



# A thermogravimetric study of the fluorination of zirconium and hafnium oxides with anhydrous hydrogen fluoride gas

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## ARTICLE INFO

### Article history:

Received 26 April 2012

Received in revised form 11 June 2012

Accepted 12 June 2012

Available online 19 June 2012

### Keywords:

Zirconium

Hafnium

Zirconium oxide

Hafnium oxide

Zirconium tetrafluoride

Hafnium tetrafluoride

Thermogravimetry

## ABSTRACT

Zircon mineral contains about 1–3% hafnium which is an undesirable impurity in the nuclear industry. A novel dry fluorination route was investigated to produce  $ZrF_4$  as a possible intermediate for the production of nuclear grade zirconium metal. The process was investigated by the reaction of pure  $ZrO_2$  and  $HfO_2$  with anhydrous hydrogen fluoride using a thermogravimetric analyzer. The findings indicate successful formation of  $ZrF_4$ ,  $HfF_4$ , and oxyfluorides identified with X-ray powder diffraction. According to the TGA experiments, the stoichiometric formation of  $ZrF_4$  was realized at 525 °C whilst that for  $HfF_4$  was not attained.

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## 1. Introduction

Zirconium occurs in nature as zircon mineral,  $Zr(Hf)SiO_4$ , with approximately 1–3% hafnium content by weight [1]. The zirconium is always associated with hafnium due to similar physical and chemical properties [2]. The presence of hafnium renders the zirconium metal less valuable in the nuclear industry, by virtue of its high neutron cross section of 105 barns compared to 0.18 barns for zirconium [3]. The large demand for hafnium-free zirconium in nuclear applications necessitates the separation of zirconium and hafnium.

Several techniques have been proposed and used to separate the two elements, solvent extraction (TBP) [4,5], liquid–liquid extraction (MIBK) [6], and extractive distillation (CEZUS) [7,8]. These aqueous routes produce zirconium tetrachloride as the precursor for the manufacture of nuclear grade zirconium metal. However, these aqueous processes are disadvantageous since they are expensive, ecologically unfriendly and involve intricate processes. Dry routes by which tetrafluorides are prepared from the metal oxides using hydrogen fluoride [9–11] or fluorine [12,13] have been proposed. The anhydrous routes present several advantages as they yield the less hygroscopic  $ZrF_4$  as the feed material for pure Zr metal production.

The conversion of  $ZrO_2$  to  $ZrF_4$  with HF was initially reported to occur at 227 °C by Robinson [10]. However a year later Robinson and Fuller claimed rapid conversion at 30 °C [14]. Since thermogravimetric studies can provide information on possible intermediates, we revisited the reaction of  $ZrO_2$  with HF to investigate the claims, and our reactions were therefore conducted from 30 to 600 °C. In our study, the fluorinations of small samples of  $MO_2$  ( $M = Zr/Hf$ ) with HF were carried out in a modified thermogravimetric analyzer (TGA). Modifications of the TGA were deemed necessary to make it acquiescent with corrosive gases. Dynamic as well as isothermal reactions were carried out and products thereof characterized using X-ray powder diffraction. All samples for analysis were handled in a dry glovebox since the tetravalent zirconium and hafnium are reported to be moisture sensitive [15,16].

## 2. Results and discussion

A pure  $ZrO_2$  sample was heated from 30 to 800 °C in a 10% HF/ $N_2$  atmosphere at a rate of 10 °C/min and the dynamic thermogravimetric curve shown in Fig. 1 was obtained. The reaction proceeds as follows: a mass gain (A) of about 4% on introduction of the reactive gas; (B) a slight decrease of about 2% in mass; (C) a further mass gain above 350 °C to yield a maximum of 6% at a temperature of 550 °C; and finally (D) a mass loss. The TG reaction profile suggests formation of intermediate compounds prior to formation of the final product. The theoretical mass gain of 35.7% which

