, therefore advanced production techniques, allowing almost any shape, are of special interest. Direct coagulation casting (DCC), used by Gauckler et al. [4–7], as a new shaping method was introduced to the nuclear field to examine the possibility to fabricate more complex shaped fuels. To test the potential of DCC the relatively simple shape of an annular pellet was investigated in this study. The DCC process is based on the destabilisation of an electrostatically stabilised ceramic suspension by time delayed in situ reactions. Enzyme catalysed reactions, as urea/urease hydrolysis, can be applied. This results in a salt creation in order to increase the ionic strength or/and in a pH-shift of the suspension towards the isoelectric point (IEP) of the powder. In both cases the viscosity of the ceramic suspension increases and a wet green body is obtained.

1.2. Aim of the study

The aim of this study was to evaluate whether the carbothermic reduction is suitable for the mixed nitride fuel production in the case of zirconium nitride as

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doi:10.1016/S0022-3115(03)00133-8

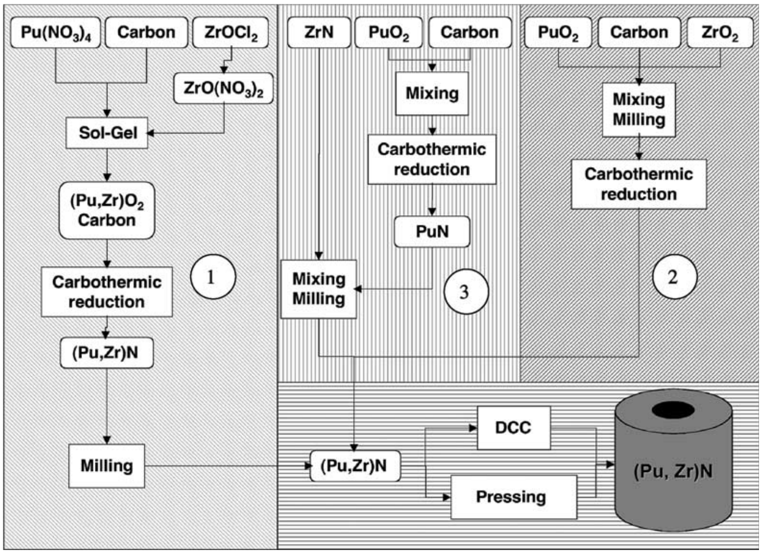

Fig. 1. Flow sheet of the production route of annular (Pu, Zr) N barrels.

matrix material, the DCC process could be used to shape nuclear fuel elements, especially in the case of zirconium nitride and whether the fabrication of conventional zirconium plutonium nitride pellets is possible.

The status quo of this study with some first results is given in this paper.

1.3. Production routes

In order to obtain mixed nitride powder three different routes (Fig. 1) were investigated. The first route comprised the PSI sol–gel method [1,8,9], which ends up with plutonium–zirconium oxide microspheres containing carbon black. The spheres were converted into the nitride by carbothermic reduction under nitrogen atmosphere. The second route directly used a mixture of plutonium oxide powder, zirconium oxide powder and carbon black for the carbothermic reduction. In the third route, commercially available zirconium nitride powder was mixed with plutonium nitride powder obtained from the reduction of the oxide with carbon. All resulting nitride powders were used to cast annular pellets via DCC. As backup shaping method, the conventional pressing method was envisaged.

2. Theoretical background

2.1. Sol–gel reaction

Ledergerber et al. [1,10,11] have given a good overview of the so-called ‘sol–gel’ process, which was recently summarised again by Streit et al. [12]. It is based on the internal gelation of pure Newtonian solutions (feed solutions) containing urea, hexamethylenetetramine (HMTA), nitric acid and a metaloxonitrate. Urea is added to a zirconyl nitrate solution to prevent the hydrolysis of the zirconyl ions as well as the complexation by the HMTA, which would result in a precipitation in the feed solution. Droplets of the feed solution are heated up in hot silicon oil, which accelerats the protonation and decomposition of HMTA. As a result ammonia is produced during this decomposition reaction, which initialises the gelation process. The hydroxide precipitated and the droplets become solid. The obtained microspheres are washed to eliminate the silicon oil and other reaction substances. Ammonia and water are removed during calcination of the microspheres.

