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Nitrides as a nuclear fuel option

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Abstract

Nitrides have been proposed to be a suitable material for fast neutronic systems from beginning of the development of nuclear fuel. Starting with the production of uranium nitride and sesquinitrides up to mixed plutonium uranium nitrides, today's developments are inert nitride matrix materials to burn plutonium or to transmute long-lived actinides in accelerator-driven sub-critical systems (ADS) or fast reactors (FR). Several authors proposed zirconium nitride as possible inert matrix material for this reason. Mixed zirconium nitrides can be fabricated by carbothermal nitridation of the oxides in a narrow temperature window. Obtaining high quality material with low carbon and oxygen content is still the major challenge. Producing mixed nitride fuels by special shaping methods, as for example direct coagulation casting or freeze drying, in comparison to conventional powder compaction enables to use this material in special shapes to optimize burn up.The history of nitride fuels at PSI will be shown up to today's CONFIRM project, dealing with plutonium zirconium nitride fuels.

Keywords: Nitrides; Nuclear applications; Powders-chemical preparation; Shaping; Sol–gel processes

1. Introduction

Supplying industrial countries with electric power is not and will not be an easy task. This is especially true when all restrictions concerning the reduction of CO_2 or waste, sustainability and low costs are considered. In the present and the near future nuclear power seems to be one sustainable solution to reduce the CO_2 output in the electric power production. In March 2004 about 440 nuclear power reactors were operating worldwide to produce about 2.6 billion MWh electricity per year and about 63 were under construction or planned.[1] As a consequence, tons of plutonium and high radioactive waste are produced every year. To reduce the toxicity of the nuclear waste concepts have been developed to transmute transuranium elements using inert matrix fuels (IMF) or to use special shapes to optimize the burn up of nuclear fuel. New IMF materials as ZrN and new shaping methods like direct coagulation casting (DCC)[2] are today of special interest in several international projects like the European Union 5th framework program collaboration on nitride fuel irradiation and modelling (CONFIRM) project[3].

From beginning of the development of nuclear fuel, nitrides have been proposed to be a suitable material for fast neutronic systems, because of their relatively high thermal conductivities and high melting points.

Just parallel to the oxide fuel production the nitrides have been examined. Starting with uranium nitrides and sesquinitrides in the late 1950s, beginning 1960s by several groups.[4–7] UN has been produced successfully by reduction of the metal and by carbothermic nitridation of the oxide. Using the carbothermic nitridation impurities of oxygen and or carbon were found in all products in various amounts. And still today UN is fabricated as replacement test material for PuN.

In the mid-1960s the fabrication of PuN and (Pu, Zr)N, as complement to the mixed oxide, starts.[8,9]

Between 1980 and 1990 the research on nitrides was not of major interest until in the beginning 1990s the search for IMF on oxide base was starting up.

Now the interest on nitrides to be used as high efficient transmutation or plutonium-burn-matrix was awaken again and several authors[10–12] proposed ZrN as IMF material. Mixed zirconium nitrides can, as mononitrides, be fabricated by carbothermic nitridation of the oxides.[3,13] Starting the

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nitride production from oxides will allow a cheap industrial production if the quality of the product is satisfying the reactor needs of low impurities and the right density. Depending on the loading of the material with fissionable material densities between 75 and 95 % of the theoretical density are envisaged. Too high impurities can affect the cladding of the fuel during irradiation, which could cause major safety problems.

First studies[11,14] deal with the fabrication and properties of (U, Zr)N followed by the production of (Pu, Zr)N.[13,15–17] Nowadays the production of mixed zirconium nitrides containing minor actinides like americium or neptunium for transmutation is the next milestone. The Advanced Fuel Cycle Initiative group examines among other things this topic[18] as well as the CONFIRM project.[3] However, the obtained nitride quality is not yet satisfying. The yield today's material has too high carbon content and is still rather a carbonitride than a nitride.[13,19]

Nuclear fuels are in general used in pellet form obtained by powder compaction. But also other fuels like sphere-pac (microsphere) or vipac (particle) fuels are in discussion and testing. Sometimes also unorthodox shapes like annular pellets or cross-forms are discussed.[20] To obtain such special fuel types different shaping methods have to be evaluated also with nitride fuels. Paul Scherrer Institute (PSI) used successfully its “sol–gel” method[11,12,19,21,22] to produce different nitride microspheres and spent some effort on developing ceramic shaping methods like DCC[2] and freeze drying (FD) on nuclear fuel.

