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A thermogravimetric study of the fluorination of zirconium and hafnium oxides with fluorine gas

Oduetse S. Monnahela [a,*], Bernard M. Vilakazi [a], Jacobus B. Wagener [a], Andreas Roodt [b], Pieter A.B. Carstens [a], Willem L. Retief [a]

[a] Applied Chemistry Department, South African Nuclear Energy Corporation Limited, P.O. Box 582, Pretoria 0001, South Africa
[b] Department of Chemistry, University of the Free State, P.O. Box 339, Bloemfontein 9300, South Africa

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ABSTRACT

The fluorination of ZrO_2 and HfO_2 and the understanding of the fundamental chemistry of formation of ZrF_4 and HfF_4 in a fluorine atmosphere were investigated using a thermobalance. The fluorination of these species was performed to understand the chemical behavior of the tetrafluoride species of these metals. Thermogravimetrical analysis indicated that the formation of ZrF_4/HfF_4 is via the oxyfluorides. X-ray powder diffraction was used to confirm the results.

1. Introduction

Zirconium and hafnium almost always occur together in nature and, due to similar properties, are very difficult to separate. Nuclear grade zirconium, which should be free of hafnium, can be produced by conventional aqueous routes [1–5] which are potentially tedious, costly and environmentally unfriendly since the waste streams contain high concentrations of ammonium salts, cyanides, and organic products. By contrast, the anhydrous routes [6–8] are more environmentally friendly, although still costly and tedious. The conventional aqueous routes produce mostly hydrated metal chlorides, which makes it difficult to minimize the oxide and hydroxide content of the $ZrCl_4/HfCl_4$, thus formed. Furthermore, the hygroscopic nature of zirconium tetrachloride rendered it not the preferred precursor for the manufacture of nuclear-grade zirconium metal [9]. Zirconium tetrafluoride is a more suitable precursor since it can be prepared in a non-hydrolyzing, non-hygroscopic [10] form, which is also less volatile than the corresponding chloride.

Zirconium tetrafluoride has been prepared by fluorination of zirconium oxide with hydrogen fluoride [6,11,12], ammonium bifluoride [13–15], fluorine gas [16], and bromium trifluoride [17]. Although the direct fluorination of zirconium oxide with fluorine gas has been described, bulk samples were used [16], and mainly the yield and conversion temperatures were reported. In this study we revisit the direct fluorination of zirconium oxide with fluorine gas using small samples. The direct fluorination of hafnium oxide was also investigated. The experiments were carried out using a modified thermogravimetric analyzer, providing information on the rate of the reaction, and the rate of formation of the tetrafluorides.

2. Results and discussion

Dynamic thermogravimetric fluorination of zirconium and hafnium oxides was conducted for the respective oxides from room temperature to 800 and 700 °C in a fluorine atmosphere. The fluorination of zirconium oxide occurs via a double-step mechanism (Fig. 1), with an initial mass increase of 7% at approximately 380 °C followed by an increase of 26% at approximately 480 °C. The latter step could be ascribed to the formation of zirconium tetrafluoride (B in Fig. 1) possibly via a zirconium oxyfluoride (A in Fig. 1) species as an intermediate. The mass loss above 600 °C is likely due to the sublimation of ZrF_4. The total mass increase for complete conversion of ZrO_2 to ZrF_4 should be 35.7%, which is slightly higher than the total mass increase (33%) shown by the

* Corresponding author. Tel.: +27 12 305 3239; fax: +27 12 305 6945.
E-mail address: Sydney.monnahela@necsa.co.za (O.S. Monnahela).

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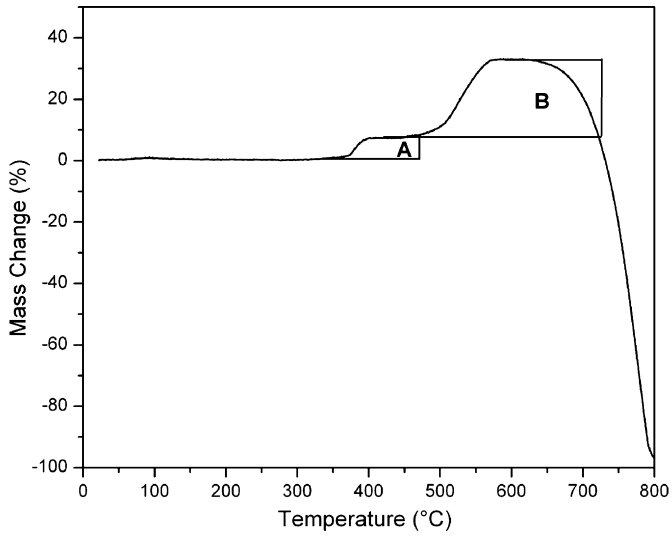

Fig. 1. Thermogravimetric curve of the reaction of ZrO_2 in a 10% F_2/N_2 atmosphere at a heating rate of 10 °C/min.