2.2. Carbothermic reduction

Different authors [1,2,13–15] have summarised the assumed reactions during the carbothermic reduction of uranium or plutonium dioxide in a nitrogen/hydrogen atmosphere. Transformed to a reaction of a general metal oxide the following equation was obtained:

$$\mathrm{M}_m\mathrm{O}_{o+u} + o\mathrm{C} + \frac{m}{2}\mathrm{N}_2 + u\mathrm{H}_2 \rightarrow m\mathrm{MN} + u\mathrm{H}_2\mathrm{O} + o\mathrm{CO}$$

In this study, the metal component was generally not a single metal. The metal term M was divided into the matrix metal $^1\mathrm{M}$ and the dopant metal $^2\mathrm{M}$ where m_1 and m_2 described the ratios. This led to a general Gibbs energy of reaction:

$$\begin{aligned}\Delta_r G^0 = {} & m_1 \Delta_f G^0(^1\mathrm{MN}) + m_2 \Delta_f G^0(^2\mathrm{MN}) \\ & - \Delta_f G^0\left((^1\mathrm{M}_{m_1})\mathrm{O}_{\frac{m_1(o+u)}{m}}\right) \\ & - \Delta_f G^0\left((^2\mathrm{M}_{m_2})\mathrm{O}_{\frac{m_2(o+u)}{m}}\right) + \frac{o}{m}\Delta_f G^0(\mathrm{CO}) \\ & + \frac{u}{m}\Delta_f G^0(\mathrm{H_2O}) + \frac{o}{m}RT\ln\frac{p(\mathrm{CO})}{p^\circ} \\ & + \frac{u}{m}RT\ln\frac{p(\mathrm{H_2O})}{p^\circ} - \frac{1}{m}RT\ln\frac{(m^2 * m_1 * m_2)}{(m_1 * m_2)^m} \\ & - \frac{u}{m}RT\ln\frac{p(\mathrm{H_2})}{p^\circ} - \frac{1}{2}RT\ln\frac{p(\mathrm{N_2})}{p}. \qquad (1)\end{aligned}$$

In the following calculations of the Gibbs free energy of reaction, the matrix metal was zirconium ($^1M = Zr$) and as dopant metal cerium, uranium, plutonium or zirconium ($^2M = Ce, U, Pu, Zr$) with a ratio of 80:20 ($m_1 = 0.8$, $m_2 = 0.2$, $m = m_1 + m_2 = 1$) was used. Only the stoichiometric cases with $o = 2$ ($u, x, y = 0$) were considered. Fig. 2 shows results for the TGA–GC measurements of zirconium oxide microspheres doped with 2.5 mol of carbon black per mol oxide. The reaction started at about 1373 K where the weight loss and the gas release started. This agrees very well with the Gibbs energy in kJ mol^{-1} calculated with Eq. (1). Fig. 3 shows the Gibbs energy as function of temperature in K. The reaction maximum, assigned to the peak of CO gas release, was observed at about 1673 K with the TGA/GC.