This work summarizes the history and used methods of nitride fuels production atPSI from 1980s up to today's CONFIRM project.

2. Methods for nitride fuel production at PSI

2.1. Carbothermic reduction and sintering

Different authors[11,12,23,24] have summarized the assumed reactions during the carbothermic nitridation of UO_2 or PuO_2 in a nitrogen–hydrogen atmosphere. Transformed to a reaction of a general metal oxide and thermochemical modeling during CONFIRM project[25] have shown that reaction temperatures between 1800 and 2000 K are necessary to convert mixed zirconium oxides to nitrides. Decarburization should be performed in a nitrogen–hydrogen atmosphere at the same temperature range.

To sinter different nitride objects (microspheres, pellets, annular pellets) from different fabrication routes, one has to take into account that the material is normally not a 100% nitride. So further carbothermic nitridation could occur. To prevent the objects to crack a slow heating ramp in the temperature range of carbothermic nitridation should be used. Then the produced gas has time to release before grains are sintered together. Using nitrides it is necessary to use nitrogen in the process gas all the time to prevent evaporation and dissociation as well as oxidation.[25]

2.2. Powder compaction

Nitride fuel pellets are conventionally produced by two different powder compactionmethods. First oxide powder is mixed with carbon black and if necessary a binder like zinc stearate and pressed to pellets. During sintering step carbothermic nitridation is performed and nitride pellets with low density are obtained. These could be milled and the obtained nitride powder is compacted a second time.

Or as second possibility oxide powders are first converted to nitrides by carbothermic nitridation and the obtained nitride powders are compacted, using if necessary a binder, and sintered, which is the today's favored route at PSI.

Combined with centerless grinding it enables to reach a specified diameter with precision in the micrometer range.

2.3. Sol–gel method

Ledergerber and co-workers[12,21,22] has given a good overview of the so-called “sol–gel” process, which was recently summarized again for mixed zirconium nitrides by Streit et al.[26] It is based on the internal gelation of pure Newtonian solutions (feed solutions) containing urea, hexamethylenetetramine (HMTA), nitric acid and a metaloxonitrate. Droplets of the feed solution are heated up in hot silicon oil, which accelerates the protonation and decomposition of HMTA. As a result ammonia is produced during this decomposition reaction, which initializes the gelation process. Hydroxide precipitated and the droplets become solid microspheres.

To yield nitride microspheres at the end a certain amount of carbon black is added to the feed solution. After gelation the carbon is finely dispersed in the microspheres. During sintering step a carbothermic nitridation takes place and sintered nitride microspheres are obtained. Starting with solutions from reprocessing this process enables a dust-free fuel production. Moreover, the homogeneity of the so-called solid solution is higher than that of a powder mixture. Microspheres of different size fractions are either directly filled into the fuel rods or are crushed and pressed to pellets before the sintering step.[27]

2.4. Direct coagulation casting (DCC)

The DCC process is based on the destabilization of electrostatic stabilized ceramic suspension by time delayed in situ reactions.[2] Enzyme catalyzed reactions, as urea/urease hydrolysis, can be used for salt creation to increase ionic strength of a suspension or for shifting the pH of the suspension to the isoelectric point (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. With DCC 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.[28–31]

At PSI the DCC method was adapted to potential nuclear fuel using ZrN powders as IMF material.[19]

2.5. *Freeze drying*

The purpose of FD is to remove a solvent from dissolved or dispersed solids and is commonly used in food industry. The principle of this method is the process of dehydrating of a frozen suspension under vacuum by sublimation.

FD enables to cast complicated shapes without being restricted on an enzyme or other organic molecules, which are strongly influenced by irradiation. FD is mostly independent from the used powder. The only challenge is to prepare a high loaded suspension with the powder/liquid system of choice. Using organic solvent with a melting point slight above room temperature and a high vapor pressure enables an easy handling even for nuclear fuel powder in glove boxes. The obtained suspension is filled into moulds and frozen. The frozen material is then dried under vacuum or low pressure. The obtained green body is dried a second time under normal pressure but higher temperatures and after this step sintering is performed.

