

High temperature behavior of simulated mixed nitrides

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Abstract. Specimen of uranium-based mixed nitrides were synthesized by high-temperature nitriding of metal powder. To investigate thermal stability, samples were annealed at high temperature in a helium atmosphere. During these experiments, the effect of increasing the exposure temperature is studied. Raising the exposure temperature results in a multifold increase of mass loss. A comparison with data on pure uranium nitride shows that increasing the complexity of the nitride systems also results in higher mass loss. Later microscopic investigation of test samples revealed that metal precipitates may be found only on the surface of test samples. Electron probe micro-analysis indicates these precipitates to be uranium metal. Nevertheless, compared to pure uranium nitride, uranium-based mixed nitrides exhibit active evaporation at lower temperatures

1. Introduction

Nuclear fuel based on mixed uranium-plutonium nitride has been considered as perspective for fast nuclear reactors with recycling fuel cycle [1]. Nevertheless, there is a serious drawback in processing and usage of uranium-based nitrides at high temperatures – namely, thermal decomposition [2, 3]. This process hinders the sintering of pellets to a high density, also leading to dissociation and evaporation of uranium and plutonium at 1700–1900 °C. Review of previous works [4] has shown that, despite the large number of theoretical and experimental data on the subject, the dissociation still remains understudied. A detailed study of thermal decomposition in uranium-based mixed nitrides is required.

Conducting experiments with fuel containing plutonium and minor actinides requires special working conditions, i.e. gloveboxes with inert atmosphere. This circumstance greatly increases the complexity of research [5]. At a certain point, one may consider using simulated fuel samples instead where active elements are replaced by chemically identical simulators.

This paper aims to provide further information for the kinetics of thermal decomposition in simulated mixed nitrides.

2. Experimental

2.1 Materials and specimens

Powder of uranium mononitride (UN) was produced by nitridation of hydrogenated uranium metal. Cold pressing was performed then to obtain green pellets. Due to the reactive nature of the metal and nitride powders, all materials are handled and stored in argon-filled gloveboxes, which provided an inert atmosphere. Samples had minimal amount of secondary oxide chemical phases. Microstructure of the uranium nitride green pellets shows open porosity channels with no cracks.



For tests at 2100 °C with mixed nitrides, plutonium mononitride (PuN) is replaced by yttrium and neodymium mononitrides (YN and NdN) which provide similar nitrogen vapor pressure. Thus, YN, NdN and Ce are selected as simulators for PuN.

Fission products are simulated by Nd, Ce, Mo, Zr, Ba, La, Sr, Y, Pr, Ru. To simplify the alloying procedure, Nd, Ce, La, Pr, and Y are substituted with an equivalent 10 and 20 wt. % amount of mischmetal (Mm). MmN was produced by hydrogenation of mischmetal prior to nitridation. The product was then mechanically admixed to uranium mononitride powder.

2.2. Thermal stability tests

Tests using Netzsch STA 449 F1 apparatus with QMS 403 C quadruple mass-spectrometer are performed to determine the threshold temperature of thermal decomposition. Measurements are conducted in high purity helium (6.0 grade) with flow rate of 100 ml/min. Additional helium refinement to < 1 ppb is performed using heated catalytic MonoTorr filter on the basis of metallic getter. The following parameters are monitored during the thermal gravimetric analysis: sample mass change; the rate of sample mass change or the derivative of mass change with respect to time, and the time dependence of sample's temperature. Thermal stability mode was enabled which means that the exposure occurs as long as the sample does not lose a predetermined mass.

Microstructural investigation of uranium mononitride samples is performed with scanning electron microscope (SEM) JEOL-6610LV equipped with EDS (energy-dispersive X-ray spectroscopy) for X-ray microanalysis.

