



## The melting behaviour of uranium/neptunium mixed oxides



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### ABSTRACT

The melting behaviour in the pseudo-binary system ( $\text{UO}_2 + \text{NpO}_2$ ) has been studied experimentally for the first time in this work with the help of laser heating under controlled atmosphere. It has been observed that the *solidus* and *liquidus* lines of this system follow an ideal solution behaviour (negligible mixing enthalpy) between the well-established solid/liquid transition temperatures of pure  $\text{UO}_2$  (3130 K) and that recently assessed for  $\text{NpO}_2$  ( $T = 3070$  K). Pre- and post-melting material characterizations performed with the help of X-ray diffraction and Raman spectroscopy are also consistent with ideal mixing of the two end members. Such behaviour follows the similar structure and bonding properties of tetravalent uranium and neptunium and the similar melting points of the two oxides. The interest of this investigation is twofold. From a technological viewpoint, it indicates that the incorporation of  $\text{NpO}_2$  in  $\text{UO}_2$  fuel or transmutation targets is a viable option to recycle neptunium without inducing any relevant change in the chemical or thermal stability of the uranium dioxide matrix, even up to the melting point. From a more fundamental perspective, it confirms that actinide dioxides, and particularly  $\text{UO}_2$ , tend to mix in a way closer to ideal, the closer are the atomic numbers, 5-f electron shell filling, atomic radii and oxygen potentials of the metals forming the pure dioxides.

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### 1. Introduction

Once minor actinides (Am, Np, Cm) are chemically separated (partitioned) from the spent nuclear fuel, they can be transmuted into lighter and less radioactive isotopes in a fast neutron reactor, resulting in a significant reduction of the nuclear waste radiotoxicity, especially on an intermediate time scale ( $10^2$  to  $10^3$  years).

In this context, two options have been considered for the transmutation of MAs in a sodium-cooled fast reactor: (a) homogeneously adding (2 to 6)% of MAs to the fuel (homogeneous mode) and (b) introducing MAs in higher amounts up to (10 to 30) wt% into transmutation targets (heterogeneous mode) [1].

Basic knowledge on (MAs + O) and (U + MAs + O) systems is thus becoming more and more interesting at high temperature especially for both the transmutation fuel fabrication and its behaviour under irradiation. The present investigation focuses on the thermal stability of neptunium-bearing oxide fuel because data are still scarce in the general (U + Np + O) system.  $^{237}\text{Np}$  is produced in a nuclear reactor through neutron irradiation of  $^{238}\text{U}$  [2]. A ternary ( $\text{UO}_2 + \text{NpO}_2 + \text{U}_3\text{O}_8$ ) phase diagram is available at

$T = 1273$  K only [3], and the evolution of phase relationships was studied by *in situ* –high temperature X-ray diffraction by Chollet *et al.* [4]. Experimental investigations need to be conducted further, especially in the vicinity of the melting transition, since such thermodynamics or physical data are fundamental for modelling the fuel behaviour under irradiation, and the completion of the phase diagram at higher temperatures. This research field is particularly relevant in the safety analysis of fast neutron reactors designed for MA transmutation, especially for the simulation of severe accidents leading to uncontrolled thermal excursions in the fuel.

In recent years, The European Commission's JRC-ITU in Karlsruhe (Germany) developed an innovative method to measure melting temperature based on quasi-containerless conditions for samples with very short duration of the heating cycles. Ever since, numerous studies have successfully proved the reliability of this technique:  $\text{UO}_{2(+x)}$  [5,6], (U, Pu) $\text{O}_2$  [7,8],  $\text{PuO}_2$  [9],  $\text{NpO}_2$  [2], (U, Th) $\text{O}_2$  [10] melting behaviour and phase diagrams at high temperatures were revisited. It has been proven that earlier values of the melting points of actinide compounds, obtained by traditional furnace heating techniques, were most probably affected by extensive high-temperature interaction between the sample and its containment. The error induced in these melting temperatures could amount to several hundred degrees Kelvin. In particular, this was shown for actinide dioxides such as  $\text{PuO}_2$  and  $\text{NpO}_2$ . The new,