At PSI FD was tested to potential nuclear fuel using ZrN powders as IMF material (results to be published).

2.6. *Characterization*

The characterization of the material is depending on the special interests from reactor safety side. For nitride fuels the major interests are the impurity contents of oxygen and carbon as well as the nitrogen content of the material. This is determined at PSI with two LECO apparatus.

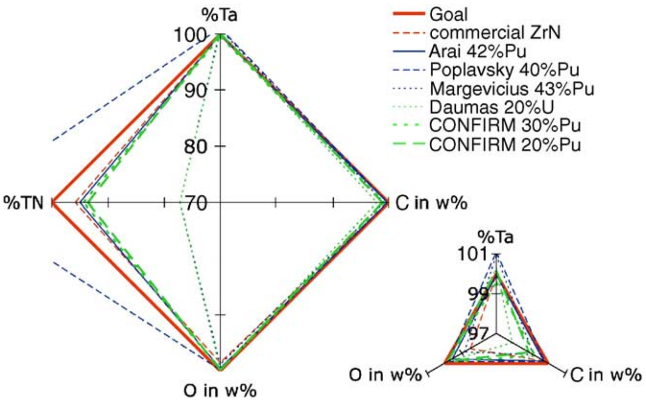

Fig. 1. Comparison of the quality of different nitride materials (Arai et al.,[15] Poplavski,[17] Margevicius, personal communication, Daumas,[11] CONFIRM, to be published).

The fabricated material should be single phased, which is controlled by X-ray diffraction (XRD). Density is determined depending on the material by gas pycnometer, water immersion or just geometrical.

A special graphic design (Fig. 1) is used in at PSI for easy comparison of the quality of different nitride powders. The lattice constant and the nitrogen content are given in relation to the theoretical constant and the theoretical nitrogen content respectively in percentage (%Ta, %TN). The carbon and oxygen content are inversed in this diagram. The best value for both is of course 0 wt.%. For this diagram the measured value is subtracted from 100 to result in a square of all target values at 100.

3. Results and discussion

3.1. *Carbothermic reduction and sintering*

Using carbothermic nitridation to convert oxides into nitrides is a simple route for fuel production. The main disadvantage of the carbothermic nitridation is the relatively high carbon and oxygen content after a first reaction. Using powders, instead of pellets or microspheres, it is possible to reduce the oxygen in the mixture by mixing the obtained carbonitride again with carbon and to treat a second time in the furnace. This possibility may result in a higher carbon contamination, depending on the decarburization step, but also in lower oxygen content. Oxygen and carbon impurities of below 1 wt.% each were obtained for mixed zirconium nitrides at PSI.

Daumas[11] used a sintering program to produce (U, Zr)N pellets at high heating rates of 500 K/h to a reaction temperature of 1875 K to convert the pressed oxide carbon mixture to the nitride. The performed calculations of Streit[19] and Jolkonnen et al.[25] show that the nitridation takes place at lower temperature when removing the produced CO rapidly. A heating rate controlled by the gas release would be ideal to increase the temperature in a more controlled manner.[32] The product composition could be improved by inserting a holding time in the thermal treatment at for example 1675 K until CO production is finished before raising the temperature to an other step. Higher gas flux should be envisaged to reduce the CO partial pressure in the reaction chamber, to prevent the material from back reaction. This might cause technical problems on further industrial scale. If nitrides should be irradiated in a reactor it is necessary to replace ^{14}N by ^{15}N in order to prevent ^{14}C production and to decrease radio toxicity in the waste.[33] In this case the relatively expensive excess of ^{15}N has to be recovered and cleaned, which might be a major technical problem.

