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Direct carbothermic reduction of actinide oxalates: Example of Nd(III) oxalate–carbon mixtures conversion

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ABSTRACT

Mixed uranium–plutonium monocarbide was obtained by carbothermic reduction of mixture of UO_2, PuO_2 and C at around 1500 °C under vacuum or argon for 4 h followed by sintering at around 1650 °C under mixture of Ar + 8%H_2 for 10 h. Moreover, PuO_2 was synthesized by oxalic precipitation followed by calcination at around 700 °C (PUREX process). This work deals with a process simplification, i.e. fabrication of carbide by calcination of actinide oxalate, precipitated in presence of carbon, at 1600 °C for 13 h under argon. In this preliminary study, neodymium was used as a surrogate of actinides. No carbon influence was noticed during calcination of neodymium oxalate into oxide. Carbon content was the same before and after calcination making possible conversion to carbide directly from mixture of neodymium oxalate and C.

1. Introduction

Since the 60s', carbide fuels have been studied all over the world for fast breeder reactors [1–6]. But about twenty years later, they were given up except in India where mixed actinide monocarbides ((U,Pu)C) are still used as an advanced fuel for liquid–metal–cooled fast breeder reactors (LMFBRs).

More recently, Gas Fast Reactor (Gen IV) development fuels aroused interest in carbide studies [7]. Mixed uranium–plutonium monocarbide ((U,Pu)C) has been chosen due to its high density [8], high thermal conductivity, good chemical compatibility with sodium coolant and stainless steel [9], and satisfactory in-pile performance of experimental pins at high burnup ($\geqslant$10 at.%).

The fabrication process of reference for mixed carbide is carbothermic reduction of a mixture of actinide oxide (UO_2 and PuO_2) and carbon, under vacuum (typically at 1 Pa, for 4 h at 1475 °C) followed by a sintering step under an Ar–H_2 atmosphere (typically argon and 8% of H_2 for 10 h at 1627 °C).

As an alternative way, in order to meet a closed fuel cycle and a possible process simplification, the one-step conversion of actinide oxalates precipitated from nitrate solution (PUREX process) into carbide was studied.

Carbothermic reduction of uranium oxides has been extensively studied [10–12]. This present work will focus on carbothermic reduction of actinide(III) oxalate. Rather than cerium, neodymium was chosen, for this first study, as an actinide surrogate for its unique oxidation degree +III and for its characteristic violet color allowing easy visual homogeneity control and visual check on the complete precipitation of this ion.

2. Experimental methods

The mixture of Nd(III) oxalate and carbon corresponding to $Nd_2(C_2O_4)_3 \cdot 10H_2O + 6C$, was prepared by mixing a Nd(III) nitrate solution (0.7 M), a concentrated $H_2C_2O_4$ solution (0.7 M) and graphite, in the stoichiometric conditions, for 30 min under stirring. A 10% excess of $H_2C_2O_4$ was added. The resulting crystallized powder was filtered, washed with water and dried at room temperature.

Thermogravimetric analysis (TG) and Differential Scanning Calorimetry (DSC) analyses were carried out with a NETZSCH STA 449C Jupiter Analyzer under argon at a rate of 5 °C min^{-1} between 25 °C and 1600 °C with isotherms at 250 °C for 1 h and at 1600 °C for 13 h. Samples of mixture, ~800 mg, were placed in an alumina crucible closed with a pinhole lid to avoid powder loss when evacuating residual air from the furnace. TG was coupled with a gas chromatography analysis (GC) with a SRA Instruments Micro-chromatograph Agilent 3000 apparatus.

For larger quantities, neodymium oxalate and carbon pellets were calcined in a Nabertherm furnace under argon with a constant rate of 5 °C min^{-1} between 25 °C and 1000 °C.

XRD patterns were collected on a Huber diffractometer by transmission using Cu Kα (λ = 1.54178 Å) radiation and on a D8

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HT diffractometer from Bruker with a position sensitive detector using Cu Kα (λ = 1.54178 Å) radiation to identify structure evolution between 25 °C and 1000 °C.

Granulometry distribution was determined with a Malvern Mastersizer X by diffraction induced by a laser.

The residual concentration of neodymium in solution was measured by Inductively Coupled Plasma–Atomic Emission Spectrometry (ICP–AES) with Perkin Elmer Optima 3100 RL system. The presence of neodymium in the solids was proved by Energy Dispersive Spectroscopy (EDS) performed on a JSM 5300 Scanning Electronic Microscope (SEM) equipped with a PGT X-ray microanalysis system (IMIX). The carbon content in the compound was measured by thermogravimetric analysis of ~100 mg of each sample at a constant rate of 5 °C min^{-1} from 25 °C to 1000 °C.