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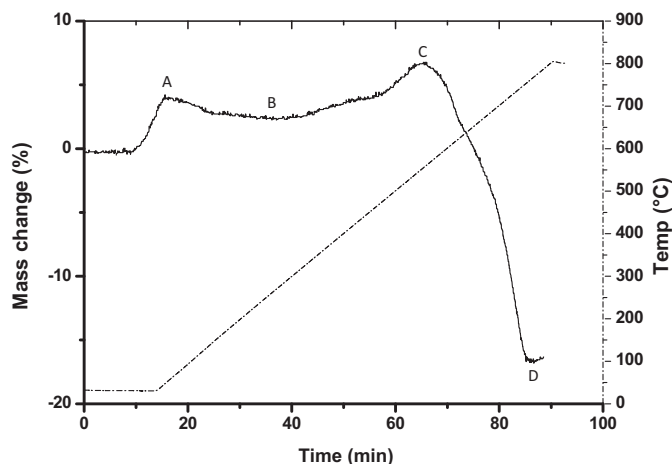


Fig. 1. Thermogravimetric curve of the reaction of  $ZrO_2$  with HF between 30 and 800 °C at a heating rate of 10 °C/min.

corresponds to complete conversion of  $ZrO_2$  to  $ZrF_4$  has not been attained in the dynamic reaction.

In order to identify the intermediate compounds, reactions of  $ZrO_2$  with 10% HF/ $N_2$  were carried out isothermally at 30, 50, 100, 150, 200, 250, 300, 350, 400, 450, 500, 525, 550, and 600 °C. No significant mass changes were observed at temperatures below 300 °C except 30 °C. As a result, the respective TG profiles of isotherms conducted below 300 °C are not included.

The TG profile of  $ZrO_2$  with HF at 30 °C yields the theoretical 35% mass gain expected for the total conversion of  $ZrO_2$  to  $ZrF_4$  (Fig. 2). However, characterization by X-ray diffraction reveals only traces of  $ZrF_4$  with  $ZrO_2$  as the major phase. This finding is not in agreement with Robinson and Fuller [14] who claim to form  $ZrF_4$  at 30 °C. This could imply strong adsorption, and the reaction at 30 °C therefore needs to be further investigated.

The TG profiles of isotherms between 300 and 600 °C illustrate characteristic mass gains that reach specific plateaus (Fig. 3). Between 300 and 500 °C, increasing mass gains were recorded till the 35% stoichiometric value anticipated for the total conversion of  $ZrO_2$  to  $ZrF_4$  was observed at 525 °C. The 525 °C temperature condition coincides with the optimum conversion temperature

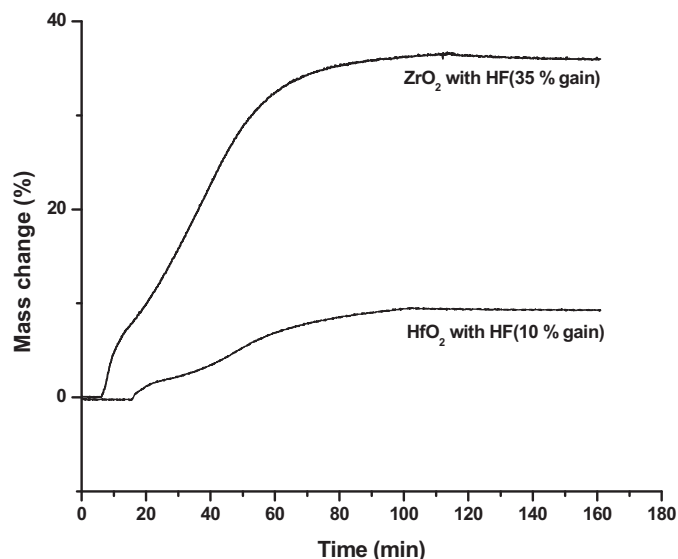


Fig. 2. Thermogravimetric curves of the reaction of  $ZrO_2$  and  $HfO_2$  with HF at 30 °C.

