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Letter to the Editors

Some aspects of the use of ZrN as an inert matrix for actinide fuels

M. Burghartz [a], G. Ledergerber [b], H. Hein [c], R.R. van der Laan [c], R.J.M. Konings [d,*]

[a] *Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland*
[b] *Kernkraftwerk Leibstadt AG, CH-5325 Leibstadt, Switzerland*
[c] *NRG, P.O. Box 25, NL-1755 ZG Petten, Netherlands*
[d] *European Commission, Joint Research Centre, Institute for Transuranium Elements, P.O. Box 2340, D-76125 Karlsruhe, Germany*

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Abstract

The sodium compatibility and the nitric acid dissolution of $(Zr_{0.80}U_{0.20})N$, prepared by carbothermic reduction of the oxide, were determined. No interaction with liquid sodium ($T = 823$ K) was observed. The material readily dissolved in nitric acid ($T = 378$–383 K). From these results it is concluded that ZrN is an attractive inert matrix in fast reactor fuels for the incineration of plutonium and minor actinides. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Uranium-free fuels are often considered for the incineration of plutonium and minor actinides. In these fuels, an inert matrix serves as the support for the actinide phase, as does the non-fissile ^{238}U-oxide for plutonium oxide in mixed oxide (MOX) fuel. However, ^{238}U is fertile and is a source for the formation of plutonium and other transuranium elements. By the use of an inert matrix, such a source is absent and hence, the incineration process can proceed further.

The concept of inert matrices for fuels and targets for incineration of actinides is being investigated for several fuel cycles. Oxide inert matrix fuels are mainly developed for the incineration of plutonium in LWR's [1–3], oxide inert matrix targets for the incineration of americium in dedicated reactors [4], generally in once-through strategies. Fuel cycles based on metal nitride are being considered for future transmutation devices such as CAPRA-type fast reactors or accelerator-driven systems for which the possibility for reprocessing of the fuels and targets is of importance.

Studies have shown that the number of candidate inert matrix materials for nitride fuels is limited [5], especially when the compatibility with PUREX reprocessing technology is taken into account. Zirconium nitride is considered one of the most promising inert matrices for nitride fuel cycles for fast reactors [5,6]. Zirconium has a low cross-section for neutron capture, the thermal conductivity of ZrN is high and ZrN is thermodynamically stable up to high temperatures. However, uncertainty exists about some of its chemical properties that are relevant to the application of ZrN in fast reactors:

1. The compatibility with sodium, the cooling medium.
2. The dissolution in nitric acid, the standard solvent for the PUREX process.

In the present letter we report the results of laboratory experiments that were performed to evaluate these aspects.

2. Materials

Pellets with composition $(Zr_{0.80}U_{0.20})N$ were prepared at the Paul Scherrer Institute. A zirconyl nitrate

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[*] Corresponding author. Tel.: +49-7247 951 391; fax: +49-7247 951 566.
E-mail address: konings@itu.fzk.de (R.J.M. Konings).

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solution was prepared by dissolving zirconyl nitrate powder, purchased from CERAC (USA), in demineralised water. The Zr concentration in the solution was 1.56 mol kg^{-1} and the molar ratio NO_3/Zr was 2. A uranyl nitrate solution was prepared from UO_3 and HNO_3. The uranium concentration was 1.6 mol kg^{-1} and the NO_3/U molar ratio 1.6. The nitrate solutions were cooled down to about 273 K, mixed with hexamethylene tetramine and urea and then dropped into a heat carrier (silicon oil of about 380 K). In this internal gelation procedure [7] the nitrates are converted to hydroxides which are converted to oxides by subsequent thermal treatment.

$(Zr_{0.80}U_{0.20})N$ was fabricated by a carbothermic reduction of the milled oxide microspheres. The milling and mixing with carbon was done in a TURBULA equipment type T2C. Measurements of the specific surface on milling time have shown that an optimum is reached after 7.5 h milling; the specific surface of the nitride is in the order of 2 m^2 g^{-1}. After milling, the powder was pressed into pellets and sintered. The pellets had a diameter of about 5 mm and densities of 69% (sample 2) and 87% (sample 3) of the theoretical density ($\rho_{th} = 8.74$ g cm^{-3}). The applied sintering programme was the following:

1. Heating under Ar/7%H_2 (to avoid formation of sesquinitride) to 1073 K within 2 h, 1 h holding time.
2. Heating under Ar/7%H_2 to 1773 K, gas change to N_2/7%H_2, 1 h holding time.
3. Heating to 2023 K, 16 h holding time.
4. Cooling to 1773 K, gas change to Ar/7%H_2, cooling to room temperature.

The crystal structure of the sintered pellets was analysed by X-ray diffraction (Philips PW100) applying Cu Kα radiation and using Ni as reference. The material was identified as single cubic phase with a lattice parameter of 467.2(2) pm. The carbon analysis shows that 2.53 wt% ($\sigma = 0.04$) carbon is present. This quite high carbon content is in agreement with the result of the lattice parameter measurements, which show a deviation from the ideal $(Zr_{0.80}U_{0.20})N$ structure [8,9].

ZrN powder used for the nitric acid dissolution tests was purchased from Aldrich (<325 mesh). The major impurities in the ZrN were Ca (1×10^{-4}%) and Mg (5×10^{-4}%) as specified by the supplier. X-ray diffraction analysis (Enraf Nonius, Cu Kα_1 radiation and using Si and W as reference) showed that the lattice parameter is 457.99(5) pm. This value is slightly higher than that reported in the literature (457.76 pm) [10], which may be due to some substitution of N by C or O in the lattice. The particle size distribution of the powder was determined to be between 0.275 and 11 μm by laser diffraction (Malvern Instruments Mastersizer 2000), the mean size being 3.6 μm. The specific surface area was found to be 2.668 m^2 g^{-1}.

