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Existence of a miscibility gap in uranium neodymium oxide materials used as nuclear fuels simulants

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ABSTRACT

During the irradiation of oxide nuclear fuels used in pressurized water reactors, many microstructural modifications occur which affect the fuel performance. This work focuses on the thermodynamic evolution of the fuel under these conditions, with a special regard to the influence of lanthanides content. For this purpose, simulant materials have been synthesized to model irradiated fuels. They consist of $(U,Nd)O_2$ doped ceramics, neodymium being added since it is the most abundant lanthanide fission product. A previous study carried out on these systems highlighted, for the first time, the possible existence of a miscibility gap in the U–Nd–O ternary system, with an experimental evidence of a biphasic equilibrium at room temperature, for a Nd content larger than 6 wt%. In the current work, high temperature X-ray diffraction experiments up to 1973 K on $(U_{0.72}Nd_{0.28})O_{2-x}$ samples are reported. The results confirm the existence of a miscibility gap. In fact, the system is monophasic at elevated temperatures and a phase separation occurs below 745 K, with two face-centered cubic phases in equilibrium. A preliminary evaluation of the tie-line associated to the biphasic system at room temperature is proposed.

1. Introduction

Understanding the behavior of irradiated oxide nuclear fuels microstructure is a big challenge since the 1960's. Moreover, during the last decades a special interest has been aimed at the so-called high burn-up structure (HBS). HBS appears in irradiated UO_2 or MOX fuels when local burn-up is above 60 MWd kg^{-1} and exhibits an increase in porosity, the formation of small subdivided grains as well as a depletion of the matrix fission gas (Rondinella and Wiss, 2010; Noirot et al., 2008). Besides, some crystallographic changes in the matrix of HBS are reported to occur as a function of burn-up (Spino and Papaioannou, 2000; Spino and Papaioannou, 2008). The fluorite-type structure, characteristic of oxides fuels, is maintained, but lattice parameters change with the burn-up, depending on the irradiation characteristics. Up to now, the reasons are not completely understood. However, among all the different parameters involved, the presence in the oxide matrix of a relatively large fraction of dissolved fission products (FP), such as Sr, Zr, Nb, Y, especially lanthanides (La, Ce, Pr, Nd, Eu, Gd and Sm) and of actinides (such as Pu, Am, Np) (Kleykamp, 1985; Kleykamp, 1993) may be a key factor. The concentration of these products continuously increases with the burn up.

A preliminary work has been focused on the specific influence of lanthanides content in the oxide nuclear fuels matrix toward their crystallographic evolutions/modifications. For this purpose, and since neodymium is the most abundant lanthanide FP, $(U,Nd)O_2$ non-irradiated oxide ceramics were prepared at different Nd contents (from 2 to 20 wt%) to simulate irradiated fuel. Crystallographic structure determination of these $(U,Nd)O_2$ samples was performed by X-Ray Diffraction (XRD) at room temperature (i.e. after sample preparation) (Desgranges et al., 2012). These experiments highlighted the existence of a biphasic domain (two FCC phases) for samples containing a Nd content higher than 6 wt%.

This biphasic domain has also been observed for other rare earths-doped UO_2 ceramics at similar concentrations, due to the existence of a miscibility gap in the ternary oxide systems (Sari et al., 1970; Lorenzelli and Touzelin, 1980). Therefore, the phenomenon observed in $(U,Nd)O_2$ may also originates from the existence of a miscibility gap. However, this cannot be thermodynamically proved until a phase separation temperature is experimentally detected. To

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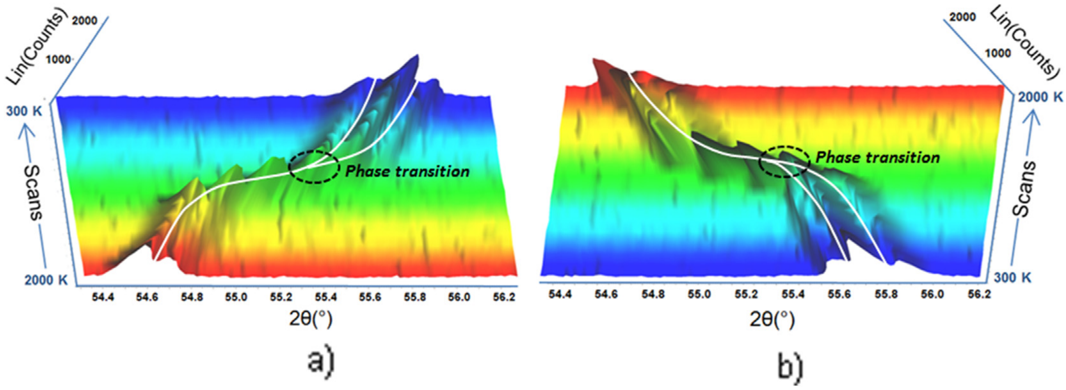

Fig. 1. Evolution of the (1 0 0) peak of the FCC structure during a) cooling and b) heating.

do so, XRD measurements as a function of temperature is best suited as this technique provides accurate information about structural evolution of the studied system.

