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Thermal stability investigation technique for uranium nitride

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ABSTRACT

Thermochemical stability of nitride nuclear fuel is an important factor that ought to be considered in fabrication processes, operation and more importantly under accidental conditions. Development of a reliable technique which determines dissociation kinetic parameters and initial temperature of UN disassociation using synchronous thermal analysis apparatus with quadruple mass-spectrometer and SEM investigations was performed. The dissociation process is found to start at temperatures higher than 1500 °C. The process comprises two stages, with a significant increase in mass loss rate at the second stage, which is due to the additional contribution of liquid uranium evaporation. The duration of isothermal exposure before uranium release depends on temperature and the initial N/U ratio and varies from several hours to a few minutes. Intense interaction of the uranium nitride with tungsten crucible was observed after 30 min exposure at 2300 °C.

1. Introduction

Until now nitride fuel was not seriously considered as perspective nuclear fuel for fast breeder reactors, and its properties are less studied than for carbide and, especially, oxide fuel. Perhaps, this was due to a complicated fabrication process and lack of commercial fast breeder reactors.

For the reactors with fast neutron spectrum, nitride fuel has various advantages over other types of ceramic fuel, the most important of all being highest density and thermal conductivity – as high as for uranium carbide. Nitride fuel is compatible with sodium. Moreover, compared to carbide fuel it exhibits higher solubility in nitric acid, higher resistance to corrosion in air and water – which is important for recycling, storing and handling spent nuclear fuel.

Currently, out-of-pile data on nitride fuel properties as well as data on its' irradiation behavior is rather scarce. The main part of data is insufficient and contradictory and cannot be used in fuel performance codes for safety case or designing fuel assemblies.

The characteristics of thermochemical stability of uranium, plutonium and mixed mononitrides are some of principal factors ought to be considered when evaluating thermal properties for fuel pins, mainly under accidental conditions. Thermochemical stability implies stability at different temperatures and equilibrium vapor pressures with no apparent dissociation. Basically, mixed nitrides are marked as highly stable based on thermodynamic calculation and separate experimental investigations (Tagawa, 1974; Oetting and Leitnaker, 1972; Hayes et al., 1990). The difference between calculated and experimental values of equilibrium vapor pressures are possibly due to physicochemical characteristics of nitrides, especially the Me/N ratio and carbon and oxygen content. Based on literature data (Alexander et al., 1969; Olson and Mulford, 1963; Inouye and Leitnaker, 1968; Gingerich, 1969; Suzuki et al., 1992), one can say that thermochemical stability of uranium mononitride, at least below 1800 °C, is high enough and excludes dissociation under partial nitrogen pressure above 100 Pa. In this case, the temperature at fuel central part must be kept below 1700 °C for providing guaranteed safety conditions when using fuel pins with helium sub layer.

Data on thermochemical stability is particularly relevant when predicting nitride fuel behavior under accidental conditions. Thus, metallic plutonium release on inner surface of the cladding at fuel center temperatures above 1800 °C was observed during Nimphe 2 experiment conducted in Phenix reactor (Renault et al., 2009). In addition, there is some data on out-of-pile experiments under thermal gradient showing above 1700 °C metallic phase precipitation and Pu evaporation, Pu transport to pellet periphery (even to the cladding surface).

Thus it is necessary to have a reliable technique of evaluating the dissociation initiation temperature of nitride fuels, also

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Table 1
Features of uranium mononitride samples.

Density (g/cm^3)	12.44
Porosity (%)	13.1
Chemical composition (wt.%)	
U	94.21
N	5.70*
C	0.14
O	0.14

* The specimens employed in the experiment were hyperstoichiometric.

allowing determining some kinetic properties of this process necessary for calculations.

The aim of this work is to develop a technique that will provide further data for various compositions of nitride fuel in view point of evaluating the effect of various parameters on the dissociation kinetics and temperature of its beginning.

2. Samples specification and experimental equipment

Due to the difficulties of dealing with materials containing plutonium, the technique was tested on samples of uranium mononitride. Uranium mononitride pellet are made by a method of carbothermal reduction in nitrogen gas flow with minimization of oxygen impurity maintenance less than 0.1 wt.%. Composition and key features based on FSUE «SRI SIA «LUCH» manufacturer data of uranium mononitride samples are listed in Table 1.

The density of UN pellets is defined by hydrostatic weighing method. A microstructure (the pores characteristic size, their quantity and distribution in section) was investigated by using metallographic microscope technique.

