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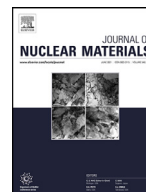
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Gonzalez Fonseca, L., Hedberg, M., Retegan Vollmer, T. (2021). Oxidation and hydrolysis of thorium doped uranium nitride fuel for use in LWR. Journal of Nuclear Materials, 555.
<http://dx.doi.org/10.1016/j.jnucmat.2021.153150>

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Oxidation and hydrolysis of thorium doped uranium nitride fuel for use in LWR

L.G. Gonzalez Fonseca*, M. Hedberg T. Retegan Vollmer

Division of Nuclear Chemistry and Industrial Materials Recycling, Department of Chemistry and Chemical Engineering, Chalmers University of Technology, 412 96 Gothenburg, Sweden



ARTICLE INFO

Article history:

Received 6 April 2021

Revised 11 June 2021

Accepted 23 June 2021

Available online 27 June 2021

Keywords:

Doped uranium nitride

SPS

Theoretical density

Porosity

Oxidation

Corrosion

Autoclave test

ABSTRACT

Uranium nitride is being investigated as a replacement for UO_2 as it shows enhanced thermal properties and seems to be a promising accident tolerant fuel (ATF) candidate. The main drawback of UN fuel is its innate low oxidation resistance in air/water environments. This becomes a challenge for the implementation of UN fuel in water-cooled reactors. The effect of thorium doping in the stability of uranium nitride microspheres and pellets sintered by spark plasma sintering (SPS) was investigated in oxidizing environments using thermogravimetric analysis and autoclave testing. It was found that during oxidation in air the density had a noticeable effect, increasing the reaction onset temperatures in pellets with higher densities. In addition, thorium doping improved the oxidation resistance of pellets in air by increasing the maximal reaction rate temperature by approximately 50 K. However, this effect was almost nonexistent in highly porous doped microspheres. The interaction with water at 373 K showed that pellets manufactured using SPS can survive unchanged for at least six hours in boiling water, which is an improvement to cold-pressed pellets. At 473 and 573 K, the pellets were oxidized and disintegration into an oxide powder was observed. Thorium-doped uranium nitride pellets did not present any improvement with respect to the oxidation resistance of UN in water at these temperatures.

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1. Introduction

Currently, uranium dioxide (UO_2) is the commercial nuclear fuel of choice, following decades of research and development in industry and power plants. Therefore, its properties, advantages, and disadvantages are well known. However, after the Fukushima Dai-ichi nuclear accident in 2011, identification and implementation of newer and safer nuclear fuel concepts became a prioritized area of research. Enhanced safety fuel concepts are commonly referred to as Accident Tolerant Fuel (ATF). ATFs are defined as fuels that exhibit improved properties compared to the current UO_2 /Zircaloy fuel system, while reducing oxidation kinetics and hydrogen production rates under accident conditions [1]. For the fuel material, disregarding cladding material, different ATF candidate fuels have been considered in the literature, such as uranium nitride (UN) and uranium silicides (U_xSi_y) [2]. Uranium nitride has been previously considered as a possible fuel for fast breeder reactors, and some properties, such as irradiation behavior, have been studied [3]. As an ATF, uranium nitride presents improved thermal proper-

ties compared to UO_2 , such as higher thermal conductivity in addition to a higher heavy metal density in the material [4]. However, its implementation as a nuclear fuel in water-cooled reactors has been limited due to its poor stability in oxidizing environments, such as the water in the primary circuit [5]. Before UN can be completely accepted as an ATF, the oxidation corrosion resistance must be enhanced to prevent dissolution of the fuel in cases of water intrusion inside the cladding.

Improving the stability of UN in oxidizing environments has proven to be a challenging task [1,2,5–7]. Several ideas have been proposed, including producing fuel pellets with low porosity levels, or coating the nitride pellets with corrosion-resistant materials [8,9]. However, it is well known that conventional pellets tend to develop cracks due to swelling and gas release, making an external surface coating ineffective if the water can leak in through the cracks. Thus, the idea of doping UN with metals that can form an oxide scale even after pellet breakdown was proposed by other authors [10]. Chromium and aluminum are known for their ability to form a chromia or alumina scale on the surface of materials, which prevents corrosion, for example of steels. However, no dopant that can form a protective film and inhibit hydrolysis has been identified for the UN system. This work investigates the effect of thorium

* Corresponding author.

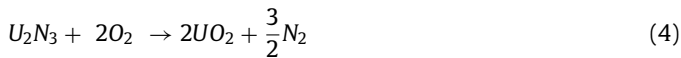
E-mail address: luig@chalmers.se (L.G. Gonzalez Fonseca).

doping in the oxidation resistance of uranium nitride microspheres and pellets sintered by SPS using thermogravimetric analysis and autoclave testing. Thorium was proposed as a possible dopant due to previous studies showing that ThO₂ is more stable and less soluble in water than UO₂ [11,12].