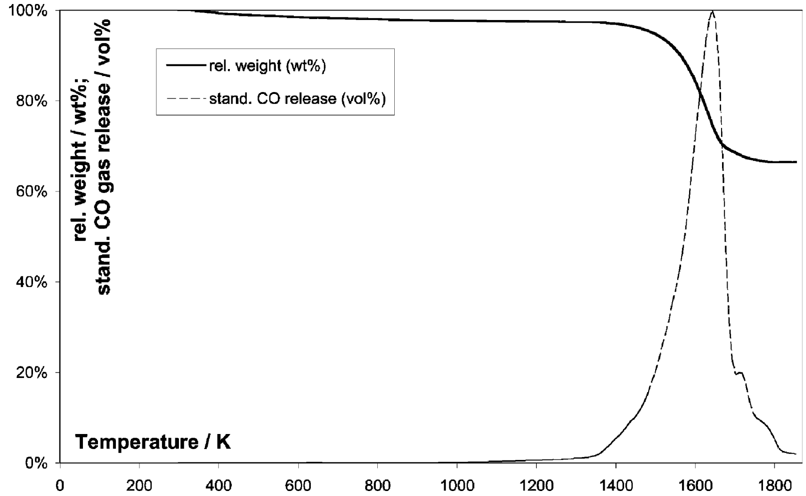

Fig. 2. TGA–GC measurements of zirconium oxide containing 2.5 mol of carbon in relation to the oxide.

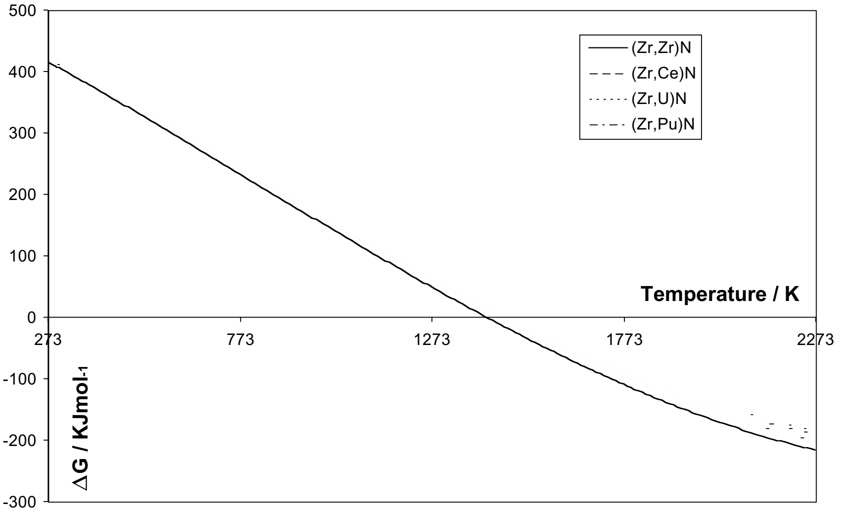

Fig. 3. Gibbs-energy of reaction calculated for carbothermic reduction of mixed zirconium oxides containing at.% Zr, Ce, U or Pu.

2.3. Direct coagulation casting

The direct coagulation process is based on the destabilisation of electrostatic stabilised ceramic suspension by time delayed in situ reactions [4]. Enzyme catalysed reactions, as urea/urease hydrolysis, can be used for salt creation to increase ionic strength of a suspension. The same reaction can also be used for shifting the pH of the suspension to the IEP of the used powder. In both cases the viscosity of the ceramic suspension increases and a wet green body is obtained. The mechanical strength of these bodies depends on the solid loading and the particle size within the suspension and can be increased by adding small quantities of alkaline swellable thickeners (AST). These macromolecules change their conformation during a pH shift to the alkaline regime during the enzymatic reaction. The reaction kinetics depends on the temperature and the enzyme concentration. In this work the hydrolysis of urea by the enzyme urease is used. At temperatures between 273 and 333 K in the pH range 4–9 the reaction:

$$NH_2CONH_2 + H_2O \xrightarrow{\text{urease}} HCO_3^- + 2NH_4^+$$

occurs. Thus the enzyme urease produces 3 mol ions from 1 mol urea substrate. This reaction increases the ion concentration in the suspension and/or shifts the pH from an acid regime to 9.

With this method it is possible to cast complex shapes with ceramic powder suspensions. The ceramic processing routes are well developed and reported for alumina powders and the urea/urease hydrolysis. Other enzyme systems are possible but not so successfully used for the DCC method [4,16–21].

In this work the DCC method is adapted to potential nuclear fuel using zirconium nitride powders as inert matrix material. A major problem in the nuclear field is the radiation influence on the enzyme. It is known that '...all enzymes can be inactivated when irradiated in solution, although the radiation doses necessary to inactivate different enzymes vary greatly...' [22]. Before working with plutonium containing samples the influence of α-irradiation and of heavy metals on urease has to be tested.