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higher value of the solid/liquid transition temperature established for plutonium dioxide naturally led to a full re-assessment of the whole ( $\text{UO}_2 + \text{PuO}_2$ ) system at high temperature. For this system, it has been observed that the oxygen potentials of both the pure end members and the intermediate compositions play a paramount role in defining the phase boundaries. These latter are largely affected by oxygen gain and losses, to the point that (urania + plutonia) phase equilibria can only be rigorously assessed within a full thermodynamic description of the ternary ( $\text{U} + \text{Pu} + \text{O}$ ) system. Similar considerations have been made for the systems ( $\text{UO}_2 + \text{ThO}_2$ ) [10] and ( $\text{ThO}_2 + \text{PuO}_2$ ) [11], in which, however, the higher chemical stability of thorium dioxide ensured behaviour of the mixed system closer to ideal even in an approximate pseudo-binary description.

Also the melting point of neptunium dioxide has been established to be more than  $T = 300 \text{ K}$  higher than that proposed in earlier research. Its oxygen potential is however closer to that of pure  $\text{UO}_2$  [12], when compared to the oxygen potential trends of  $\text{PuO}_2$  or  $\text{ThO}_2$ . It is therefore legitimate to wonder about both the thermal and chemical stability of the mixed system ( $\text{UO}_2 + \text{NpO}_2$ ) at high temperature, up to melting. In particular, can this system be satisfactorily described within a pseudo-binary plane? How good is the approximation of considering mixing ideal (i.e. without excess enthalpy) in this pseudo-binary system? These are some of the essential questions that the present experimental work deals with for the very first time.

## 2. Materials and methods

### 2.1. Sample preparation

Disks of  $(\text{U}_{1-y}\text{Np}_y)\text{O}_2$ , with  $y = 0.1, 0.2, 0.3$  and  $0.7$  were prepared at the LEFCA facility (CEA Cadarache, France), starting from  $\text{UO}_2$  and  $\text{NpO}_2$  powders. Uranium dioxide powder was produced by a wet fabrication route based on the formation of ammonium diuranate (ADU) from uranyl nitrate precipitated with ammonia. The particles obtained were then atomized and dried, leading to spherical-shaped agglomerates of roughly  $20 \mu\text{m}$ . The sum of impurities is below  $192 \cdot 10^{-6}$  (Table 1). The purity of the  $\text{NpO}_2$  powder, provided in 1995 by CEA/VALRHO, was determined by ICP-AES analysis. It contains less than 0.4 wt% impurities (Table 1). Raw powder was ground and mixed in the appropriate ratios and first calcined under a reducing atmosphere (i.e.,  $\text{Ar}/5\%\text{H}_2$ ) at  $T = 1773 \text{ K}$  for 20 h. Powders subsequently underwent an intermediate grinding before being sieved and pressed into pellets in an automatic press at 390 MPa. Pellets were sintered 24 h at  $T = 2023 \text{ K}$  in an atmosphere of  $\text{Ar}/\text{H}_2$ , leading to 80% density and size of 6 mm in diameter and 2.5 mm in thickness, suitable for the sample holder of melting temperature measurement apparatus. Phase composition and O/M ratios were checked by powder X-ray diffraction (PXRD) [4] with an expanded uncertainty on  $y$  reported in Table 2 as  $\text{U}(x(\text{NpO}_2))$  and  $\text{U}(\text{O}/\text{M}) = \pm 0.01$  on the O/M ratio. This latter value could be less precise in uranium-rich samples due to the strong tendency to oxidation of uranium dioxide in contact with even low traces of oxygen.