3. Results

3.1. Uranium nitride

Mass loss of a uranium nitride sample heated up to 2100°C is performed (Figure 1). The sample exposed for 35 min lost a total 2 % of its mass, starting losing mass already at the stage of heating (1600–1700 °C). After reaching the isotherm, mass loss happened in two stages: the average rate of mass loss increases up to ≈ 0.09 mg/min, and later during exposure mass loss accelerates up to ≈ 0.012 μ g/min. Prior to acceleration, the mass of the samples decreases by ≈ 2.5 mg, and the total mass loss of sample is about 3.5 mg (1.9 % of the total mass of the sample). At 2100 °C the average rate of mass loss increases after 10 min exposure. Mass loss data performed over other UN samples at this exposure temperature show similar kinetics. If thermal exposure is reduced to 2000°C, the acceleration of mass loss begins after 50 min of exposure (Figure 2). At isothermal exposure the average rate of mass loss increases up to ≈ 0.03 mg/min, then mass loss accelerates up to ≈ 0.05 μ g/min. Decreasing of exposure temperature results in slowdown of losing mass. The average rate of mass loss becomes smaller.

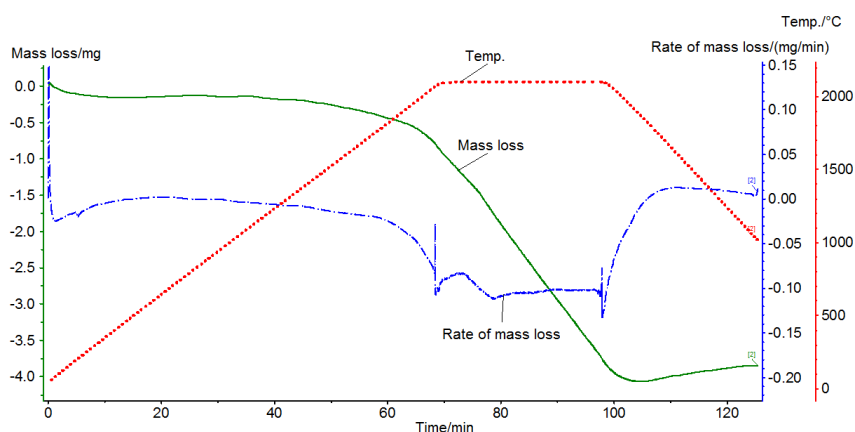


Figure 1. Dependence of mass loss and rate of mass loss on temperature and isothermal exposure duration (2100 °C) for uranium nitride sample.

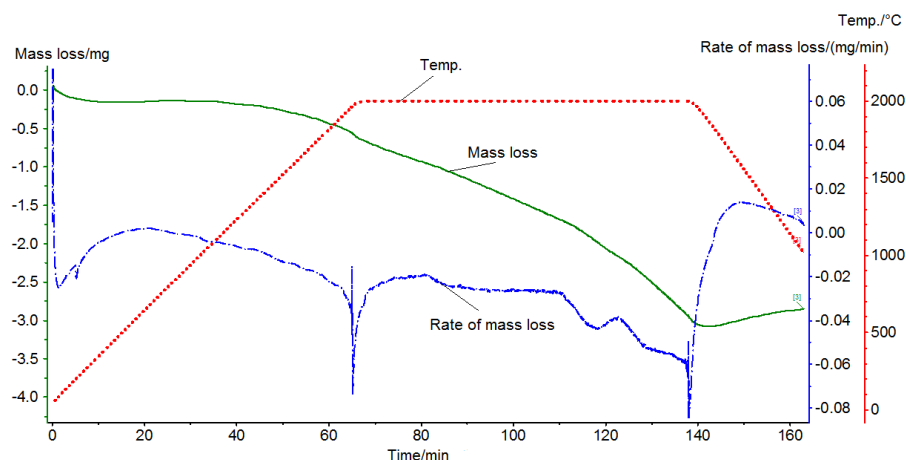


Figure 2. Dependence of mass loss and rate of mass loss on temperature and isothermal exposure duration (2000 °C) for uranium nitride sample.

After thermal stability tests, UN samples were additionally studied using scanning electron microscopy (Figure 3). Electron probe micro-analysis showed that uranium-rich precipitates were formed. The size of precipitates varied from 0.1 to 6.0 μm . Decreasing exposure temperature from 2100 °C to 2000 °C resulted in lower precipitate sizes.