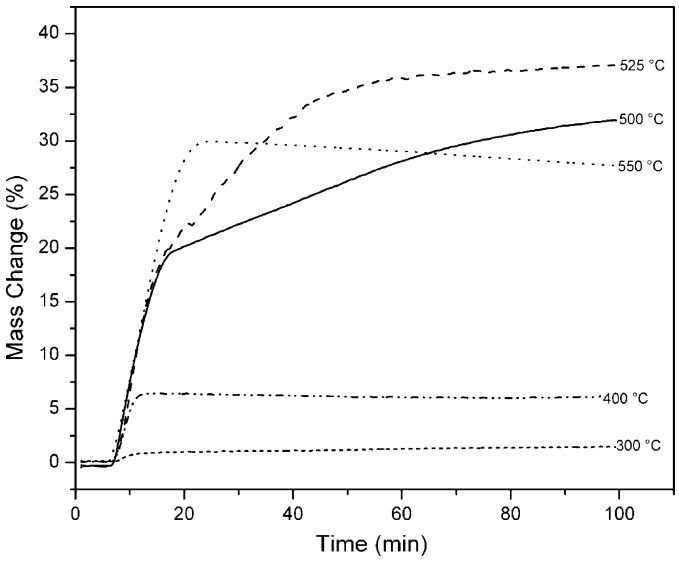

Fig. 3. Thermogravimetric curves of the reactions of ZrO_2 with fluorine at isothermal temperatures of 300, 400, 500, 525, and 550 °C.

thermogravimetric results. The zirconium oxyfluoride whose formation from ZrO_2 corresponds to a 7% mass increase could be ascribed to the formation of non-stoichiometric zirconium oxyfluorides.

The reaction of hafnium oxide with fluorine occurs via a four-step reaction mechanism (Fig. 2), with mass gains of 1, 12, 3, and 2% respectively, amounting to an overall mass gain of 18%. This behavior could also be ascribed to formation of intermediates (A–C in Fig. 2) before the formation of hafnium tetrafluoride (D in Fig. 2). The total mass gain of this reaction (18%) is also somewhat less than the calculated mass gain for the conversion of HfO_2 to HfF_4 (20.9%). It can, as for the ZrO_2 reaction, be postulated that the intermediates may be oxyfluorides of hafnium.

In an attempt to isolate the intermediate compounds, fluorinations were carried out at selected isothermal temperatures of 300, 400, 500, 525, and 550 °C for zirconium oxide (Fig. 3) and 300, 400, 500, 550, 580, and 600 °C for hafnium oxide (Fig. 4).

Zirconium oxide reacts partially with fluorine at 300 °C to yield an insignificant mass increase (Fig. 3). The XRD analysis of the sample showed a trace amount of zirconium oxyfluoride ($Zr_3O_2F_8$) (Fig. 5). The intermediate $Zr_3O_2F_8$ was previously synthesized by Papiernik et al. [18]. At 400 °C the mass increase is only 6%, which is in good correlation with part A of Fig. 1 with XRD confirming the formation of some zirconium tetrafluoride as well as oxyfluorides (Fig. 5). At 500 °C the mass increase is 34% showing trace amounts of the starting material and complete conversion at 525 °C (37%) as confirmed by XRD (Fig. 6). Although Chrétien and Gaudreau [19] observed a significant mass loss of about 3.4% already at 500 °C in one week due to sublimation of ZrF_4 it was not observed by us at 525 °C. The conversion at 525 °C occurs via a double-step mechanism. The formation of zirconium tetrafluoride appeared in multiple phases as confirmed by XRD. At higher temperature (550 °C) the mass increase is only 29%, which could be indicative of two simultaneous reactions, namely product formation and mass loss due to sublimation. Even at this high temperature a very small amount of zirconium oxide and oxyfluorides were observed by XRD (Fig. 6), which could be due to the insufficient reaction time. Papiernik et al. [18] studied the solid state reaction of ZrO_2–ZrF_4 systems. They also found that the intermediates ($Zr(OF)_{3.8}$ and