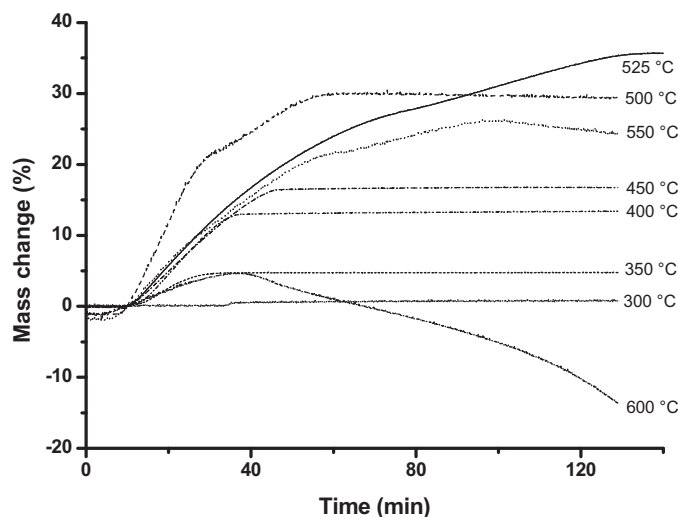


Fig. 3. Thermogravimetric curve of the reaction of  $ZrO_2$  with HF at isothermal temperatures of 300, 350, 400, 450, 500, 525, 550 and 600 °C.

reported by both Haendler et al. [17] and Monnabela et al. [13] on using fluorine as the fluorinating agent. At 300 and 350 °C there was a 1 and 4% mass gain, respectively, and the XRD revealed  $ZrO_2$  as the major phase and phases of  $Zr_3O_2F_8$  (Fig. 4) which were previously isolated by Holmberg [18]. A 13% mass gain was obtained at 400 °C with the XRD showing  $Zr_{0.33}F_{3.33}O_{0.33}$  and  $ZrO_2$  phases (Fig. 4). About 16% mass gain was recorded at 450 °C, with XRD confirming phases of  $ZrF_4$  in addition to the  $ZrO_2$  phase (Fig. 4).

At 500 and 525 °C where mass gains of 29 and 35% (Fig. 3) were recorded, phases of  $Zr_{0.13}F_{1.4}O_{0.33}$ ,  $Zr_{0.33}F_{3.33}O_{0.33}$ ,  $ZrF_4$  and traces of  $ZrO_2$  were identified (Fig. 5). The  $Zr_{0.13}F_{1.4}O_{0.33}$  has previously been isolated by Papiernik et al. [19]. This oxyfluoride was also found by Rivas et al. [20] on heating the hydrated  $ZrF_4$  at 327 °C for 24 h. An initial mass gain of 24% followed by mass loss was observed at 550 °C. The mass loss can be ascribed to sublimation of the formed  $ZrF_4$  since sublimation experiments conducted by heating the pure commercial  $ZrF_4$  from 30 to 800 °C at a heating rate of 10 °C/min under nitrogen atmosphere (Fig. 6) gave a sublimation temperature of 687 °C. This behavior is in agreement with the sublimation

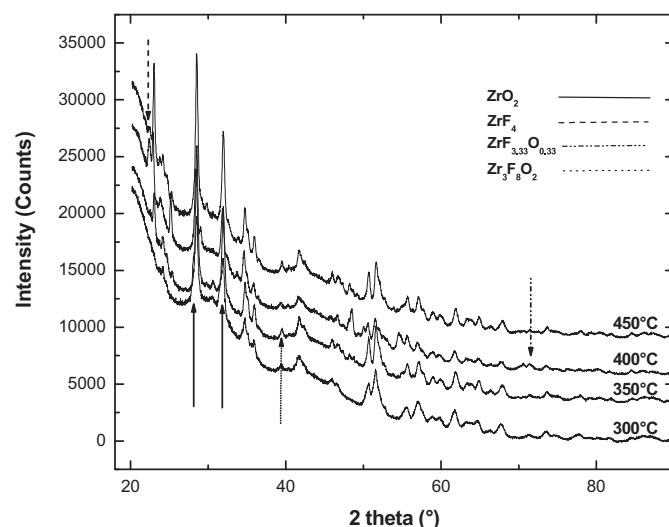


Fig. 4. XRD patterns of the products obtained when  $ZrO_2$  was treated with HF at isothermal temperatures of 300, 350, 400 and 450 °C.