3. Experimental results and discussion

3.1. Sol–gel

Carbon black and a dispersant were added to a solution of HMTA and urea in water, and after dispersing the 'HMTA-C-solution' was ready to use. Metal solutions were prepared by dissolving the metallic nitrate salt in water. The different metal solutions were mixed for gelation in a fix ratio to obtain the 'M-solution'. The ratio of the solutions was such that the metal part of the end product contained 80% zirconium and 20 at.% of the second metal (Zr, Ce, Nd, U or Pu) component. The HMTA-C-solution was cooled down to about 274 K in the feed reservoir of the gelation system. While stirring the M-solution was slowly added. This resulting feed solution contained 1.20 mol% HMTA, 1.05 mol% urea and 2.50 mol% carbon in reference to the metal. It was stirred and cooled during the whole gelation process. The solution was passed through a nozzle with a diameter of 550 or 600 μm. The obtained droplets were falling into hot silicon oil, where the gelation reaction took place and microspheres were obtained. The spheres were washed with actrel, ammonia and methanol to remove silicon oil, water and organics. The green microspheres were dried in a rotary kiln at 383 K and calcined at 873 K for 4 h under an argon–hydrogen (8%) atmosphere.

3.2. Carbothermic reduction

The calcined microspheres were heated up under a nitrogen–hydrogen (7%) atmosphere with 300 K h^{-1} to a reaction level at 1673 K. After 8 h the furnace was heated up to 1873 K for additional 8 h. The cooling procedure was done under an argon–hydrogen (8%) atmosphere.

The golden coloured microspheres of ZrN, $Ce_{0.2}Zr_{0.8}N$, $Nd_{0.2}Zr_{0.8}N$, $U_{0.2}Zr_{0.8}N$, $Pu_{0.2}Zr_{0.8}N$ have densities between 91% and 103% TD. The microstructures of the spheres (Fig. 4) show rather big pores due to the high gas release during reduction and a second (black) phase. This phase most likely consists of unreacted material e.g. of metal oxide and carbon black, which explains the overestimated theoretical densities. This is emphasised by the results of the chemical analysis of the samples shown in Fig. 5. For an easy comparison

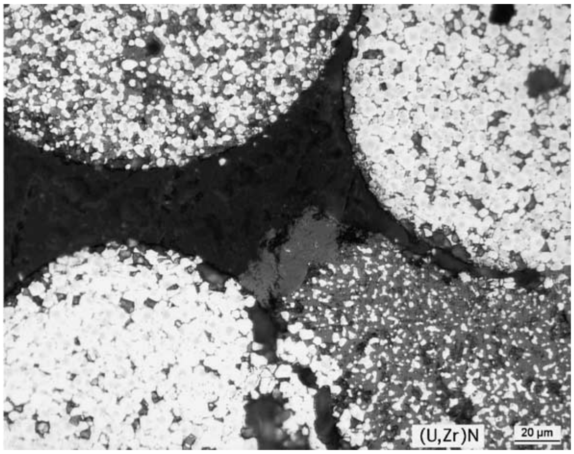

Fig. 4. Ceramography of $U_{0.2}Zr_{0.8}N$ microspheres.

