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Melting point determination of uranium nitride and uranium plutonium nitride: A laser heating study

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ABSTRACT

Understanding of the behaviour of nuclear material in extreme conditions is essential for the analyses of the operation limits of nuclear fuels, and prediction of possible nuclear reaction accidents. In this context, the high temperature behaviour of uranium nitride and mixed uranium–plutonium nitrides has been studied in the present work by laser heating under controlled atmosphere coupled with fast multi-wavelength pyrometry. Such an approach has allowed performing a thermal arrest analysis and establishing the solid–liquid phase boundaries in the investigated compositions, whereby non-congruent vaporisation was avoided by setting a suitable nitrogen overpressure. In addition, the normal spectral emissivities of the current samples were determined by radiance spectroscopy. Besides revealing a slightly more metallic optical behaviour in plutonium-containing compositions, this latter characterisation led to the determination of the real melting/solidification temperatures of the investigated nitrides. It is confirmed that UN melts congruently at (3120 ± 30) K in a nitrogen pressure of 0.25 MPa (2.5 bar). The melting/solidification temperatures decrease in plutonium containing samples, reaching (3045 ± 25) K for $x(\text{PuN}) = 0.2$, a composition of interest for potential applications of this material as a nuclear fuel. Besides their fundamental importance, the current results are useful for a deeper understanding of the nitride fuel behaviour under accidental conditions, whereby uncontrolled thermal excursions might occur in the nuclear reactor core.

1. Introduction

Uranium nitride (UN) and mixed uranium–plutonium nitride (U,Pu)N exhibit a number of favourable nuclear fuel properties when compared to conventional oxide fuels, including high fissile atom density and high thermal conductivity [1,2]. A complete knowledge of the high temperature behaviour of these materials is therefore fundamental for the fuel design and safety, as it defines the performance limits of a fuel element itself [3].

Whilst problems and proposed solutions concerning the nitride synthesis are addressed in another publication [4], the current paper deals with the measurements of solid/liquid equilibria in uranium nitride and one mixed uranium–plutonium mononitride. In the present research, the melting behaviour of sol–gel synthesized nitrides has been investigated by a recently developed quasi-containerless fast laser heating technique, coupled with multi-wavelength spectro-pyrometry for the measurement of temperature. The phase diagram of the U–N binary system has been widely studied [5–9] at temperatures well below melting, and has notably been reported in the compilation works of Okamoto [10] and of Uno et al. [11]. Uranium mononitride (UN), dinitride (UN_2) and sesquinitride (U_2N_3) are the stable compounds observed in this material system. UN and UN_2 are envisaged in the NaCl type face-centred and cubic CaF_2-type face-centred cubic respectively with ($Fm{-}3m$) space group both, while U_2N_3 crystallizes in a body centred cubic structure at low temperature (α-U_2N_3) and in a hexagonal structure at higher temperature (β-U_2N_3) [12,13] envisaged in the ($Ia{-}3$) space group. The high-temperature properties and the phase stability of the U–N system have been summarized by Hayes et al. [14] and more recently by Chevalier et al. [15]. The congruent melting point of UN has been published as 3123 ± 30 K [16,17] for a nitrogen pressure superior or equal to 2.5 atm. Other values (2923 ± 100 K [18] and 2753 ± 50 K [15]) have been reported in the literature, but are considered to be too low and unreliable [15]. The present temperature determination by a pyrometric method requires knowing some UN optical properties such as the reflectivity, the transmissivity and, especially, the emissivity. In this field, the only direct reflectivity measurements (at room temperature) were reported by Arakawa and Williams [19].

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Uranium–plutonium mixed nitrides (U,Pu)N crystallize in the same NaCl-type structure, as UN and PuN [10]. Although UN and PuN form a continuous solid solution, a large deviation from Vegard's law was observed, suggesting the non-ideality of the solution [20]. Two different melting temperatures for the composition $U_{0.8}Pu_{0.2}N$, 2633 and 3053 ± 20 K, have been proposed by Huebotter [21] and Nightingale [22], respectively. No data about the optical properties of these mixed nitrides are available in the literature.

Considering the high volatility of these nitrides at high temperature [23,24] and their strong tendency to react with an even low amount of oxygen [25], only very few data have been published on their high temperature behaviour. These were obtained by heating, in dedicated furnaces, nitride samples under a nitrogen overpressure, mostly at the price of costly and cumbersome experimental facilities. Technical difficulties were even increased in the investigation of radioactive samples, for which the experimental setup had to be mounted in suitable shielded cells or glove boxes.

In this context, the current investigation aims at providing more and extra data on the high temperature behaviour of UN and (U,Pu)N by using a modern heating approach based on remote laser irradiation. It is possible, with this technique, to perform a thermal analysis up to very high temperature (well beyond melting) on a sample mounted in a radiation-shielded autoclave under controlled atmosphere. In the present setup, neither the heating agent (the laser) nor the measuring devices (the pyrometers) are in contact with the pressurised and radioactive environment, which makes the entire experimental procedure much easier and more flexible compared with more traditional ones. As a result, a consistently larger number of experimental data have been collected, allowing for a statistical analysis. Furthermore, some novel data about the spectral emissivities of the investigated compounds have been measured thanks to the employment of pyrometers operating at different wavelengths in the visible and near-infrared domains. After laser melting, the samples were finally characterised by X-ray diffraction (XRD) and by Scanning Electron Microscopy (SEM).