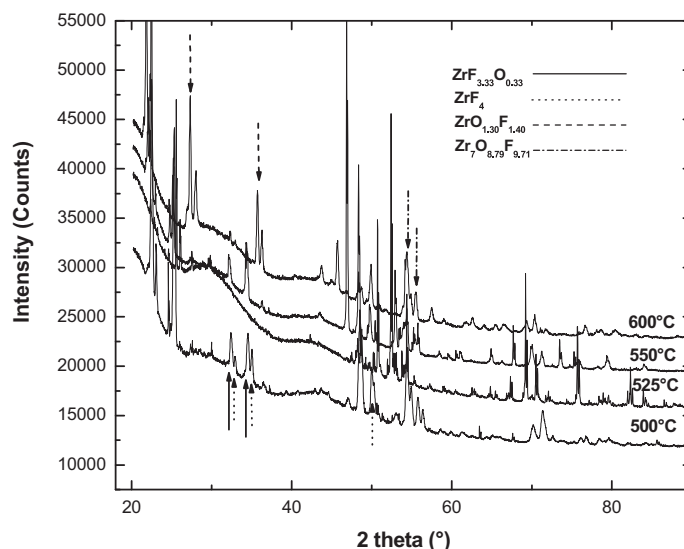


Fig. 5. XRD patterns of the products obtained when  $\text{ZrO}_2$  was treated with HF at isothermal temperatures of 500, 525, 550 and 600 °C.

reported by Atkins et al. [16] on heating  $\text{ZrF}_4$  in argon atmosphere. Phases of  $\text{ZrF}_4$  were revealed by XRD at the isotherm of 550 °C (Fig. 5). At 600 °C only 4% mass gain was obtained which suggests conditions more favorable to sublimation. Apart from the  $\text{ZrF}_4$  phase, the  $\text{Zr}_{8.79}\text{F}_{9.71}$  phase was also identified by XRD (Fig. 5) at this isothermal temperature.

The isothermal experiments yield higher mass gains as compared to the dynamic experiment. This could be due to conditions more suitable to forming intermediates as opposed to the dynamic run with constant heating. Atkins et al. [16] and Waters [21] identified the  $\text{ZrOF}_2$  oxyfluoride as an intermediate on heating the hydrated  $\text{ZrF}_4$  in air at 300 °C, with further heating yielding the  $\text{ZrO}_2$ . We do not observe this oxyfluoride in our investigation through hydrofluorination of the  $\text{ZrO}_2$ .

Similar to the reaction profile for  $\text{ZrO}_2$  with HF, isothermal as well as dynamic thermogravimetric hydrofluorination of  $\text{HfO}_2$  were carried out. The TG profile for the dynamic reaction (Fig. 7) depicts an initial mass gain (A) of 2% due possibly to absorption of HF on  $\text{HfO}_2$ , followed by (B) mass loss due to desorption of HF, another mass gain (C) to yield a total of 14% for the conversion of  $\text{HfO}_2$  to  $\text{HfF}_4$  and finally the mass loss (D) due to sublimation of the converted  $\text{HfF}_4$ . A summary of the isothermal TG curves is depicted in Fig. 8. As in the

reactions involving  $\text{ZrO}_2$  with HF, higher reaction temperatures resulted in higher mass uptake. At 30 °C there was 10% (Fig. 2) mass gain and  $\text{HfO}_2$  was the only phase detected by XRD. At 300, 350 and 400 °C, mass gain increases of 2, 10 and 11% were, respectively, recorded but only the  $\text{HfO}_2$  phase was detected by XRD (Fig. 9).

At 450 and 500 °C there was 13 and 17% mass gains recorded (Fig. 8). There was 19% mass gain recorded at each isotherm of 550 and 580 °C. The XRD analysis confirmed formation of  $\text{HfF}_4$ ,  $\text{Hf}_2\text{OF}_6$  and traces of  $\text{HfO}_2$  at temperatures between 450 and 580 °C (Fig. 10). The  $\text{Hf}_2\text{OF}_6$  phase has been previously isolated by Rickard and Waters [22] on heating the tetrafluoride monohydrate in air. The stoichiometric value of 20% anticipated for the total conversion of  $\text{HfO}_2$  to  $\text{HfF}_4$  was not realized. At 600 °C there was an initial mass gain to 9% followed by mass loss suggesting reactions occurring simultaneously, where  $\text{HfF}_4$  undergoes sublimation as it is formed. The XRD showed phases of  $\text{HfF}_4$  and  $\text{Hf}_2\text{OF}_6$  at this temperature (Fig. 10). In our study,  $\text{Hf}_2\text{OF}_6$  was the only oxyfluoride identified, however this does not preclude the presence of other oxyfluorides since this is one of only two entries in the current X-ray diffraction database. A summary of the intermediates and products formed is given in Table 1.

