



Controlling the oxygen potential to improve the densification and the solid solution formation of uranium–plutonium mixed oxides



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ARTICLE INFO

Article history:

Received 18 July 2013

Accepted 15 December 2013

Available online 22 December 2013

ABSTRACT

Diffusion mechanisms occurring during the sintering of oxide ceramics are affected by the oxygen content of the atmosphere, as it imposes the nature and the concentration of structural defects in the material. Thus, the oxygen partial pressure, $p(\text{O}_2)$, of the sintering gas has to be precisely controlled, otherwise a large dispersion in various parameters, critical for the manufacturing of ceramics such as nuclear oxides fuels, is likely to occur.

In the present work, the densification behaviour and the solid solution formation of a mixed uranium–plutonium oxide (MOX) were investigated. The initial mixture, composed of 70% UO_2 + 30% PuO_2 , was studied at $p(\text{O}_2)$ ranging from 10^{-15} to 10^{-4} atm up to 1873 K both with dilatometry and *in situ* high temperature X-ray diffraction.

This study has shown that the initial oxides UO_{2+x} and PuO_{2-x} first densify during heating and then the solid solution formation starts at about 200 K higher. The densification and the formation of the solid solution both occur at a lower temperature when $p(\text{O}_2)$ increases.

Based on this result, it is possible to better define the sintering atmosphere, eventually leading to optimized parameters such as density, oxygen stoichiometry and cations homogenization of nuclear ceramics and of a wide range of industrial ceramic materials.

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1. Introduction

Up to now, the oxygen partial pressure, $p(\text{O}_2)$, of the sintering gas in equilibrium with an oxide ceramics is neither precisely monitored nor controlled during the industrial sintering of nuclear ceramics. This leads to a large dispersion in critical parameters like density, oxygen stoichiometry and cation homogenization. This dispersion originates from diffusion phenomena occurring during sintering (i.e. densification, grain growth, solid solution formation, etc.) which are governed by the nature and the concentration of structural defects imposed by $p(\text{O}_2)$ [1–6]. Monitoring the latter during sintering is thus essential to achieve a better control of the diffusion mechanisms, leading to a more thorough understanding of the fundamental phenomena involved during sintering, ultimately leading to suitable microstructures.

In the frame of the 4th generation Sodium Fast Reactors (SFR), an experimental prototype, ASTRID, is being currently under development [7]. Mixed uranium–plutonium oxide (MOX) fuel with plutonium content close to 30% is considered as a candidate

fuel for the above reactor and the research work regarding fuel fabrication is under process.

Currently, the fabrication of MOX fuel for fast neutron reactors is based on the traditional powder metallurgy process. Powders of uranium and plutonium dioxides are ground together in appropriate ratios until an intimate mixture is obtained. The mixture is pre-compacted, granulated and/or sieved then pressed as green compacts. The material is sintered at 1973 K under a reducing atmosphere composed of Ar + 5% H_2 , leading to dense pellets with an oxygen to metal ratio (O/M) < 2.00.

If sintering is performed under an oxidizing atmosphere, the concentration of cation vacancies increases and activates the diffusion. For example, $\text{U}_{0.94}\text{Pu}_{0.06}\text{O}_{2.17}$ pellets shrink to 97% of their theoretical density with a 4 h cycle at 1323 K under CO_2 . The same result can be obtained under reducing conditions but it requires a higher temperature of 1973 K [8]. Also, the formation of the solid solution from a mixture made up of 18% PuO_2 and 82% UO_2 after 2 h at 1873 K is strongly sensitive to $p(\text{O}_2)$. Under Argon + 3% Air, the solid solution fully forms whereas under Ar + 5% H_2 , it is limited to 20% and therefore, the material is heterogeneous [9]. Under H_2 , the formation of the solid solution starts at 1573 K but requires 8 h at 1873 K for completion [10]. Under CO_2 , only 2 h at 1473 K are needed for solid solution formation [11].