2. Theory

2.1. Oxidation of UN and ThN in air

The oxidation mechanisms for uranium nitrides in air has been studied previously by different authors [13,14]. Depending on the oxidation environment and temperature, different products, such as UO₂, U₃O₈, or UO₃, can be expected. Dell et al. [15] studied the reaction mechanism, and they found that in air, the transformation of UN powders into UO₂ starts at 473 K following Reaction 1. Nitrogen released in the reaction can either combine with another nitrogen and form N₂ or react with UN to form U₂N₃, as shown in Reactions 2 and 3. They also concluded that a sandwich structure is formed with UO₂ as the outer layer, followed by a U₂N₃, and UN in the bulk.



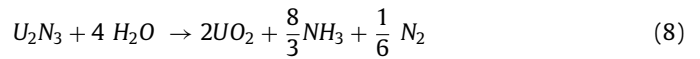
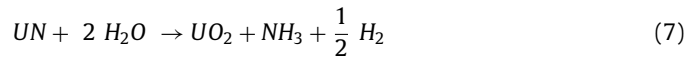
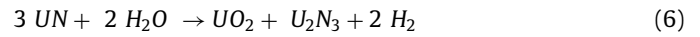
Due to the chemical potential gradient, the oxygen will react in the interface and migrate through the oxide lattice by vacancy exchange, further oxidizing the UN and U₂N₃ in the bulk of the material Eq. 1 and (4) [13]. A UO₃ phase has been observed starting at 523 K. As temperature rises, UO₃ is converted into U₃O₈, which is the final oxidation product [13,14]. Thorium oxidation chemistry is simpler because thorium is present only in a +4 oxidation state in the oxide compound, therefore the only product observed is ThO₂ [16].



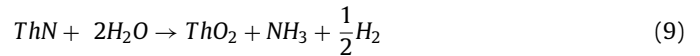
2.2. Hydrolysis of UN and ThN

In aqueous or steam environments it is known that UN will react to produce UO₂ according to the following reactions proposed by Rao et al. [14]. They theorized that the lower oxidation potential

of water molecules compared to O₂ was the reason for the production of UO₂ instead of higher oxides, such as U₃O₈ or UO₃. Formation of U₂N₃ has also been observed during these reactions, depending on the material properties, as explained by Dell et al. [17]. The produced U₂N₃ is further oxidized to UO₂. The production of ammonia as a byproduct is also undesirable, as this will modify the water chemistry in the coolant.



As with oxidation in air, thorium nitride hydrolyses into ThO₂ without the presence of any higher nitrides (Reaction 9), as studied by Sugihara et al [16]. They proposed that no higher nitrides were formed because of the large differences in the crystal structure between ThN and the intermediates Th₂N₂O or Th₃N₄. Therefore, long movement of Th atoms must happen to allow the insertion of nitrogen in the structure. Alternatively, shorter movements of uranium atoms in U₂N₃ are necessary for the atoms to be positioned at a similar distance than in the UN lattice.



3. Experimental

3.1. Materials

UN microspheres were produced through an internal gelation method, followed by carbothermic reduction and nitridation. The synthesis process and characterization of microspheres, in addition to the pellet's sintering parameters, have been described elsewhere [18]. Microspheres of UO₂ were produced using the same procedure, excluding the addition of carbon, and the nitridation step during heating. Doped and undoped UN pellets were then manufactured using SPS, pressing the microspheres without material grinding or the use of binders. Sintering temperatures between 1723 and 2023 K, and pressures between 50 and 100 MPa were used to achieve different porosity in the pellets. Pellets of UO₂ were pressed using a manual hydraulic press. The pressure used was 2GPa which was held for 5 minutes. The as-pressed UO₂ pellets were sintered at 1923 K for 6 hours. A summary of the elemental composition and properties of the materials used in this study are listed in Table 1. Density variations in pellets were obtained due to different sintering parameters used during SPS. Composition differences between samples can be attributed to the difference in distribution of carbon in each batch of microspheres.

Table 1

Elemental composition of UN and (U,Th)N microspheres produced by the internal gelation method. The lattice parameter was determined using X-ray diffraction prior to pressing and sintering of the materials. The density of the pellets is listed as percent of theoretical density (%TD). The confidence level for the uncertainties is 2 σ , and n.d. denotes that values were not determined.