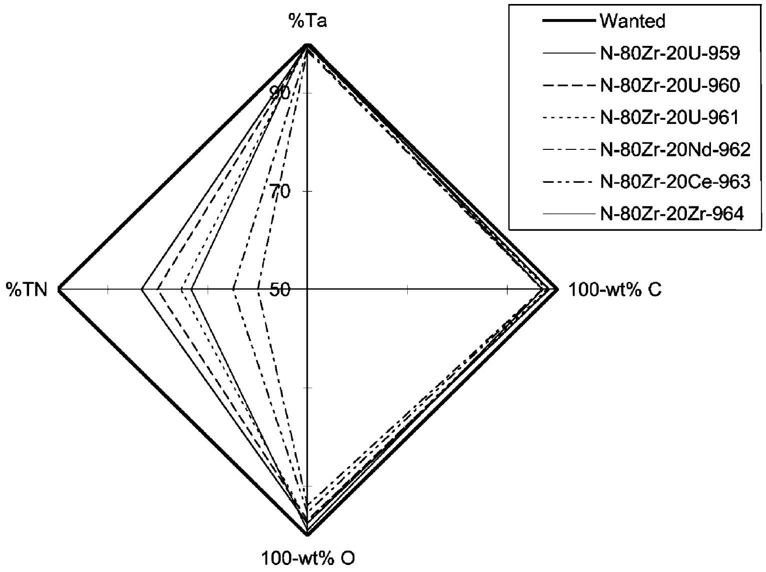

Fig. 5. Summary of the analytical results of XRD, C, N and O of doped microspheres.

of the different nitride powder qualities, the lattice constant and the nitrogen content are given in relation to the theoretical lattice constant in percent (% Ta) respectively the theoretical nitrogen content in percent (% TN). To have a simple diagram the carbon and oxygen contents are inversed by subtracting from 100.

To obtain better materials the powder route was tested with different oxide powders, which were mixed with carbon black to perform the carboreduction with the same thermal treatment as the microspheres. The obtained powders (ZrN, $Nd_{0.25}Zr_{0.75}N$, $Hf_{0.25}Zr_{0.75}N$, $U_{0.25}Zr_{0.75}N$, $Pu_{0.25}Zr_{0.75}N$) showed better results for the oxygen content and the lattice constant. A higher carbon content was observed due to a higher ratio of carbon black at the beginning of the reduction of the powders compared with the microspheres. The lower nitrogen content found needs further investigations. Fig. 6 summarises the analytical results of some of the produced

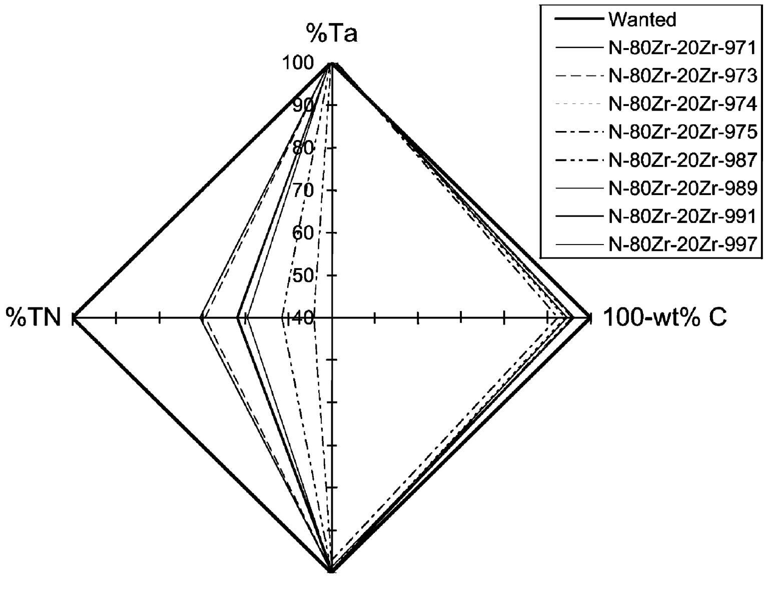

Fig. 6. Summary of the analytical results of XRD, C, N and O of self-made zirconium nitride.

zirconium nitride powders. In general it was possible to produce mixed zirconium carbonitrides. Further experiments, not part of this study, have improved the carbon to nitrogen ratio.