Similar disks with different compositions  $y = 0.02, 0.05, 0.20, 0.50, 0.75$  and  $0.85$  with an expanded uncertainty  $U_r$  of  $\pm 1\%$  have been prepared by gel-supported precipitation (or sol-gel external gelation) at JRC-ITU Karlsruhe. The purity of the sol-gel liquid solution is provided in Table 1. The uranyl nitrate solution was mixed with an acidic solution of  $^{237}\text{Np}$  to achieve a mole stoichiometry  $\text{Np}/(\text{U} + \text{Np})$  of 0.02, 0.05, 0.20, 0.50, 0.75 and 0.85. Those ratios have been checked by Inductively Coupled Plasma – Mass Spectrometry. An organic thickener (Methocel, Dow Chemicals®) was added in order to increase the viscosity of the solution. The

TABLE 1

Main impurities in  $\text{mg} \cdot \text{kg}^{-1}$  for the starting materials used in the study.

Material	$\text{NpO}_2$ CEA	$\text{UO}_2$ CEA	$\text{UO}_2$ ITU	$(\text{U}_{1-y}\text{Np}_y)\text{O}_2$ ITU
Provenance	CEA/ VALRHO		Advanced nuclear materials Co.	
State	Powder	Concentration/ $\text{mg} \cdot \text{kg}^{-1}$ powder	Pellet	sol-gel liquid solution
Li			<1	
B			<1	
C			56	
N			11.7	
F			6.8	
Na	400	§	6.1	15.4
Mg		‡		89
Al	400	‡	208	3.2
Si		1.7	4.8	
P			1	
S			40	
Cl			44	
K				5.7
Ca	700	§		212
Ti		‡	1	
V		<0.2	<1	
Cr	300	§	1.3	
Mn		§		
Fe	1000	7.5	11.3	28.4
Co		‡		
Ni		1.5	1.7	
Cu		§	1.8	3.86
Zn		§		27
As				12.5
Y			<1	
Zr		§	2.3	
Mo		‡	<1	
In		‡		
Sn		<3		2.1
Ba			3	
Ce			<1	
W		§		
Pb		§	1	4.98
Bi		<2.3		
Th		<1.7		5.35

‡: Sum of those elements are below  $2 \cdot 10^{-6}$ .

§: Sum of those elements is below  $8 \cdot 10^{-6}$ .

solution was then dropped in an ammonia bath where the droplet to particle conversion took place thanks to the hydrolysis of the metal ions. The resulting powder was washed, dried and then calcined at  $T = 873 \text{ K}$  in air (2 h) to remove organics and then at  $T = 973 \text{ K}$  in  $\text{Ar}/\text{H}_2$  (2 h). The disks were then sintered at  $T = 1923 \text{ K}$  (4 h) under  $\text{Ar}/\text{H}_2$ . As detailed elsewhere [14], the O/M ratios of these compounds are equal to  $(2.00 \pm 0.01)$  ( $\text{U}(\text{O}/\text{M})$ ).

Pure neptunium dioxide samples were prepared as described by Böhler *et al.* [2]. The starting material was a 99.87 wt% pure powder. Disks 6 mm in diameter and (1.2 to 1.5) mm in thickness were obtained using a bi-directional press. They were then sintered for 8 h in an  $\text{Ar}/\text{H}_2$  flux at  $T = 1973 \text{ K}$  with  $\text{H}_2\text{O}$  at concentration approximately  $1500 \cdot 10^{-6}$  to densify the disks, then heat-treated twice in air for 8 h at  $T = 1123 \text{ K}$ , and for 12 h at  $T = 2000 \text{ K}$  just before the laser experiments in order to obtain a composition as close as possible to the exact  $\text{O}/\text{Np} = 2$  stoichiometry. No weight change was observed after a second annealing, and this was considered a satisfactory test that the stoichiometric composition ( $\text{O}/\text{Np} = 2$ ) had been reached. For pure uranium dioxide, commercial pellets produced and sintered by Advanced Nuclear materials Co.® were employed (Table 1).

Natural uranium was employed in all the current samples, consisting for 99.3% of  $^{238}\text{U}$ , and for 0.7% of  $^{235}\text{U}$ . Over 99.9% of the current neptunium consisted of  $^{237}\text{Np}$ .

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