X-ray phase and structural analysis of uranium nitride pellets was conducted on Bruker D8 DISCOVER diffractometer with DAVINCI design using CuK_α radiation (40 kV, 40 mA). For phase identification Bruker AXS DIFFRAC.EVA v.2.1 software was used as well as the international database ICDD PDF-2. Structural analysis was conducted using the analysis technique for the full profile of the sample's diffraction pattern using DIFFRAC.TOPAS v.4.2 software.

The typical X-ray spectrum with lines corresponding to the master phase of uranium nitride for all samples (UN – red dashes) is shown in Fig. 1. The lines of possible additional phases UO_2, UC_{1+x} are also marked. Using the common knowledge of so-called corundum numbers, the quantitative content of identified phases in the sample is evaluated: UN – 96.4%; UO_2 – 1.84%; UC_{1+x} – 1.76% and the elemental composition is determined: U – 94.28%; O – 0.19%; N – 5.38%; C – 0.15%. Increased oxygen content is most likely due to the air oxidation of samples' surface. It must be noted that the results of this quantitative analysis are approximate, because the structural phase state is omitted during calculation (Table 1).

The profile analysis of X-ray lines of UN master phase indicates that every line consists of a sharp intense line and some halo (Fig. 2, black line).

Thus, the evaluation of the full diffraction pattern profile was conducted assuming the presence of two phases with similar lattice parameters. The approximation error of the X-ray spectrum is sufficiently lesser in this case comparing to single-phase calculation, but the obtained lattice parameters differ insignificantly, which apparently indicates that the observed halo is inherent to the thin surface layer with highly distorted structure after polishing. Therefore, the average lattice parameter for all samples amounts 489.70 ± 0.03 pm, while the half-width of the X-ray line (531) β_{real} amounts 0.55° which indicates small structure distortion in near-surface layers.

Microstructural investigation of uranium mononitride samples was performed with scanning electron microscope JEOL-6610LV equipped with EDS and WDS for X-ray microanalysis.

All samples were polished and etched by mixture of 50 vol.% H_2SO_4 + 50 vol.% H_2O_2 to reveal the grain structure.

A typical microstructure image of the samples is shown in Fig. 3. It can be seen that the grain size amounts ~10 μm, pore size amounts ~3 μm, and the porosity mostly is open.

The results of X-ray microanalysis show that nitrogen content at different positions varies from 5.28% to 5.55% with an average value of 5.46% which is in good accord with manufacturer's data and X-ray analysis. Carbon and oxygen content were inaccessible by this measurement technique, because on the one hand such small quantities were comparable to measurement error of EDS, and on the other hand no surface-cleaning apparatus was available which could remove carbon or oxygen contamination.

On the ground of incoming inspection, the value of nitrogen to uranium ratio N/U for the samples of batch 32 exceeds unity and amounts 1.027, i.e. belongs to the hyperstoichiometric region (Fig. 4).

Synchronous thermal analysis tests using Netzsch STA 449 F1 apparatus with quadruple mass-spectrometer QMS 403 C were performed to determine the top threshold of thermal stability of the experimental uranium mononitride samples. Regular fuel elements are filled with helium, therefore the measurements were conducted in high purity helium (6.0 qualification) with flow rate of 100 ml/min. Additional helium refinement to <1 ppb was performed using heated catalytic MonoTorr®filter on the basis of metallic getter. Open tungsten crucibles were used with thermogravimetry holders. During experiment the following parameters

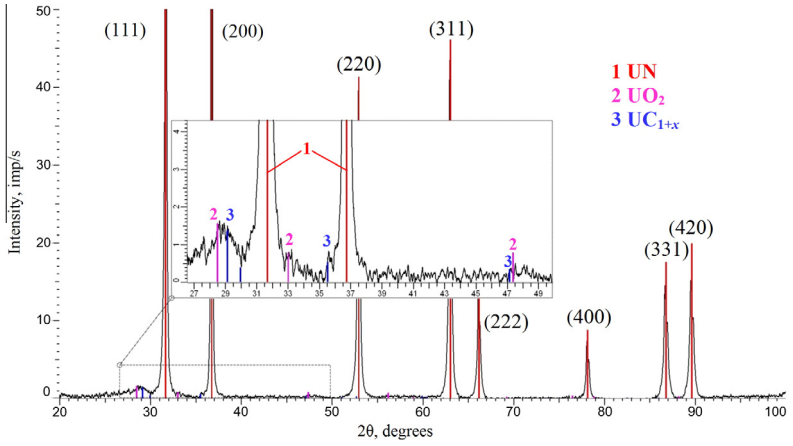

Fig. 1. X-ray spectrum of uranium mononitride. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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