2. Experimental section

2.1. UN and (U,Pu)N Samples

The nitride samples were prepared by carbothermal reduction under N_2 of carbonous oxides beads produced by coupling external sol–gel and carbothermal reduction methods. This process, fully described by Carvajal-Nunez et al. [4], has also been employed to ensure the synthesis of (Zr,U)N [26].

According to the X-ray diffraction (XRD) collected with a Bruker Bragg–Brentano D8 advanced diffractometer (Cu Kα1 radiation), rocksalt-type solid solutions (*Fm*–3*m*) have been produced for both UN and (U,Pu)N samples.

2.2. Laser melting

2.2.1. Laser heating pulses

UN and (U, Pu)N samples were mounted in a controlled-atmosphere autoclave closed by a gas – proof quartz window 10 mm thick. Physical contact to their mount was limited by using three radically arranged graphite screws to hold them in place. In some case, zirconium oxide based ceramic glue produced by Advanced Materials Inc.® was used to fix the sample. Independently, only a small portion of the sample surface was irradiated by a heating laser beam, so that the hot material was only in contact with cooler parts of the same composition. This self-containing (or quasi-containerless) character of the current measurements greatly reduced or completely ruled out problems such as uncontrolled interaction between the sample and its containment, typically encountered in nitrides at high temperatures.

These specimens were studied at very high temperature by laser heating combined with fast pyrometry (Fig. 1), as described by Manara et al. [27].

The heating agent was a Nd:YAG 4.5 kW cw laser radiating at 1064.5 nm, programmable with a complex power/time profile, allowing thermal cycles of variable duration. The laser beam, conveyed by fiber optics, impinged on the sample surface on an approximately circular area of 3 mm in diameter, heating it beyond melting for variable time durations (from a few tens of ms to a few hundreds ms). The invariance of the recorded phase transition temperatures with the dwelling time in the liquid state could thus be checked, to study the possible occurrence of phenomena out of the thermodynamic equilibrium (such as segregation or non-congruent vaporisation). The high power laser pulse was then switched off and the sample let cool naturally. Cycles of three successive melting pulses were performed in each experiment. During the intervals between pulses (lasting several seconds), the sample temperature has decreased to an intermediate level, close to the pyrometer's detection limit (approximately 1400 K). Avoiding full cooling to room temperature between the melting pulses ensured a better mechanical stability of the sample throughout repeated shots, which lead to an improved result reproducibility. Finite element simulations of the heating cycles (Böhler et al. [28]), supported by micro-imaging of the quenched samples, ensured that at the beginning of the cooling process homogeneous temperature was produced in the laser irradiated area for a depth of a few tens μm. Thermal analysis was then performed on the cooling stage of the cycle.

2.2.2. Temperature measurements

The sample temperature was measured on a spot of 0.5 mm in diameter at the centre of the laser-heated area by means of a pyrometer equipped with a fast logarithmic amplifier (adjusting the time of about 10 μs to 1% of log output) and operating at 655 nm [26]. It was calibrated against a standard tungsten-ribbon lamp in the range of 1800–2500 K, ensuring traceability to the international temperature scale of 1990 [29]. Beyond this temperature, the validity of the calibration, as well as the quality of the optical windows and the alignment, were tested by measuring in situ the melting radiance temperatures of molybdenum and tungsten (2530 K and 3207 K, respectively, at 653 nm (Bedford et al. [30]).

A further spectro-pyrometer, based on a linear array of 256 Si photodiodes, was used to record the sample thermal radiance in the range of 488–1011 nm. This instrument allows a more complete spectral analysis, whereby its main disadvantage is in the poorer time resolution (one spectrum per millisecond at best) [27]. Due to low signal-to-noise ratio, only the range of 550–920 nm was useful for the current measurements. The photodiode at 649 nm was calibrated up to 2500 K using the tungsten-ribbon lamp and this calibration was transferred to a tubular-cavity variable-temperature graphite blackbody-furnace up to 3500 K. The remaining photodiodes were then calibrated with this blackbody, allowing a conversion of output signal to spectral radiance over the entire useful wavelength range. The measured radiance spectra recorded in the vicinity of the melting/solidification points were fitted by least-squares regression to Planck's distribution law for blackbody radiance, modified by a wavelength- and temperature-dependent function assumed to represent the normal spectral emissivity (NSE or ε_λ). Although such an approach is known to be affected by low numerical accuracy [31], compared to other techniques, it can be considered as acceptable for materials, like the current uranium and plutonium nitrides, which are known to display a regular emissivity behaviour (continuous and monotonous trend as a function of λ). The normal