Sample name	Nitrogen Content (wt-%)	Carbon Content (wt-%)	Oxygen Content (wt-%)	Lattice Parameters (Å)	% TD
UN-1	5.2 ± 0.1	0.27 ± 0.01	0.574 ± 0.002	4.896 ± 0.004	90.5 ± 0.5
UN-2	5.0 ± 0.1	0.6 ± 0.1	0.23 ± 0.02	4.896 ± 0.002	94.3 ± 0.4
UN-4	n.d.	2.0 ± 0.1	n.d.	n.d.	92.5 ± 0.8
UN-5	5.3 ± 0.2	0.2 ± 0.1	0.08 ± 0.02	4.894 ± 0.002	93.1 ± 0.4
UN-6	4.02 ± 0.04	2.3 ± 0.4	0.24 ± 0.06	4.92 ± 0.02	90 ± 1
UN-7	5.3 ± 0.2	0.01 ± 0.03	0.09 ± 0.02	4.892 ± 0.002	98.2 ± 0.4
(U ₉₅ Th ₅)N	5.6 ± 0.4	0.010 ± 0.002	0.26 ± 0.02	4.913 ± 0.006	95.2 ± 0.6
(U ₉₀ Th ₁₀)N	5.3 ± 0.4	0.3 ± 0.1	0.4 ± 0.1	4.924 ± 0.002	97.7 ± 0.6
(U ₈₀ Th ₂₀)N-1	5.1 ± 0.1	0.5 ± 0.1	0.6 ± 0.1	n.d.	90.4 ± 0.3
(U ₈₀ Th ₂₀)N-2	3.5 ± 0.2	2.4 ± 0.1	0.37 ± 0.02	4.99 ± 0.01	95.0 ± 0.9
UO ₂	0.19 ± 0.01	n.d.	12.1 ± 0.8	5.45 ± 0.01	92.4 ± 0.2

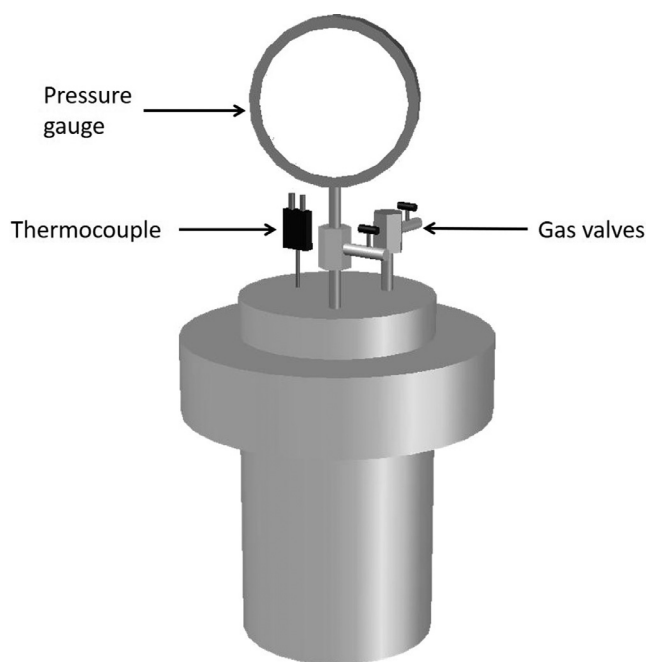


Fig. 1. Representation of the autoclave used for water/steam interaction experiments.

3.2. Methods

The oxidation tests were performed in an oxygen-containing environment using a thermogravimetric analyzer (TGA Q-500 from TA instruments). Pellets were cracked into small pieces by application of mechanical pressure using an agate mortar. Samples of approx. 10–20 mg were placed in a basket made of alumina and introduced into the instrument. The temperature was increased at a heating rate of 5 K/min up to 1173 K. A mixture of 90% synthetic air (AGA, 99.99%) and 10% N₂ (99.996%) was used throughout the heating process with a flow of 100 mL/min. The final oxygen content in the oxidizing gas was 18.9%. The oxidized samples were cooled to room temperature at a rate of 15 K/min. The mass change was monitored with $\pm 10 \mu\text{g}$ accuracy. The TGA results were analyzed with respect to mass change of the samples during the experiment, reaction onset temperature and maximal reaction rate temperature. The reaction onset temperature was defined as the temperature where 5% of the final mass change was obtained. The maximal rate temperature was determined as the maximum peak value of the first derivative of the mass change graphs. A buoyancy correction was performed by measuring the mass change of an empty sample holder and subtracting it from the values of the TGAs obtained for all the samples.

Water/steam corrosion tests were performed first in a glass beaker containing 500 mL of ultra-pure water ($18.2 \text{ M}\Omega\cdot\text{cm}$), which was heated until boiling. The pellet was weighed and placed in a platinum basket, which was then introduced into the boiling water. After 6 hours the pellet was taken out, dried with an absorbing tissue, and weighted to determine any mass change. The next set of experiments were carried out in a stainless steel autoclave, provided by Parr instruments, with maximum temperature and pressure limits of 623 K and 20 MPa, respectively. A schematic representation of the autoclave system can be seen in Fig. 1. Ultra-pure water ($18.2 \text{ M}\Omega\cdot\text{cm}$) was used throughout this study to investigate its interaction with the fuel. The pellet was placed in a stainless steel sieve basket designed to achieve a larger interface between the pellet and water. The autoclave was tightly closed and purged several times with argon to remove oxygen from the auto-

clave. The argon-purged autoclave was left at 1 MPa over-pressure over night to check for leakages. Before the interaction experiments, the autoclave atmosphere was purged once again with argon and the pressure in the autoclave was adjusted to atmospheric pressure before the heating process was performed. Temperature was increased to 373, 473, or 573 K, and was then maintained for two hours before turning off the heating mantle. The autoclave was left to cool overnight before opening.