In this work, high temperature XRD study of a $(U,Nd)O_2$ sample is presented, carried out in order to evidence the existence of such miscibility gap.

2. Experimental procedure

The analyzed sample is a $(U_{0.72}Nd_{0.28})O_2$ non-irradiated ceramic. It was prepared by mixing of Nd_2O_3 (20 wt%) and UO_2 powders. Even if a biphasic domain can be already detected for a Nd content of 6% (Desgranges et al., 2012), this value of 20 wt% was chosen in order to have a clearer definition of each phase. Specific compositions of each phase will be discussed later. Powders were mixed, pressed at 450 MPa and sintered under He with 5% H_2 atmosphere, at 1973 K during 72 h. Room temperature XRD characterization after preparation showed no signature of the initial Nd_2O_3 compound (Desgranges et al., 2011).

High temperature XRD diffraction analyses of this sample was carried out in a Bragg Bentano θ–θ BRUKER D8 Advance X-Ray diffractometer, equipped with a heating stage for in-situ measurements. This instrument is implemented in a glove box at the LEFCA facility (CEA Cadarache, France) dedicated to nuclear materials study. The X-ray beam is provided by a conventional tube source (Kα1 + Kα2 radiation, $\lambda = 1.5406$ and 1.5444 Å) operating at 40 kV and 40 mA. The signal was detected by a LynX'Eye fast-counting Position Sensitive Detector (PSD) (Chollet et al., 2013; Truphémus et al., 2012).

From a general point of view, the experiment consists in the realization of a reductive (mix He–5%H_2) annealing treatment of the sample, followed during the whole experience by XRD measurements. XRD patterns are recorded at intervals of 50, 100 or 200 K. The thermal path followed consists in three steps. First, the sample is reduced at 1973 K during 140 min. Previous work shows that this procedure is appropriate[12]. Second, the sample is cooled down to room temperature at a very slow rate to avoid kinetic or diffusional limitations (average rate: 0.01 K s^{-1}) and XRD patterns recorded. Third, the sample is heated to 1973 K at the same rate and XRD patterns recorded. The objective of this last heating is to obtain a comparison between crystallographic evolution of $(U,Nd)O_{2-x}$ during both cooling and heating phases.

Patterns were refined with the Rietveld method using TOPAS software (Bruker AXS GmhH, 2013). The structural model chosen is based on the UO_2 structure: a FCC matrix with (0,0,0) sites containing both Nd^{3+} and U^{4+} cations. Peak type used was a POV-type, background was refined with a 4-order Chebychev polynomial, and preferred orientation was not considered. Other refined parameters were the instrumental values "zero error" and "sample displacement". EVA software was also used for preliminary observations of patterns and graphical representation (Bruker AXS GmhH, 2009).

3. Results

Figs. 1 and 2 show the patterns obtained during heating and cooling, in the partial range of 54–57° (2θ). Each peak is composed of two diffraction lines, provided by Kα1 + Kα2 sources Different phenomena take place at low and high temperatures. Above 745 K, only one typical FCC contribution is observed. Below, the FCC contribution is splitted, revealing a biphasic system in this range. This behavior seems reversible during the subsequent heating. However, a quantitative refinement is necessary to go further and to confirm this reversible behavior.

Lattice parameters are presented in Fig. 3. The error is estimated lower than 0.0016 Å from TOPAS determination. All phases detected are of FCC-type. The refinement allowed determining the phase transition temperature. It lies between 745 and 800 K, during heating as well as during cooling. Thus, the evolution in temperature is reversible.

Within biphasic areas, one phase has indeed a lattice parameter very similar to UO_2, and the other is quite smaller (this is discussed later in this article). However, the difference between phases 1 and 2 becomes smaller with increasing temperature, until the lattice parameter reaches a final value which corresponds to the lattice parameter of monophasic system, as illustrated in Fig. 3.

4. Discussion

This result evidences the existence of a miscibility gap in the $(U_{0.72}Nd_{0.28})O_{2-x}$ system. Two FCC phases coexist in the sample at low temperature and change in a single phase at high temperature. This phase separation is reversible with temperature, which confirms the thermodynamic equilibrium of the material and discards the possibility that the biphasic areas originate from the sample preparation. This is consistent with a previous Raman spectroscopy study performed on $(U,Nd)O_2$ samples (Desgranges et al., 2012).

A miscibility gap exists in other rare earth-dopes oxides fuels, such as $(U_{1-y}Pu_y)O_{2-x}$ and $(U_{1-y}Ce_y)O_{2-x}$, for $y \geq 0.2$ (Guéneau et al., 2011; Norris and Kay, 1983). In both system, one phase is close to stoichiometry and the other is hypo-stoichiometric. Even if the valence state of Nd (3+) is not the same of Pu and Ce (3+ but also 4+), which leads to different electronics situations during dissolution of the cation into the UO_2 lattice, it can be assumed, by