3.3. Direct coagulation casting

The IEP of commercially available zirconium nitride powder (AlfaAesar, 99.5%, Hf < 3%, Lot 63 560) was found at pH 5.6, measuring the electric sonic amplitude (ESA). This is too low to use the urea/urease hydrolysis when shifting the pH. However, as we also can create salt at the buffer pH = 9 of the urea decomposition reaction the destabilisation of the suspension by the ionic strength was used. To reach a higher stiffness of the wet green body AST's were used. Commercial zirconium nitride was added to an emulsion made from urea (8.75 mol%), citric acid diammonium salt (1 mol%), Aculyn (2.5 wt% of polymer in emulsion) and water. After dispersing the suspension four droplets of octanol were added to reduce the surface tension. After adding urease the suspension was shaken for 30 min before filling the moulds. The moulds were protected against drying up for 19 h. After drying for 4 days the pins were removed and after an additional day the pellets were demoulded. After drying 2 days in the exsiccator the pellets (Fig. 7(a)) were dried for 24 h at 383 K. The sinter program for the pellets has a first so-called de-waxing step at 973 K reached by a heating ramp of 450 $\mathrm{K\,h^{-1}}$ hold for 3 h. With a ramp of 450 $\mathrm{K\,h^{-1}}$ the pellets were heated up to 1423 K to heat further with a ramp of 67 $\mathrm{K\,h^{-1}}$ to a maximum of 2023 K, which was hold for 2 h. This was followed by a controlled cooling ramp (250 $\mathrm{K\,h^{-1}}$) till 1273 K were reached. From this point the furnace was cooled down by natural convection. The atmosphere in the reaction tube was argon with 7% hydrogen except the sintering time (end of de-waxing till start cooling down), where a nitrogen atmosphere with 8% hydrogen was used. Fig. 7(b) shows the first sintered zirconium nitride annular pellet. With DCC it was possible to shape annular zirconium nitride pellets. The used enzyme reaction takes about 24 h to solidify the used suspension. Using a radioactive suspension will degenerate the enzyme during this time by irradiation. Therefore further investigations are necessary to know more about the stability of urease during irradiation or to speed up the solidification reaction by choosing an other enzyme to use the pH shift.

3.4. Pellet pressing

As backup route it was decided to use conventional pellet pressing. Powder was weighed to yield a pellet of about 10 mm height and about 8.5 mm diameter, without any binder or other additions. The powder was pressed with about 20 kN for 20 s. For the radioactive material in the automatic press zinc stearate was used as a smear additive to protect the press tools. The yield green pellets (ZrN, $\mathrm{Nd_{0.25}Zr_{0.75}N}$, $\mathrm{Hf_{0.25}Zr_{0.75}N}$, $\mathrm{U_{0.25}Zr_{0.75}N}$, $\mathrm{Pu_{0.25}Zr_{0.75}N}$) were sintered with the same program as the