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In this work, we studied the densification of a mixture of 70% UO_2 + 30% PuO_2 under various atmospheres by dilatometry. The results are compared to those obtained on pure UO_2 and PuO_2 . A special attention was paid to carefully monitor $p(\text{O}_2)$ at the inlet and/or outlet of the sintering furnace, and studies were carried out under a wide domain of $p(\text{O}_2)$ ranging from 10^{-15} to 10^{-4} atm at 1873 K (including SFR usual range). Based on the thermodynamic model proposed by Lindemer and Besmann [12–14], sintering under such a wide range of oxygen potential will lead to the formation of hypo or hyperstoichiometric oxides.

To go further, high temperature X-ray diffraction (HT-XRD) experiments were performed to study the kinetics of formation of the $\text{U}_{0.7}\text{Pu}_{0.3}\text{O}_{2\pm x}$ solid solution under various $p(\text{O}_2)$. These two characterization techniques are complementary and allowed a better understanding of the effect of $p(\text{O}_2)$ during the sintering of uranium and plutonium mixed oxide fuels.

2. Experimental

2.1. Atmospheres

To cover the 10^{-15} to 10^{-4} atm range of $p(\text{O}_2)$ at 1873 K, two types of atmospheres were used: (1) $p(\text{O}_2)$ increases with the dissociation of gas with temperature (mixtures of argon or helium + 5% H_2 without humidification and with 5000 or 28000 ppm H_2O were used) and (2) $p(\text{O}_2)$ is fixed, independent of temperature and only function of the initial composition (two mixtures of argon or helium with an initial content of 100 and 500 ppm of oxygen were selected).

Oxygen potential $\Delta\bar{G}(\text{O}_2)$ is generally defined by the thermodynamic relationship:

$$\Delta\bar{G}(\text{O}_2) = R \cdot T \cdot \ln\left(\frac{p(\text{O}_2)}{p(\text{O}_2)^*}\right) \quad (1)$$

where R is the gas constant, T the temperature, $p(\text{O}_2)$ the oxygen partial pressure and $p(\text{O}_2)^*$ is the standard-state pressure.

To calculate the oxygen potential of a gas dissociated when the temperature increases, it is necessary to determine the relationship between $p(\text{O}_2)$ and temperature. For $\text{Ar}/\text{H}_2/\text{H}_2\text{O}$ mixtures, $p(\text{O}_2)$ can be calculated from the thermodynamic equilibrium (2).



At equilibrium, the Gibbs free energy of reaction (2) is zero and leads to the following expression of $p(\text{O}_2)$.

$$p(\text{O}_2) = \exp\left(\frac{-\Delta G_T^\circ}{R \cdot T} - 2 \cdot \ln\left(\frac{p(\text{H}_2)}{p(\text{H}_2\text{O})}\right)\right) \quad (3)$$

SAGE software [15] (Solgasmix-based Advanced Gibbs Energy minimizer) was used to calculate the most thermodynamically stable composition in specific conditions of temperature and pressure, in the different phases of the system. Thus, the relation between $p(\text{O}_2)$ and temperature for $\text{Ar}/\text{H}_2/\text{H}_2\text{O}$ mixtures was determined and shown in Fig. 1b. The atmospheres chosen cover oxygen potentials ranging from -600 and -300 $\text{kJ}\cdot\text{mol}^{-1}$ at 1873 K (Fig. 1b).

Argon mixtures with 100 or 500 ppm of O_2 have a constant $p(\text{O}_2)$ at $1 \cdot 10^{-4}$ and $5 \cdot 10^{-4}$ atm, respectively (Fig. 1a). The corresponding oxygen potentials were calculated and their evolution as a function of temperature plotted in Fig. 1a. The oxygen potential at 1873 K ranges between -200 and -100 $\text{kJ}\cdot\text{mol}^{-1}$.