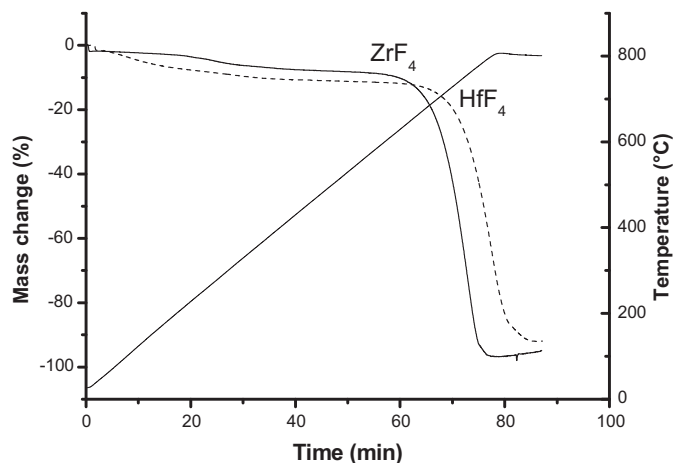


Fig. 6. An overlay of the thermogravimetric curves of the decomposition of the commercial  $\text{ZrF}_4$  and  $\text{HfF}_4$  heated from 30 to 800 °C in nitrogen atmosphere.

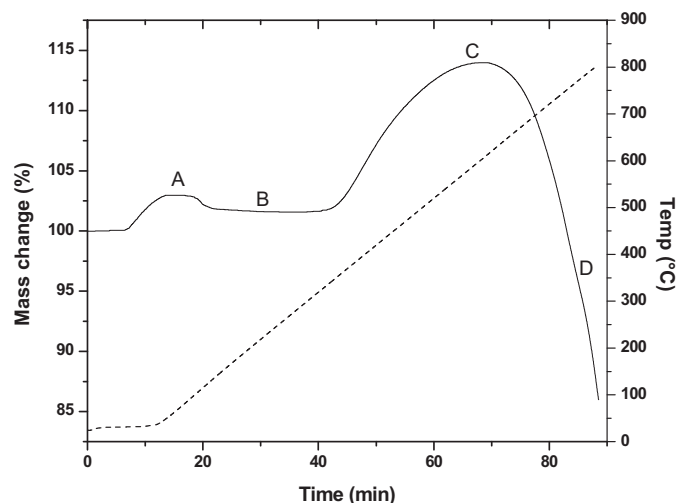


Fig. 7. Thermogravimetric curve of the reaction of  $\text{HfO}_2$  with HF heated from 30 to 800 °C at a heating rate of 10 °C/min.

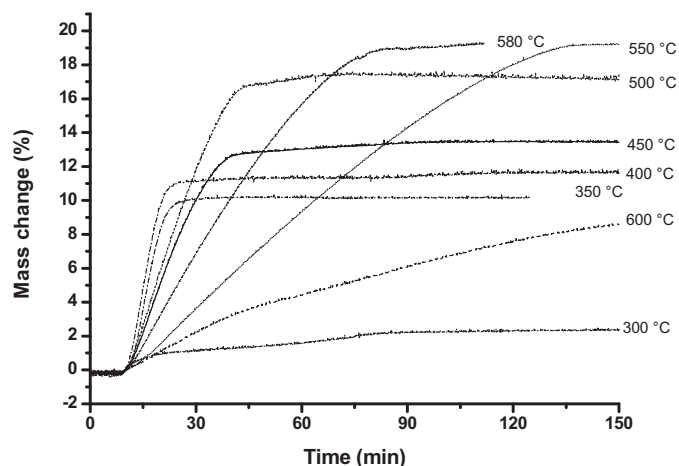


Fig. 8. Thermogravimetric curves of the reaction of  $\text{HfO}_2$  with HF at isothermal temperatures of 300, 350, 400, 450, 500, 550, 580 and 600 °C.