3.2. *Powder compaction*

Several experiments in the frame of the CONFIRM project with mixed zirconium nitrides were performed. It was found that compaction is possible but high carbon content will lead

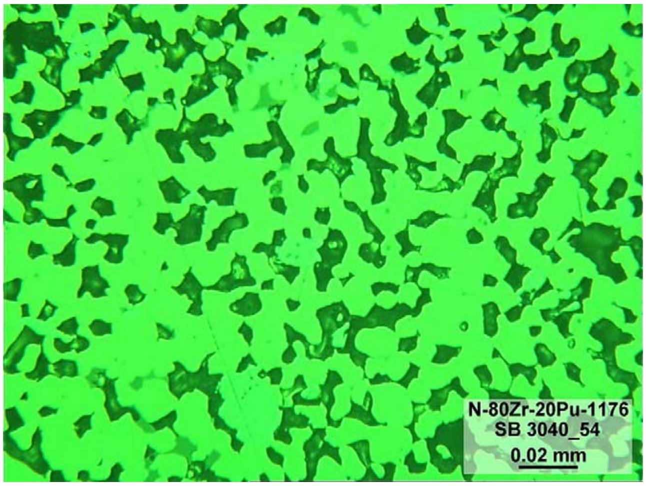

Fig. 2. Ceramography of a $(Pu_{0.2}Zr_{0.8})N$ pellet showing a porosity of 18.5%.

to cracks in the pellets during sintering. The used mixed zirconium nitride powders are easy to handle, except the neodymium containing powder, which oxidizes on air.

(Pu, Zr)N pellets fabricated for CONFIRM project will be irradiated in the Studsvik test reactor. In this campaign it was found that it was not possible to reach higher densities than in the range of 78–81.5 %TD. This could be explained by the hardness of the powder particles before compaction. Ceramography in Fig. 2 shows clearly the big pores, which are surrounded by sintered particles. Another fact is, that a nitride with a relatively high oxygen content shows a higher density. The reason here fore could be that oxygen acts as a sintering aid.

To reach higher densities with mixed zirconium nitride powders further process optimizations have to be done or other shaping methods, like FD or DCC have to be used.

3.3. Sol–gel method

With the method of internal gelation different nitride microspheres were produced at PSI:[13,14,27,34] UN, (U, Pu)N, ZrN, (CeZr)N, (Nd, Zr)N, (U, Zr)N and (Pu, Zr)N.

The different colors of the spheres, shown in Fig. 3, indicate the different impurity levels of the different material.

In general they show a to high content of oxygen and especially carbon (1–5 wt.%), which is not satisfying.

It is not achieved to complete the carbothermic nitridation to convert the whole oxide into nitride. This is due to the fixed positions of carbon in the microspheres. With this method only one carbothermic nitridation is possible, which disables an optimization by repeating the reaction.

Further optimization may lead to a production route of carbonitride microspheres out of solutions obtained from reprocessing, but high quality nitride powders will not be accessible.

3.4. Direct coagulation casting

The usability of DCC in the nuclear nitride fuel production was tested at PSI.[19,26,35] It was possible to cast ZrN with the DCC method using the increasing of ionic concentration as well as the addition of AST with the urea/urease enzyme system. In both cases annular ZrN pellets were obtained and sintered. No cracks were found in the sintered pellet as could be seen in Fig. 4. The surface structure of the shown pellet is manly depending on the greasing of the mould, which has to be improved. Ceramography of the cut