Pellets that did not pulverize during the exposure experiments were cut, polished, and characterized using a Leo Ultra 55 SEM equipped with an EDX detector to observe the effect of the heating treatment on the surface of the pellet. The measurements were carried out in high vacuum with a high voltage ranging from 10–30 kV. In cases where the pellets did not survive, the water was filtered, using a Grade 1 Whatman® filter paper, to recover the residual powder. The powders were let to dry in air for at least 24 hours. Dissolution of uranium and thorium in the simulated coolant water was measured using a Thermo-Fisher inductively coupled plasma mass spectrometer (ICP-MS). The nitrogen and oxygen contents were measured in the recovered powders using a LECO TC-436DR. Powders were also investigated by X-ray diffraction (XRD) using a BRUKER D2 PHASER XRD, which includes monochromatic Cu ($\lambda = 1.54184 \text{ \AA}$) radiation source in 2θ range of $20^\circ - 144^\circ$, with a lynxeye detector. The operation voltage and current used were 30 kV and 10 mA, respectively.

4. Results and discussion

4.1. Oxidation of nitride fuels in air

Thermogravimetric analyses were used to study the behavior of different samples of UN and Th-doped UN materials under an oxygen atmosphere. Results are presented in Fig. 2. It can be seen that there was a slow increase in mass at the beginning of the treatment, and after the onset temperature the mass gain increased rapidly. A small weight loss was observed for the (U95Th5)N and UN-7 low porosity microspheres after 773 K, which was attributed to nitrogen gas being slowly released from the pores as suggested by other authors [13,19,20].

For the UN-1 high porosity and (U90Th10)N microspheres, the maximal mass gain was higher than in the other two samples and could correspond to the formation of UO₃ according to the expected weight change, 13.5% for pure UN and 12.9% for (U90Th10)N. The measured highest weight change is above the expected values (less than 0.5% difference), which can be attributed to nitrogen gas developed during the reaction and trapped in the material [14]. The possibility to produce UO₃ was attributed to the higher porosity and starting oxygen content of these two samples compared to the rest. Following decomposition to U₃O₈ could be expected once the temperature was increased above 773 K [14]. This was corroborated by the presence of peaks with negative reaction rate in the derivative of the TGA (Fig. 3) and a weight decrease of approximately 2%, as expected by the calculations.

Reaction onset temperatures and maximal reaction rate temperatures for the TGAs are summarized in Table 2. For comparison purposes, the onset temperature was defined as the temperature where 5% of the final mass increase was reached. Uranium nitride microspheres showed onset temperatures between 519 and 550 K. Thorium doped microspheres showed a lower range for onset temperatures, between 516 and 524 K. The maximal reaction rate temperatures for microspheres were similar to each other, varying between 573 and 600 K, with the low porosity sample (UN-7) having the highest temperature. No clear correlation was found between the doping level and the oxidation temperatures of highly porous materials, such as microspheres.