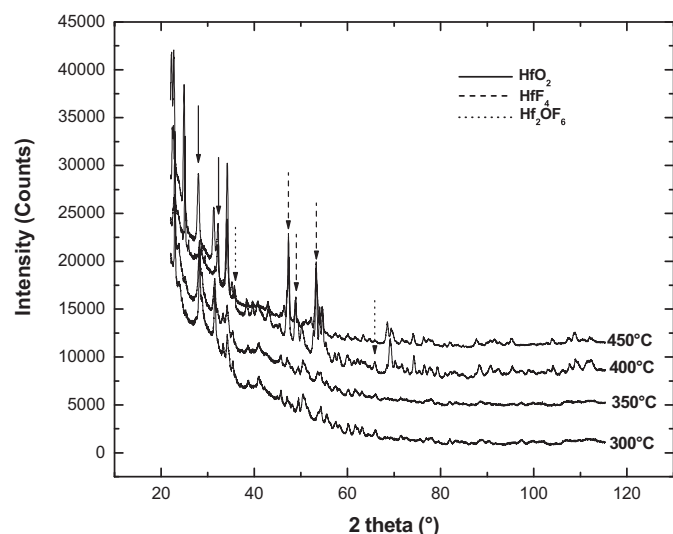


Fig. 9. XRD patterns of the products obtained when  $\text{HfO}_2$  was treated with HF at isothermal temperatures of 300, 350, 400 and 450 °C.

Table 1

Reaction intermediates and products species identified through XRD.

ZrO <sub>2</sub> with HF	HfO <sub>2</sub> with HF
ZrO <sub>2</sub>	HfO <sub>2</sub>
Zr <sub>3</sub> O <sub>2</sub> F <sub>8</sub>	Hf <sub>2</sub> OF <sub>6</sub>
ZrO <sub>0.33</sub> F <sub>1.33</sub>	HfF <sub>4</sub>
ZrO <sub>1.3</sub> F <sub>1.4</sub>	
ZrO <sub>8.79</sub> F <sub>9.71</sub>	
ZrF <sub>4</sub>	

Comparison of the thermogravimetric curves of isotherms of ZrO<sub>2</sub> with HF (Fig. 3) and those of HfO<sub>2</sub> (Fig. 8) reveals a rapid change in mass for the latter and thus faster reactions compared to the former. This is in good agreement with Williams and Weaver [23] who reported that HfO<sub>2</sub> reacts faster than ZrO<sub>2</sub>.

### 3. Conclusions

The thermogravimetric investigations and X-ray powder diffraction identification confirm production of ZrF<sub>4</sub> and HfF<sub>4</sub> from the oxides through fluorination with HF. The tetrafluorides are potential precursors for separation of Zr and Hf and subsequent Zr metal

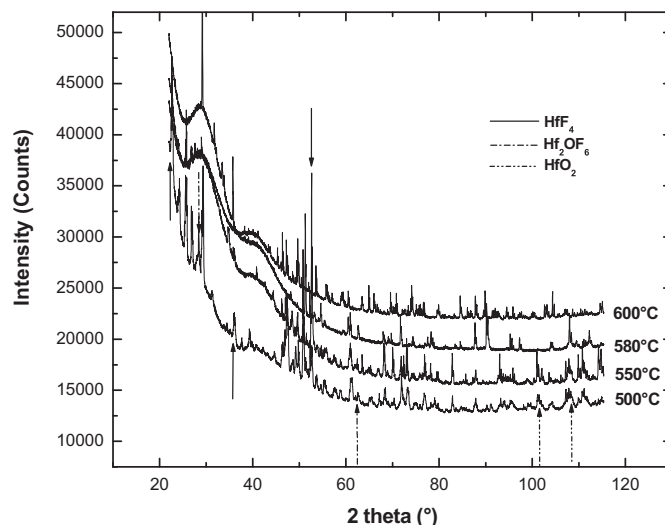


Fig. 10. XRD patterns of the products obtained when  $\text{HfO}_2$  was treated with HF at isothermal temperatures of 500, 550, 580 and 600 °C.

production. The theoretical mass gain for ZrF<sub>4</sub> formation was realized at an isothermal temperature of 525 °C. The dynamic experiments of the oxides showed formation of intermediates prior to formation of the product. The presence of intermediate oxyfluorides was confirmed on experiments done at specific isotherms.