3. Results

3.1. Compatibility with sodium

Pellets of (Zr,U)N were enclosed in stainless steel capsules (AISI 316 L) together with solid sodium (Métaux Spéciaux, Grade ER, oxygen content less than 30 ppm). The volume ratio of the pellet and the sodium was 1:3. The steel capsules were carefully outgassed at 773 K in vacuum after which they were transferred to an argon-filled glove box, in which the loading was done. After the capsules were closed with a screw cap and a copper sealing ring, they were sealed into quartz and heated for 72 h at 823 K.

X-ray radiography of the capsule (Fig. 1) showed that the pellets were still intact after the test. Next, the capsules were opened and the sodium was dissolved in ethanol to recover the pellets. Visual inspection showed no indications of chemical interaction between pellet and sodium. SEM analysis confirmed this observation (Fig. 2).

3.2. Dissolution in nitric acid

Dissolution tests in nitric acid were performed to investigate the compatibility with the PUREX reprocessing technology. For this purpose (Zr,U)N disks were

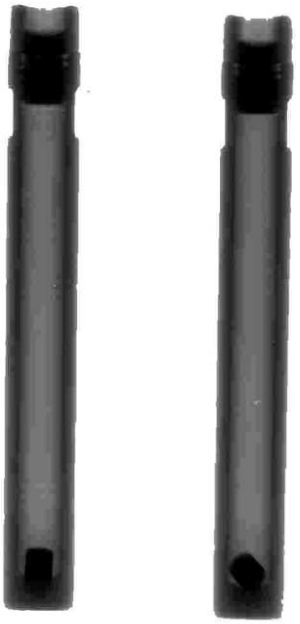

Fig. 1. The X-ray photographs of the (Zr,U)N pellets in sodium after heating for 72 h at 550°C. Left sample 2 that had a density of 69% and right sample 3 that had a density of 87% of the theoretical one.

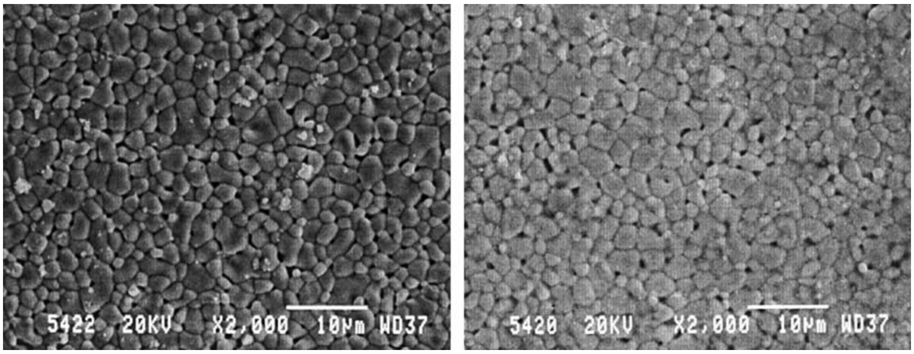

Fig. 2. Scanning electron microscopic images of sample 3 before (left) and after (right) the sodium compatibility test.

reacted with 50 ml nitric acid (10 mol dm^{-3}) at 378–383 K under reflux conditions. For comparison ZrN powder was also dissolved under similar conditions. The maximum duration of the test was 10 h. After the tests the material that was not dissolved was weighed and characterised by X-ray diffraction.

The tests showed that the (Zr,U)N discs readily reacted with the acid solution (Fig. 3). 85% of the material had reacted after 6 h. The remaining material was identified by X-ray diffraction as a mixture of ZrN and ZrO_2. The dissolution of the ZrN powder proceeded even more quickly, as can be expected from the much higher specific surface area. The latter results can be compared to the experiments by Kleykamp [6], who observed very slow dissolution of slabs of ZrN (89% density): 1.5% of the initial mass was dissolved after 34 h. Kleykamp obtained for the rate constant of dissolution $k = 0.17$ mg cm^{-2} h^{-1}. When our results for the ZrN powder are fitted to a similar linear equation ($\Delta m/F_0 = kt$ in which F_0 is the initial specific geometric surface) and assuming the incubation period to be less than 1 h, we obtain $k = 0.74$ mg cm^{-2} h^{-1}.

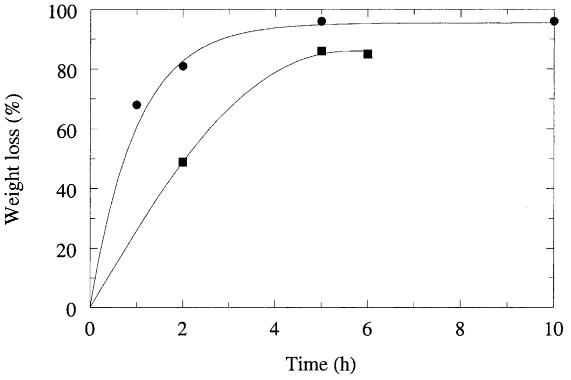

Fig. 3. The dissolution in boiling nitric acid as a function of time: (●) ZrN powder and (■) $(Zr_{0.8}U_{0.2})N$ pellet.

4. Conclusions

The results of our experiments show that (Zr,U)N is compatible with sodium and is soluble in nitric acid. This confirms that ZrN is an attractive inert matrix for fast reactor application. However, confirmation of the results using (Zr,Pu)N and, eventually, (Zr,Am)N is needed.

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