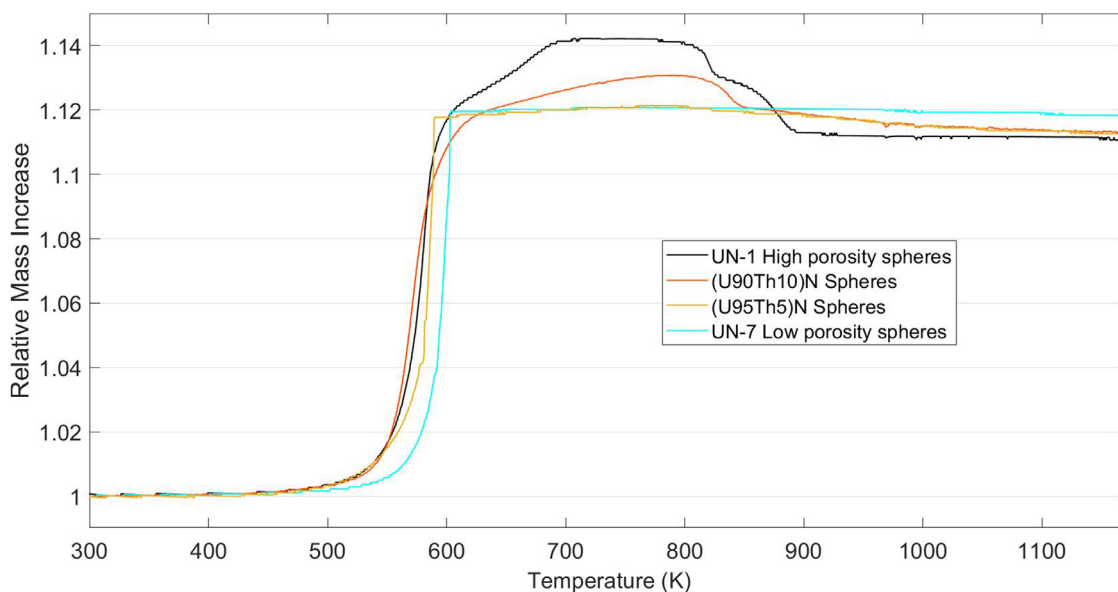


Fig. 2. TGAs for oxidation of uranium nitride and (U,Th)N microspheres using a mixture of 90% synthetic air and 10% N₂ with a flow rate of 100 mL/min.

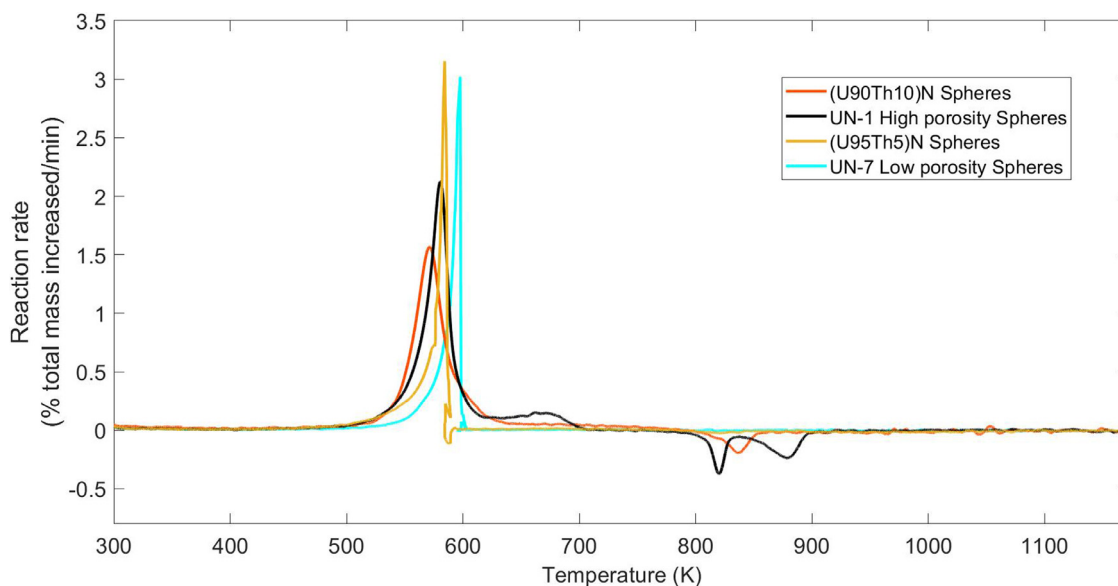


Fig. 3. Derivative of the TGAs of UN and Th-doped UN microspheres showing the reaction rate as mass increase per unit of time.

Two sets of pellets were selected for the TGA analysis with either high or low porosity, and for each, a doped and undoped pellet were used. To obtain the low porosity pellets, temperatures of 1923 K and 75 MPa pressure were used in the SPS. For high porosity pellets, either the temperature was reduced to 1723 K or the pressure to 40 MPa. The TGAs for the pellets are compared in Fig. 4.

UN-1 pellet with high porosity (~10%) showed a maximal reaction temperature at 603 K; a small improvement compared to the microspheres. It can also be seen that for the UN-7 pellet with low porosity (~2%), both the onset and maximal reaction rate temperatures were drastically increased to 679 and 853–873 K, respectively. As the reaction rates were slower for high density pellets, a maximal reaction rate temperature was difficult to determine, therefore, a temperature range was listed for these samples instead. The maximal reaction rate values for low porosity pellets was comparable to the standard UO₂.

The high porosity pellets have an oxidation behavior similar to the microspheres, as the reaction rates have a high maximum peak in the TGA at 633 K or below. On the contrary, the maximal reaction rates of low porosity pellets were not as high and occurred at significantly higher temperatures (873–923 K). These results are comparable with studies done previously by other authors [14,15,19,20] in pellets manufactured using UN powders instead of microspheres. The similarity in behavior between high porosity pellets and microspheres could be explained by the existence of a porosity threshold or a logarithmic correlation between the reaction rate and the porosity. At low porosity, the surface area available for reaction is small, and therefore the transport of oxygen through the oxide layer would be the limiting step. As the porosity increases, the surface area also increases, which allows a faster oxidation. Once the porosity exceeds the threshold, oxygen transport through the oxide layer becomes less important.