3. Results

3.1. Precipitation of neodymium oxalate in the presence of carbon

At the end of precipitation step, neodymium, evidenced by its violet characteristic color, is no more visible in the solution suggesting a high yield for Nd(III) oxalate precipitation. This was confirmed by an analysis of Nd(III) content in the residual solution by ICP–AES (~1.0 mg/l) and also by the weight of the precipitated solid (6.319 g) close to the expected mass (6.34 g) of the mixture of $Nd_2(C_2O_4)_3 \cdot 10H_2O + 6C$ (experimental yield ~99.7%).

The presence of neodymium in the precipitate was verified by EDS (Fig. 1(a)).

3.2. Conversion of a mixture of neodymium oxalate and carbon into neodymium oxide and carbon

A typical TG plot of the conversion of a mixture of neodymium oxalate and carbon into neodymium oxide and carbon is shown in Fig. 2.

At each intermediate step, the molecular formula were determined from mass loss, and/or by structural analysis.

XRD investigations, shown in Fig. 3, confirmed the identity of crystallized compounds before and after the heat treatment, respectively, mixture of graphite 2H and neodymium oxalate decahydrate and mixture of graphite 2H and the final oxide.

The presence of Nd in calcined powder was confirmed by EDS analysis (Fig. 1(b)).

The same calcination route was carried out on higher quantity (~1 g pellets) under argon in a furnace. The mass loss (exp: 49.7%; cal: 49.3%) confirms the conversion of oxalate into oxide. Then, the mass loss during heating of the residual solid ($Nd_2O_3 + 6C$) under air at 1000 °C, enabled the determination of carbon content (3C by Nd).

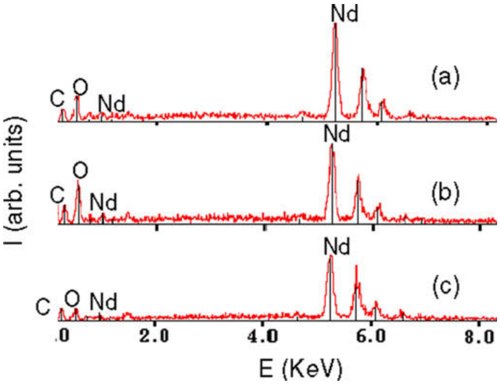

Fig. 1. EDS analyses of neodymium oxalate decahydrate (a), oxide (b) and carbide (c).

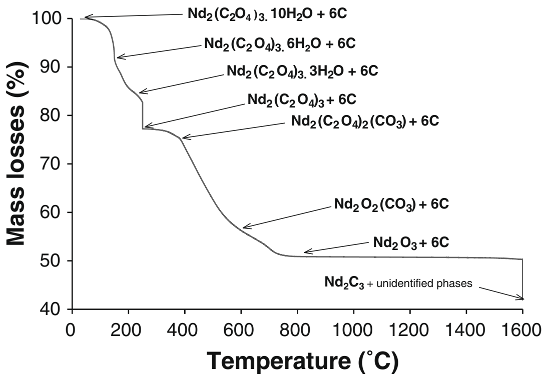

Fig. 2. TG plot starting from a $Nd_2(C_2O_4)_3 \cdot 10H_2O + 6C$ sample under argon up to 1600 °C.

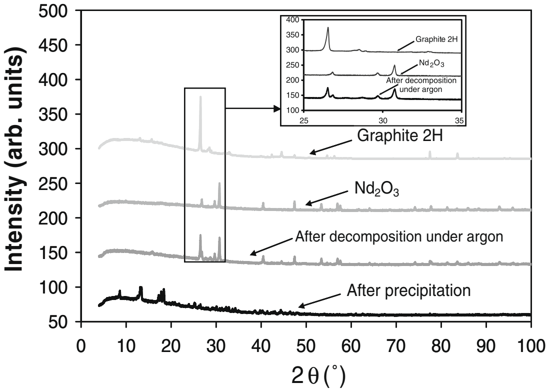

Fig. 3. XRD patterns before and after the heat treatment.

After the 1000 °C calcination, pellet shrinkage was observed corresponding to a grain growth phenomena rather than a real sintering process as indicated by an increase of the grain size (36–81 μm) measured by granulometry scattering.

3.3. Conversion of the mixture of neodymium oxalate and carbon into neodymium carbide

The Fig. 4 shows the CO–CO_2 release (GC measurement) during the heating of neodymium oxalate and carbon to obtain neodymium carbide. From 1600 °C, a mass loss is observed in TG analysis under argon and a departure of carbon monoxide is detected by GC. This loss of CO and the global mass loss allowed confirming the formation of neodymium carbide.