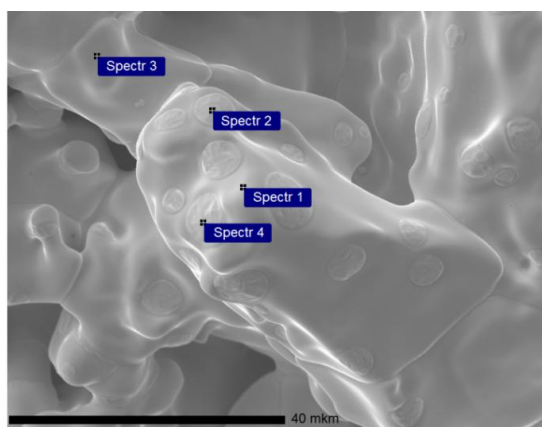


Figure 3. Microstructure and electron probe micro- analysis of uranium mononitride sample exposed at 2100 °C:

Spectr 1 (N – 48.9 at.%, U – 51.1 at.%);
Spectr 2 (U – 100.0 at.%);
Spectr 3 (N – 46.6 at.%, U – 53.4 at.%);
Spectr 4 (U – 100.0 at.%).

Summing up facts mentioned above, the second stage of mass loss may be explained (i.e. severe increase in rate of mass loss during exposure at high temperature – see Figure 1,2). Evaporation of uranium mononitride leads to nitrogen depletion: the N/U ratio of uranium mononitride gradually decreases, and dissociation begins when composition reaches equilibrium at given temperature and partial pressure of nitrogen in the gas atmosphere which then leads to precipitation of uranium metal. The precipitated phase remains in liquid state, since test temperature exceeds the melting temperature of uranium. Moreover, vapor pressure of uranium is large enough to initiate its evaporation and yet increases the rate of weight loss.

The precipitated phase was distributed evenly over the non-restrained surface of the sample. However, no precipitates were found on sample's surface which was in contact with the crucible during tests. Evidently, the crucible restrained access of helium to the surface of the sample in these areas. This resulted in a higher partial pressure of nitrogen over this surface and stabilized UN.

3.2. Uranium-based mixed nitride

Mass loss of a UN+20 wt.%MmN sample heated up to 2100°C is performed (Figure 4). In (U,Mm)N samples mass loss due to evaporation begin at temperatures above 1480°C. Comparing to uranium mononitride, the rate of mass loss is significantly increased in mixed nitrides: 0.12 mg/min for UN,

0.75 mg/min for UN+10 wt.% MmN, and 0.91 mg/min for UN+20 wt.%MmN. During isothermal exposure, the maximum rate of mass loss is about 20% lower. Acceleration of evaporation, nevertheless, does not lead to dissociation.

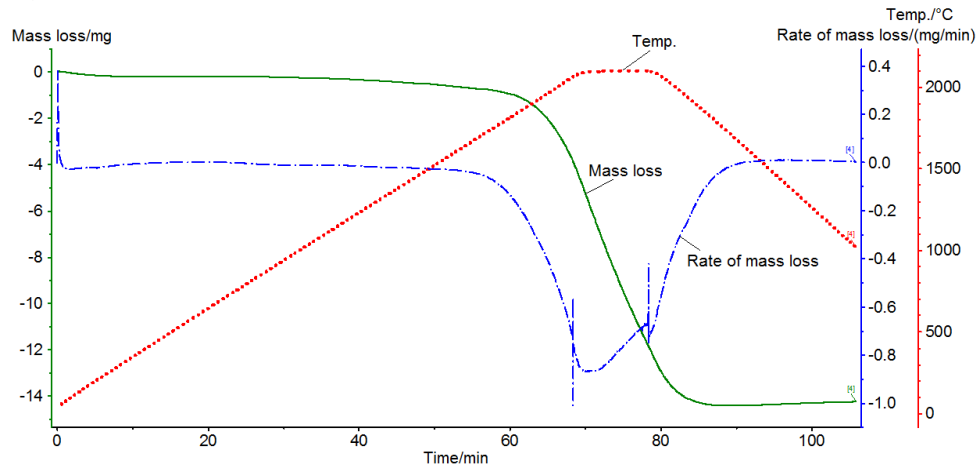


Figure 4. Dependence of mass loss, rate of weight loss for UN+20% MmN samples on temperature and duration of isothermal exposure.