Table 2

Oxidation reactions temperatures for UN and (U,Th)N microspheres and pellets with different levels of porosity. n.d. denotes that values were not determined. The confidence level for the uncertainties is 2σ .

Sample	Total Porosity (% volume)	Average microsphere size (μm)	Onset temperature (K)	Maximal reaction rate temperature (K)
UN-1 High porosity spheres	71	970 ± 78	519	580
(U90Th10)N Spheres	n.d.	n.d.	524	573
(U95Th5)N Spheres	66	916 ± 52	516	584
UN-7 Low porosity spheres	58	896 ± 36	547	598
UN-1 High porosity pellet	9.5	-	510	603
UN-7 Low porosity pellet	1.8	-	679	853-873
(U80Th20)N-1 High porosity Pellet	9.6	-	615	633
(U90Th10)N Low porosity Pellet	2.3	-	679	903-923
UO ₂ Pellet	7.6	-	621	638

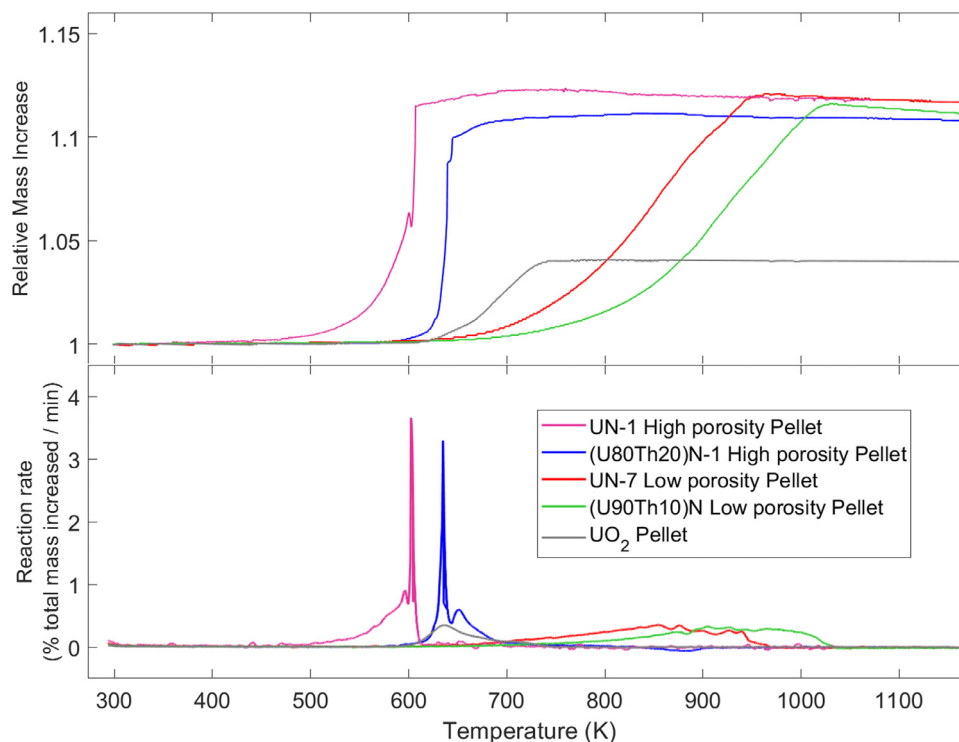


Fig. 4. Upper: TGAs for oxidation of UN and (U,Th)N pellets with high and low porosity compared to the standard UO₂. Lower: Derivative of the TGAs showing the reaction rate as mass increase per unit of time.

Thorium effect on the oxidation could be clearly observed in the doped pellets, unlike in the microspheres. Both the reaction onset temperature and the maximum reaction rate temperature were increased with respect to the undoped pellet with similar porosity. For example, Th-doped pellet with low porosity [(U90Th10)N] presented a reaction onset temperature at 679 K, compared to 615 K for the undoped pellet. This suggests a favorable effect of thorium on the oxidation resistance of UN in air.

The final products of the oxidation of UN and ThN in an oxygen atmosphere should be U₃O₈ [13] and ThO₂ [16], respectively. Therefore, a theoretical mass increase of 11.4% and 7.3% is expected for pure samples. As the thorium content in some of the samples was 10% or 20% mol ratio with uranium, the final mass increase was expected to be 11.0% and 10.6%, respectively. The final mass gain of all UN samples was measured to be 11.9% after the buoyancy correction. Higher than expected mass increase values were also measured for the thorium doped materials in the TGA analysis. This behavior is most likely caused by the development of nitrogen gas during the reaction of UN with O₂, which is trapped in the pores or crystal structure of the powders, as this has been reported previously [13,19,20]. In the calculations, it is assumed that

all N₂ is completely released. Therefore, if part of this gas is dissolved in the crystal structure or trapped in the pores, the weight is expected to increase. Nonetheless, this weight shift should not affect the trends observed for the reaction onset temperatures and maximal reaction rates temperatures.