The presence of neodymium in carbide was noticed by EDS analysis (Fig. 1(c)).

XRD investigations showed a mixture of Nd_2C_3 and Nd_2O_3 due to an incomplete reaction and the spontaneous carbide oxidation at the surface, in air and at room temperature (when opening TGA furnace and during its storage). Note that some additional phases are also observed in low quantity.

4. Discussion

The proposed reaction mechanism leading to neodymium oxide under argon is detailed in Fig. 5.

Neodymium oxalate trihydrate, anhydrous neodymium oxalate and Nd(III) dioxymonocarbonate $Nd_2O_2(CO_3)$ have been reported

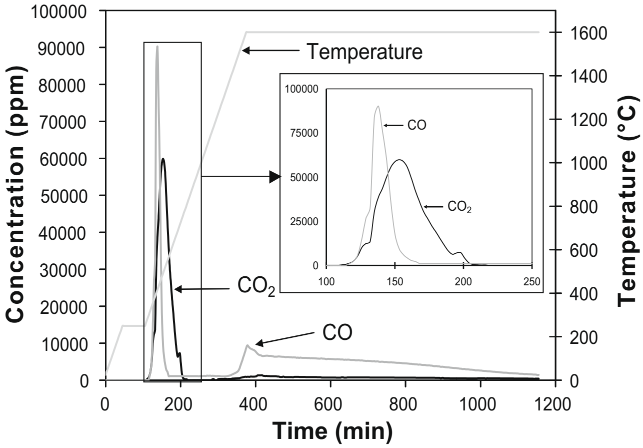

Fig. 4. CO–CO$_2$ release during TG under argon of $Nd_2(C_2O_4)_3 \cdot 10H_2O$ + 6C sample.

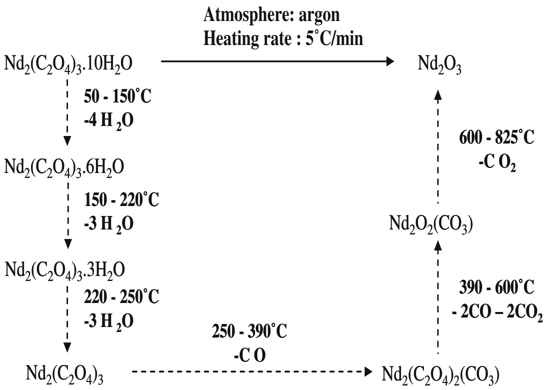

Fig. 5. Reaction path of the thermal conversion of $Nd_2(C_2O_4)_3 \cdot 10H_2O$.

as an intermediate compound during decomposition studies in air [13–16]. The lanthanide oxalato-carbonate, $Ln_2(C_2O_4)_2(CO_3)$ formation, as an intermediate compounds was supported with past works on ytterbium [17], and plutonium [18].

The evolution of the X-ray pattern of neodymium oxalate during heating in argon showed the transformation of the decahydrate into an amorphous phase at 80 °C and the crystallization of the neodymium oxide at about 800 °C.

The initial carbon added in the neodymium nitrate solution does not react with Nd, neither during oxalate formation step (precipitation step), nor during neodymium oxide formation (conversion step). The initial carbon content is maintained allowing a complete carbothermic reduction at 1600 °C under Ar:

$$Nd_2O_3 + 6C \rightarrow Nd_2C_3 + 3CO(g).$$

Regarding CO release, the reaction between oxide and carbon rapidly occurs when a 1600 °C temperature is reached due to easy diffusion of CO from solid compounds. The CO release then decreases presumably because of powder densification and hence CO diffusion slowing. However, 13 hours' isotherm is not sufficient for a complete reaction.

A longer time and/or a higher temperature and/or an argon flow increase could improve pure carbide formation. Studies of these parameters are in progress.

The high reactivity of carbide in air atmosphere, even at room temperature, evidenced the necessity of a few handling and storage precautions. Characterization by XRD of carbides immediately after TGA has to be organized.

5. Conclusion

The reaction mechanism occurring during the thermal transformation of $Nd_2^{III}(C_2O_4)_3 \cdot 10H_2O$ into oxide in the presence of carbon was investigated under argon using thermogravimetric analysis and structural characterization of the intermediate solid compounds. Then, carbothermic reduction of neodymium oxide into sesquicarbide was studied by TG analysis and structural characterization of the final solid. These studies allowed the synthesis of carbide from solution of neodymium nitrate using precipitation and calcination in one step.

Further studies on uranium and plutonium based fuels are planned. The simplification of the carbothermic process is very important when using highly radioactive elements.

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