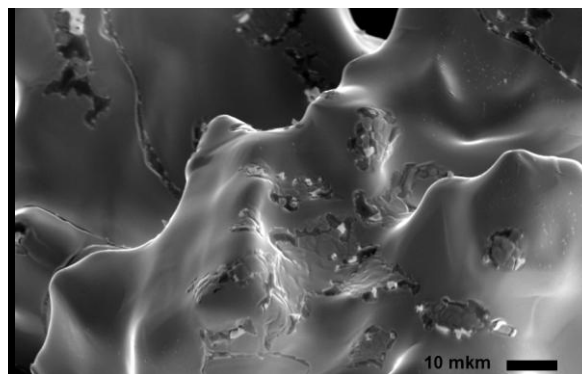


Figure 5. Microstructure of UN+20% MmN sample exposed at 2100 °C.

The resulting microstructure of (U,Mm)N after tests is shown on Figure 5. The distribution of elements in both samples is similar. Ce, La and Nd were evenly distributed along the examined surface.

X-Ray analysis showed that lines are split in two: UN and (U,Me)N meaning that MmN dissolved in UN (Figure 6.). Precipitates of MmN were not observed.

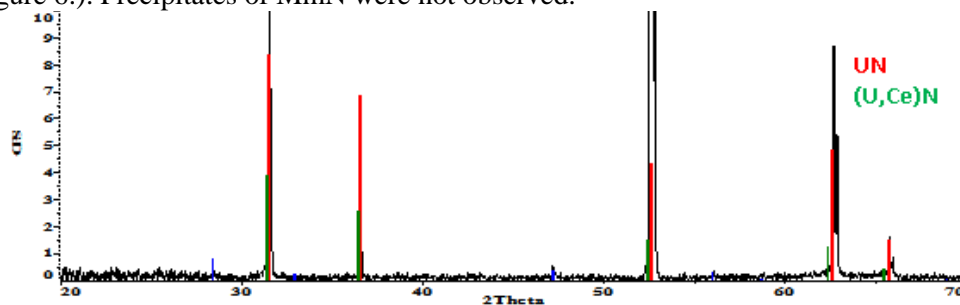


Figure 6. X-ray pattern of UN+20 wt.% Mm sample.

4. Discussion

Evaporation of uranium mononitride leads to nitrogen depletion: the N/U ratio of uranium mononitride gradually decreases, and dissociation begins when composition reaches equilibrium at given temperature and partial pressure of nitrogen in the gas atmosphere which then leads to precipitation of uranium metal. The precipitated phase remains in liquid state, since test temperature exceeds the melting temperature of uranium dioxide. Moreover, vapor pressure of uranium is large enough to initiate its evaporation and yet increases the rate of mass loss.

Mass loss due to evaporation occurs at a much higher rate in mixed uranium nitride samples with 10–20 wt.% of MmN. However, no dissociation happens since precipitates of uranium metal or mischmetal nitrides are not found on the surface of samples.

Both evaporation and dissociation of uranium nitride is strongly dependent on the partial pressure of nitrogen. Low partial pressure of nitrogen in helium leads to dissociation at test temperatures.

Summary

This study addressed one of the key problems with using mixed uranium-based nitrides in closed nuclear fuel cycle: namely the influence of minor actinides and fission products on high-temperature sintering of recycled green pellets. Thermal stability tests conducted both with pure uranium nitride (UN) samples and simfuel samples containing 20 wt.% mischmetal (Mm) show that samples with complex chemical composition are sufficiently less stable than pure UN. For samples with 20 wt. % Mm dissociation temperature drops by 200–300°C. Therefore, it is extremely important to carefully choose the high-temperature processing mode for this fuel so dissociation can be prevented. Both fission products and minor actinides will hinder the performance of mixed nitride fuel. Further work is needed, possibly aimed at selecting proper additives which could increase the dissociation temperature of mixed uranium-based nitrides.

Acknowledgements

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