4.2. Oxidation tests in water/steam

Due to the feedback obtained during the exposure of thorium doped pellets in air, it was expected that some corrosion resistance might also be achieved in water environments. Therefore, pellets were also tested in an autoclave to study their interaction with water at temperatures up to 573 K and pressures of up to 8.5 MPa, resembling conditions found in a boiling water reactor (BWR). It was observed that uranium nitride pellets sintered in SPS were able to survive at 373 K with no evident mass change for at least six hours in the closed autoclave. As can be seen in the SEM/EDX in Fig. 5, the distribution of oxygen towards the edge of the pellet seems to be homogeneous, which suggests that no extensive reaction with water occurred in the exposure experiment performed. These results are an improvement from exposure experiments of

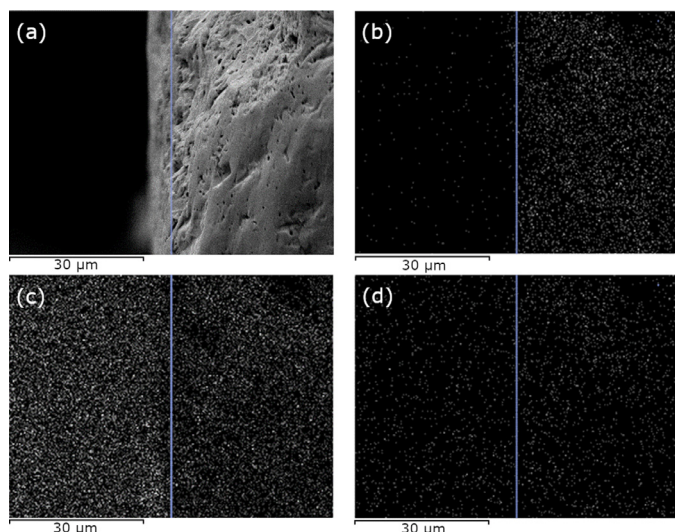


Fig. 5. SEM image (a) with nitrogen (b), carbon (c) and oxygen (d) distribution on the edge of the UN-2 pellet after interaction with water at 373 K for six hours. The blue line indicates the edge of the pellet seen by the EDX.

cold pressed nitride pellets to boiling water, performed previously by Herman et al. [10], where the low density UN pellets crumbled after two hours in boiling water.

Pellets subjected to higher temperatures and pressures were not able to survive, and complete disintegration into a black powder was observed after heat treatment. The solutions were filtered, and the uranium and thorium concentrations were measured in the remaining solutions to observe if any dissolution had occurred during the corrosion experiment. A summary of the results obtained are listed in Table 3. A small amount of these elements was measured, although the solubility of UO_2 and ThO_2 in water has been reported to be negligible [12].

The nitrogen and oxygen contents were measured in the product powders to observe if the reaction had been completed. It was observed that at 473 K and 1.5 MPa pressure, the pure UN sample (UN-6) was not completely oxidized and still contained 0.71 wt-% nitrogen. It was confirmed that the powder was a mixture of UN and UO_2 after examination of the X-Ray diffractogram (Fig. 6). In addition, the oxygen content was measured to be 12.9%, which is higher than expected for pure UO_2 (11.8%). The higher oxygen content in all of the residual powders was attributed to the presence of water, which was later corroborated using TGA measurement in an inert atmosphere.

A thorium doped pellet [(U80Th20)N-2] was subjected to the same test as the non-doped pellet. A similar behavior was observed regarding the incomplete oxidation of the pellets compared to the undoped material. Thoria (ThO_2) signals were observed in the XRD (Fig. 6) in addition to the diffraction peaks of UN and UO_2 . The nitrogen content measured was 0.29%, which is lower than for the undoped pellet and suggests a further reaction com-

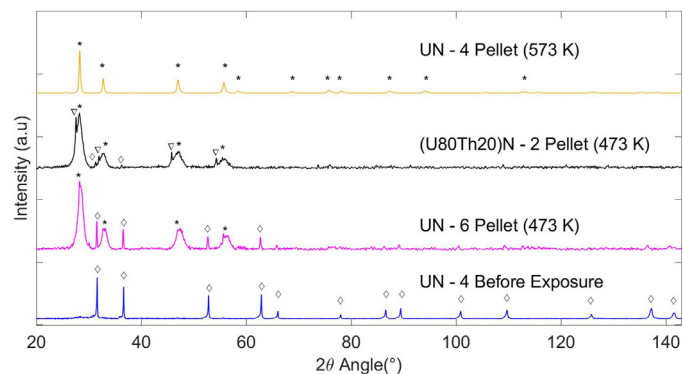


Fig. 6. X-Ray diffractograms for powders collected after pellet disintegration in the corrosion testing, where UN(\diamond), UO_2 (*), or ThO_2 (∇) peaks were identified and compared to the XRD for a pure UN sample before the exposure experiment.

pletion. This could be expected due to the higher reactivity of ThN compared to UN [16]. Oxygen content measured for this sample was 14.87%, the highest of all the samples.