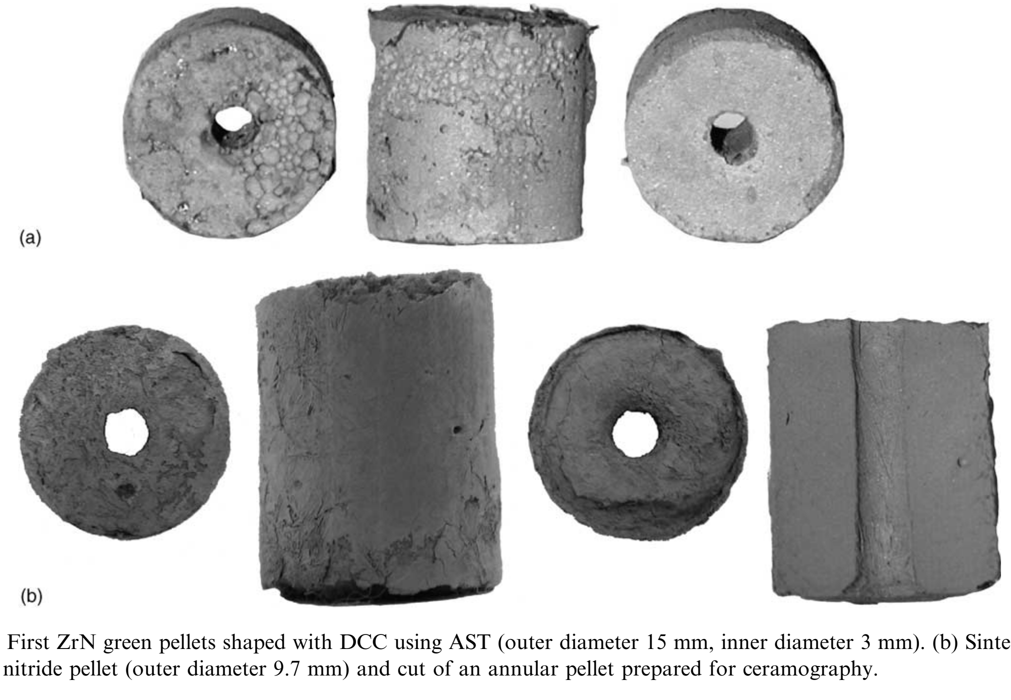

Fig. 7. (a) First ZrN green pellets shaped with DCC using AST (outer diameter 15 mm, inner diameter 3 mm). (b) Sintered annular zirconium nitride pellet (outer diameter 9.7 mm) and cut of an annular pellet prepared for ceramography.

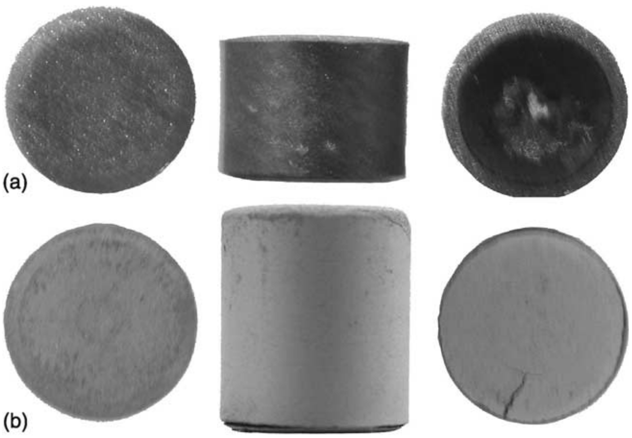

Fig. 8. (a) Sintered plutonium zirconium nitride pellet with a diameter of 7.11 mm and height of 5.05 mm. (b) Sintered zirconium nitride pellet with a diameter of 8.14 mm and height of 9.58 mm.

DCC pellets. Fig. 8(a) shows a sintered $Pu_{0.25}Zr_{0.75}N$ pressed pellet produced from self-made powder. The average geometric density of the pellet batch was found to be approximately 99% TD. Pure zirconium nitride pellets (Fig. 8(b)) showed densities between 70% and 80% TD. Only one phase was observable in the XRD. Chemical analyses are ongoing. Ceramographies of the inactive pellets showed no cracks and no larger pores. It was possible to press pellets out of the self-made nitride powders with relative high quantities of carbon and oxygen. An further improvement of the powder should result in pellets with higher density.

4. Conclusions and outlook

It has been shown, that the calculated Gibbs energy for carbothermic reduction fits well with the experimental results of the carbothermic reduction. The quality of the yield powders is not yet satisfying. Further improvements are on the way.

Direct coagulation casting with zirconium nitride works in principle using the increase of the ionic strength combined with AST. The stability of the urease enzyme in a suspension containing an α-emitter may be a major problem in the nuclear field. This aspect needs further investigation. The use of an other enzyme system using the pH-shift for coagulation reaction seems to be more promising than the urease system.

It was shown that it is possible to produce (Pu, Zr) N pellets by carbothermic reduction followed by conventional powder pressing. In order to decrease the impurity of the product, the composition of the initial powders as well as the parameters for the carboreduction have to be improved.

For irradiation experiments in the framework of the CONFIRM project [23,24] the production of pressed (Pu, Zr) N pellets with 20% and 30% plutonium will be performed.

Acknowledgement

This work is performed as PhD thesis of the first author at PSI, Villigen, Switzerland.

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