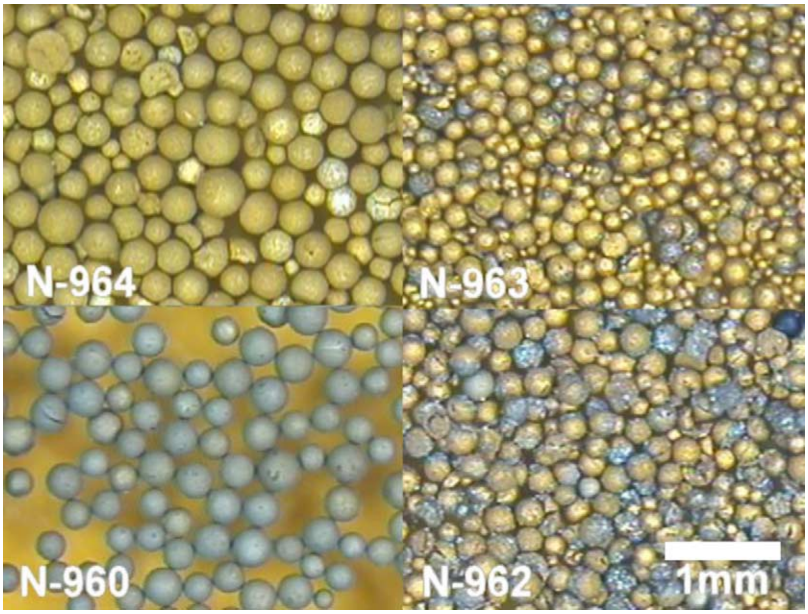

Fig. 3. Sintered ZrN microspheses (N-964) and spheres doped with Ce (N-963), Nd (N-962) and U (N-960).

Fig. 4. Sintered annular ZrN pellet fabricated by DCC (outer diameter: 9.7 mm) and cut for ceramography on right side.

pellet was not successfully finished, due to the hardness of the material.

(Pu, Zr)N pellets could not be produced by DCC so far, because it was not possible to coagulate the ZrN with the urea/urease system in a short time period. Both used methods need about 24 h to solidify the suspension. But fast reaction is the main prerequisite to use DCC with radioactive material, because of its influence on the enzyme system. Irradiation, heavy metals and water radicals have a strong destructive influence on large organic molecules like enzymes.[19] Using the pH-shift as a fast reaction would be the only opportunity to shape radioactive material with DCC. For mixed zirconium nitrides another enzyme system has to be used which ends its reaction at a pH range between 5 and 6, due to the IEP of ZrN, and not at 9 as the used one.

3.5. Freeze drying

Learning from DCC that large organic molecules could complicate shaping processes in nuclear fuel production the idea was born to use FD instead. First experiments with ZrN powder show good results in the same quality range, which was achieved with DCC.

The shaping processes using an organic solvent and ZrN powder result in week porous green bodies, which get slightly stiffer after thermal drying and much more after sintering. Fig. 5 shows a batch of green annular freeze-dried ZrN pellets after demoulding. Optimizations of the process concerning mould and performing of the single steps are ongoing.

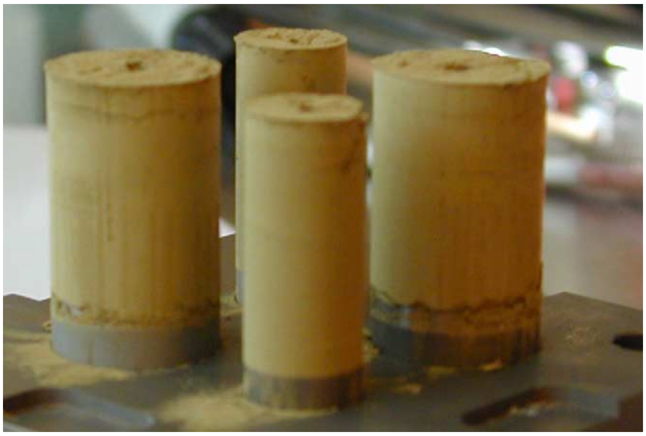

Fig. 5. Green annular ZrN pellets fabricated by FD (outer diameters: 10–15 mm) before thermal drying step.

4. Conclusion

A series of nitride products have been prepared by means of different methods. It was shown that it is possible to produce nitride fuel microspheres with PSI "sol–gel" method but the nitride quality is not really satisfying. The carbon content is too high and the final product is rather a carbonitride than a nitride.

The fabrication of nitride power using the carbothermic nitridation from the oxides is not the best way to produce high quality nitrides, but it is the cheapest way and will be the procedure of choice when producing nitride fuel in industrial scale. It has been shown that it is possible to produce (Pu, Zr)N fuel with carbon and oxygen impurities below 1 wt.% each. This quality is not yet good enough to speak from a high quality nitride, but might be acceptable for reactor usage. Nevertheless the quality has to be improved.

Compacting nitride powder was possible but the reached densities of around 80% TD were not satisfying. To obtain higher densities or more complicated shapes DCC and FD were envisaged. DCC is in principle possible and reaches nearly 100% TD with non-radioactive power but the so far used enzyme system is not suitable for actinide containing material. FD seems to be an easy method to obtained more complicated shapes. But the procedure has to be tested with actinide containing material.

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