Lastly, a UN pellet (UN-4) was tested at 573 K. Both the oxygen content in the powder and the absence of other peaks besides UO_2 in the X-ray diffractogram point to a complete oxidation of UN into UO_2 .

Results reported in the literature have shown that UN pellets with similar porosity also started to oxidize at 473 K in conditions similar to those of this study [17]. The presence of a U_2N_3 phase remaining in the products after hydrolysis has been reported before, however it was not observed in this work. Moreover, other interaction studies between steam and UN pellets at temperatures of 573 K and higher, at atmospheric pressure, showed no mass change in pellets pressed with SPS [5]. However, the higher temperature needed for reaction was attributed to the lower steam pressure used in those experiments. In the present study, pressurized batch experiments were performed, and results more similar to Dell et al. [17] were obtained.

As mentioned previously, the formation of thoria (ThO_2) during the reaction was confirmed with the XRD (Fig. 6), suggesting that a separation of the ThO_2 and UO_2 occurs during oxidation, even though a solid solution has been reported for the UO_2 - ThO_2 system [21,22]. The mechanism for the hydrolysis of (U,Th)N leading to phase separation is yet unclear and further investigation is still necessary. However, for the purpose of this study, it is possible to conclude that a thoria layer was either not formed or was unstable at the conditions of the experiment and spalled off. Therefore, at the conditions of these tests, thorium showed no indication of significantly improving the corrosion resistance of UN pellets in water.

Although the conditions used in this study resemble the operating conditions of a BWR, other parameters can be controlled in a real reactor that were not controlled in our tests, such as oxidation potential or the pH of the water. These changes could cause a variation in the fuel-coolant interaction, and therefore, different results might be obtained.

Table 3

Water corrosion tests results. Sample UN-5 was tested in boiling water in air, while the rest of the samples were tested in the autoclave and flushed with argon. The N and O content was measured only for the powders filtered after reaction. n.m. represents non-measurable values. The confidence level for uncertainties is 2σ .

Sample Name	Max Temperature in Test (K)	Pressure (MPa)	Pellet disintegration	U conc (mg/L)	Th conc. (mg/L)	N content in powders (wt-%)	O content in powders (wt-%)
UN-5	373 (air)	0.1	No	n.m.	-	-	-
UN-2	373	0.2	No	n.m.	-	-	-
UN-6	473	1.5	Yes	1.9	-	0.71 ± 0.04	12.9 ± 0.2
UN-4	573	8.5	Yes	4.0	-	0.04 ± 0.01	11.59 ± 0.04
(U80Th20) N-2	473	1.5	Yes	6.6	0.9	0.29 ± 0.01	14.87 ± 0.05

5. Conclusions

The effect of thorium doping in the corrosion resistance of uranium nitride has not been reported before. Therefore, in this work the oxidation and hydrolysis behavior of thorium-doped UN microspheres and pellets was studied.

It was found that during oxidation of UN in air, the high porosity in the microspheres allowed for the formation of UO_3 which was decomposed into U_3O_8 . Low porosity pellets (~2% porosity) showed much slower reaction kinetics during the heating process compared to the high porosity pellets (~10%).

Thorium-doped UN pellets showed an increase in both the reaction onset temperature and maximal reaction rate temperature compared to undoped pellets with similar densities, which is an indication of improvement in the oxidation resistance of UN in air.

It was also shown that UN pellets sintered using SPS were able to survive the interaction with water at 373 K and low pressures (0.1–0.2 MPa) with zero mass change. However, an incomplete hydrolysis of UN was observed at 473 K (1.5 MPa), with pellets disintegrating into UO_2 powder, leaving some UN unreacted. Water exposure at 573 K (8.5 MPa) showed a complete transformation of the UN pellet into UO_2 powder.

Thorium-doped UN pellets exposed to water at 473 K and 1.5 MPa pressure lost their integrity and the material was transformed into a mixture of UO_2 , ThO_2 , and UN. Therefore, no significant improvement due to thorium doping of the pellets was observed in the corrosion resistance of UN in water, at the conditions and reaction times investigated in this work.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

L.G. Gonzalez Fonseca: Data curation, Formal analysis, Investigation, Methodology, Resources, Validation, Visualization, Writing - original draft. **M. Hedberg:** Conceptualization, Formal analysis, Methodology, Supervision, Writing - review & editing. **T. Retegan Vollmer:** Supervision, Writing - review & editing.

Acknowledgments

This research was financially supported by the Swedish Foundation for Strategic Research (SSF), project number EM16-0031.

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