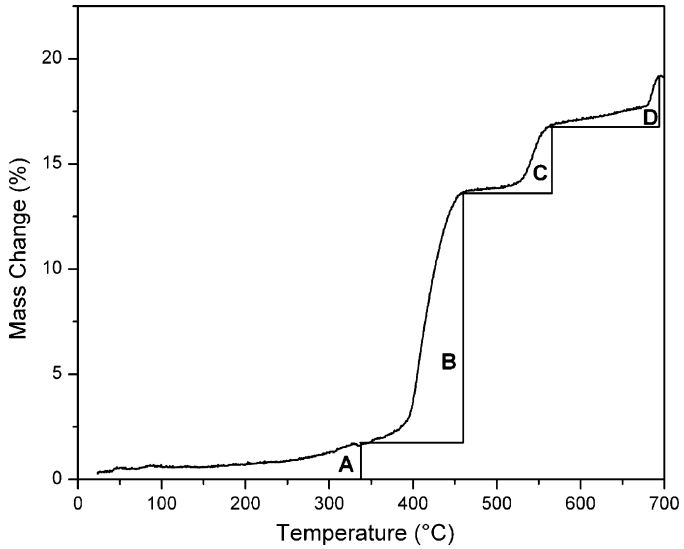

Fig. 2. Thermogravimetric curve of the reaction of HfO_2 in a 10% F_2/N_2 atmosphere at a heating rate of 10 °C/min.

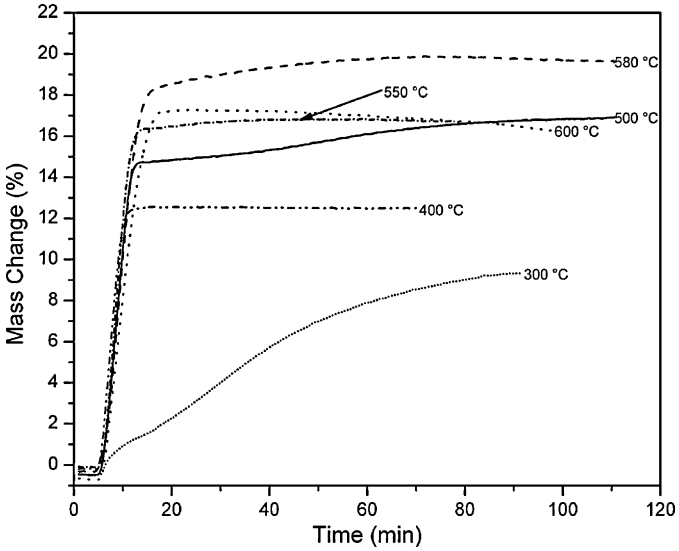

Fig. 4. Thermogravimetric curves of the reactions of HfO_2 with F_2 at isothermal temperatures of 300, 400, 500, 550, 580, and 600 °C.

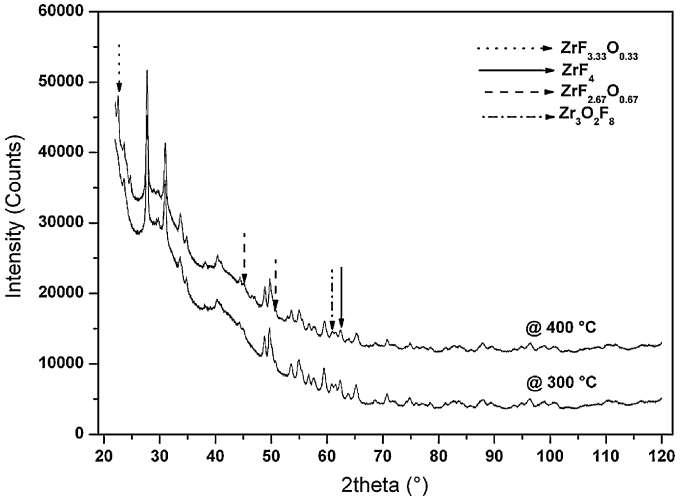

Fig. 5. XRD results of the fluorinated ZrO_2 at 300 and 400 °C, showing the presence of $ZrF_{3.33}O_{0.33}$, $ZrF_{2.67}O_{0.67}$, $Zr_3O_2F_8$ and ZrF_4.

Table 1
Possible zirconium and hafnium oxyfluoride intermediate based on theoretical mass change for complete conversion to indicate species.

$ZrO_2 + F_2$ reactions		$HfO_2 + F_2$ reactions	
Intermediates	Theoretical mass change (%)	Intermediates	Theoretical mass change (%)
$ZrOF_2$	17	$HfOF_2$	10.5
Zr_2OF_6	24.4	Hf_2OF_6	15.7
$Zr_3O_2F_8$	23.8	$Hf_3O_2F_8$	13.9
$Zr_7O_9F_{10}$	12.8	HfF_4	20.9
ZrF_4	35.7		

$Zr(OF)_{2.7}$) occur between 550 and 750 °C. The XRD analyzes of all the isothermal reactions showed that ZrF_4 forms via a plethora of zirconium oxyfluorides, which overlaps with one other.