Isotherms conducted at temperatures above 550 and 600 °C for ZrO<sub>2</sub> and HfO<sub>2</sub>, respectively, already showed signs of sublimation of the tetrafluorides. This suggests that 525 °C is the optimum temperature for the conversion of zirconium oxide. Sublimation experiments done on the commercial ZrF<sub>4</sub> and HfF<sub>4</sub> illustrate that sublimation occurs at 687 and 733 °C, respectively. Only one hafnium oxyfluoride, Hf<sub>2</sub>OF<sub>6</sub>, was identified whilst a host of zirconium oxyfluorides was formed and confirmed by XRD on treating the oxides with HF. The Hf<sub>3</sub>O<sub>2</sub>F<sub>8</sub> identified by Rickard and Waters [22] on heating the hydrated HfF<sub>4</sub> in air could not be observed in our findings.

Although the 35% mass gain required for the conversion of ZrO<sub>2</sub> to ZrF<sub>4</sub> was achieved at 30 °C, XRD could only confirm traces of ZrF<sub>4</sub> and the ZrO<sub>2</sub> starting material as the major phase at this temperature. It is thought that adsorption of HF might at least partially contribute to the large mass gain. Phases of ZrF<sub>4</sub> were seen from temperatures of 450 °C according to our study.

## 4. Experimental

### 4.1. Apparatus

Experimental runs were performed on a modified [24] Perkin Elmer TGS-2 thermogravimetric analyzer. An inert gas was continuously purged through the chamber of the weighing mechanism to avoid interaction of the corrosive gases with the highly sensitive electronics and mechanics of the weighing mechanism. The details of the thermobalance protection have been described by Birks and Tattam [25]. Nickel is quickly passivated against fluorination, hence all metallic parts including the sample pan were changed to nickel. Tung and Friedland [26] also states that nickel or nickel alloy are stable in fluorine atmosphere.

### 4.2. Materials

Dilute mixtures of 10% HF/N<sub>2</sub> were prepared in a 20 L stainless steel cylinder with the HF supplied by Pelchem, a Necsa subsidiary. The metal oxide and fluoride samples were purchased from Sigma Aldrich: ZrO<sub>2</sub> [pure], HfO<sub>2</sub> [98%], ZrF<sub>4</sub> [99.9%] and HfF<sub>4</sub> [99%].

#### 4.3. Method

Dynamic fluorination runs of the oxides were performed by placing approximately 20 mg ZrO<sub>2</sub> or HfO<sub>2</sub> sample on a nickel pan within the TG furnace in a dry nitrogen atmosphere. The 10% HF/N<sub>2</sub> was introduced, allowed to equilibrate at 30 °C, and then the temperature was elevated to 800 °C at a heating rate of 10 °C/min. Isothermal reactions were conducted by heating the ZrO<sub>2</sub> or HfO<sub>2</sub> to the desired temperature under nitrogen purge gas, and then introducing 10% HF/N<sub>2</sub> reactive gas.

The sublimation temperature of the commercial metal fluorides was determined by heating the samples from 30 to 800 °C at 10 °C/min under dry nitrogen purge gas.

#### 4.4. X-ray powder diffraction

X-ray powder patterns of the commercial MO<sub>2</sub>, MF<sub>4</sub> (M = Zr, Hf) as well as the reaction products of the isothermal reactions were recorded using a Bruker D8 Advance powder diffractometer. The samples were loaded in a sealed enclosed sample holder, specially designed to protect samples against environmental moisture. Loading was done inside a dry nitrogen glovebox. Sample probing was done using the 8 keV Cu-Kα radiations with the phases identified using the Bruker's Eva software in conjunction with the 2007 PDF-2 ICDD database.

#### Acknowledgments

This work has been funded by the Department of Science and Technology under the Advanced Metals Initiative. We wish to express sincere appreciation to the South African Nuclear Energy Corporation for the use of their facilities including the XRD

instrument. The authors would also like to express sincere appreciation to Dr. Hester Oosthuizen for the insightful discussions.

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