In a furnace, oxygen potential is not only imposed by the composition of the inlet gas but also by the change in oxygen content resulting from interactions with the material and the initial O/M ratio [16]. Measuring the oxygen potential of gas *in situ* at 1973 K during sintering is not feasible. However, it is possible to estimate it by measuring $p(\text{O}_2)$ at the inlet and the outlet of the

furnace, which is usually not done and may give new insights into the process [17,18].

$p(\text{O}_2)$ is directly monitored with a solid-state electrolyte cell or indirectly measured with a moisture probe. Both ways were investigated in this study. The moisture content in gas was determined with a capacity probe device (from Vaisala company). Two yttria stabilized zirconia probes (YSZ), from Setnag, were chosen. One, operated at 948 K, measured the actual oxygen partial pressure of the gas whereas the other, operated at 1073 K, imposed and monitored the oxygen partial pressure of a gas (oxygen probe associated with an oxygen pump).

It is well known that the $p(\text{O}_2)$ in equilibrium with the fuel is determined by the composition of the sintering atmosphere. To allow the system to reach equilibrium at each temperature, a slow heating rate was used in this study and also an important renewal of gas is ensured to have a good flow of gas around the pellet.

2.2. Preparation, sintering and characterization of fuel samples

2.2.1. Raw materials and sample preparation

Scanning electron microscopy (SEM) images (Fig. 2) show that UO_2 powder is composed of 50 μm large spherical agglomerates consisting of crystallites of submicrometer size. PuO_2 powder consists in 0.5 μm thick flakes.

Specific surface areas measured by the BET method, carbon content obtained from carbon/nitrogen analysis as well as other characteristics of the two starting powders are summarized in Table 1.

The UO_2/PuO_2 mixture was made at the LEFCA facility (CEA Cadarache, France), by a powder metallurgy process optimized for small amounts of powder (40 g). 70% of UO_{2+x} and 30% of PuO_2 powders were mixed for 4 h in a ball mill using metallic uranium balls. Then, the mixture was sieved to 160 μm without pre-compaction. This simple process of powder preparation results in an intimate contact between both precursors without affecting the specific surface area.

1 gram of each powder, i.e. UO_2 , PuO_2 and 70% UO_2 + 30% PuO_2 mixture, were pressed into green cylinders of 6 mm in diameter and height. A simple uniaxial press was used for making green pellets. No die lubricant was used while compaction.

2.2.2. Dilatometry experiments

A SETARAM TMA92-16.18 vertical dilatometer was used for this study. The furnace is composed of a graphite heater protected by an alumina tube. The sample holder and the probe are made of alumina, allowing measurements up to 1873 K. The axial change in length was measured using a flat probe and a Linear Voltage Differential Transformer. The accuracy of the measurement is of ± 0.01 μm .

A force of 0.05 N was applied to the sample through the probe connected to an electromagnetic device controlled via Calipso DB V 1.051. This software also controls the temperature measured with a thermocouple located above the sample. B-type and W thermocouples were used under oxidizing and reducing atmospheres, respectively. The thermal cycle consisted in heating at 1 $\text{K}\cdot\text{min}^{-1}$, 4 h isothermal soak at 1873 K and cooling at 7 $\text{K}\cdot\text{min}^{-1}$. Input gas flow was 14 $\text{L}\cdot\text{h}^{-1}$, which is the highest flow rate achievable. The expansion of the system was corrected by measuring a reference sample of alumina and subtracting its contribution.

2.2.3. High temperature X-ray diffraction (HT-XRD)

The formation of the $\text{U}_{0.7}\text{Pu}_{0.3}\text{O}_{2\pm x}$ solid solution was studied using a Bragg–Brentano θ – θ Bruker D8 Advance X-ray diffractometer installed in a glove-box. The instrument is equipped with a Cu anticathode ($K\alpha_1$: $\lambda = 1.5406$ \AA + $K\alpha_2$: $\lambda = 1.5444$ \AA) operating

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