Haendler et al. [20] cite that the conversion of zirconium oxide to zirconium tetrafluoride is complete at 525 °C, and no reaction occurs at 100 °C which is in accordance with our findings. There is, however, a discrepancy at 400 °C where we have approximately 20% less product than Haendler (6% vs. 29%). This could be attributed to physical factors such as a difference in particle sizes or difference in experimental methods.

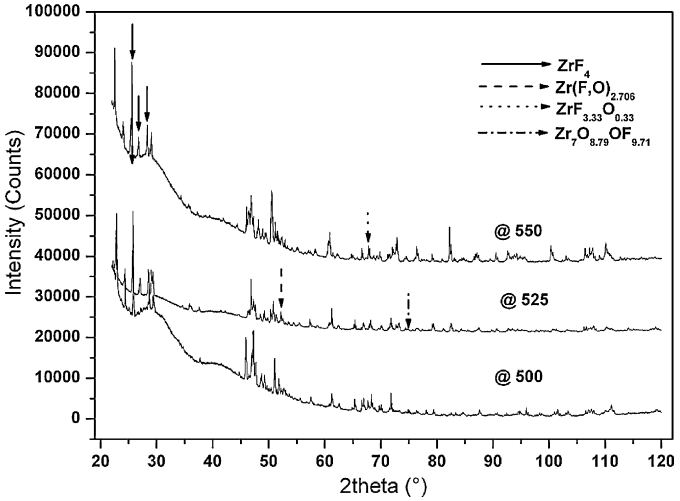

Fig. 6. XRD results of the fluorinated ZrO_2 at 500, 525 and 550 °C, showing the presence of ZrF_4.

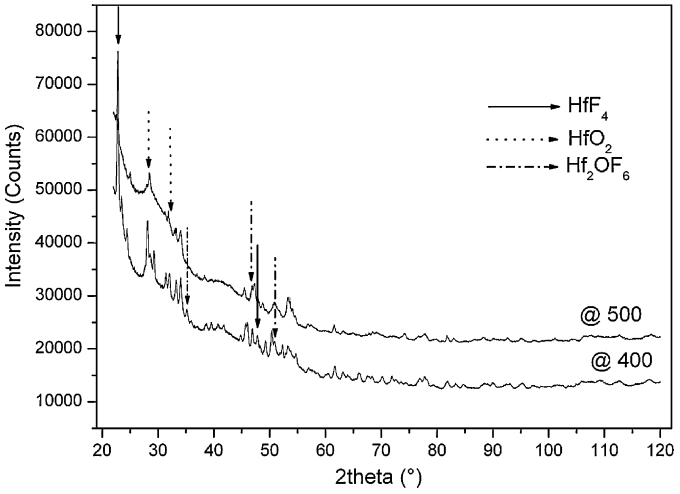

Fig. 7. XRD results of the fluorinated HfO_2 at 400 and 500 °C, showing the presence of HfO_2, Hf_2OF_6 and HfF_4.

Fig. 4 depicts the isothermal reactions of hafnium oxide with fluorine at 300, 400, 500, 550, 580, and 600 °C. The formation of hafnium tetrafluoride probably occurs via oxyfluorides, of which only one hafnium oxyfluoride phase, Hf_2OF_6, could be identified by the XRD database. Hafnium oxide reacts with fluorine at 300 °C with a mass increase of approximately 9%. This could theoretically be ascribed to a proposed hafnium oxyfluoride, $HfOF_2$, which will give a 10.5% mass increase (Table 1). However, the XRD data indicates mainly the starting material. At 400 °C the mass increase was 12% with the XRD (Fig. 7) confirming the formation of hafnium tetrafluoride and the oxyfluoride, Hf_2OF_6. At both 500 and 550 °C the mass increase was 17% illustrating a mixture of hafnium oxyfluoride and hafnium tetrafluoride (major phase), and complete conversion (20%) at 580 °C as confirmed by XRD (Fig. 8), although a very small amount of HfO_2 was still observed by XRD. At 600 °C sublimation has already started to dominate. More work is needed to identify intermediate compounds, possibly with elemental analysis combined with spectroscopy.

The thermogravimetric curves in Fig. 3 (fluorination of ZrO_2) and Fig. 4 (fluorination of HfO_2) have a distinctive shape. With the exception of the lowest temperature in each series, the reaction is initially very rapid, but then levels off or proceeds at a much slower

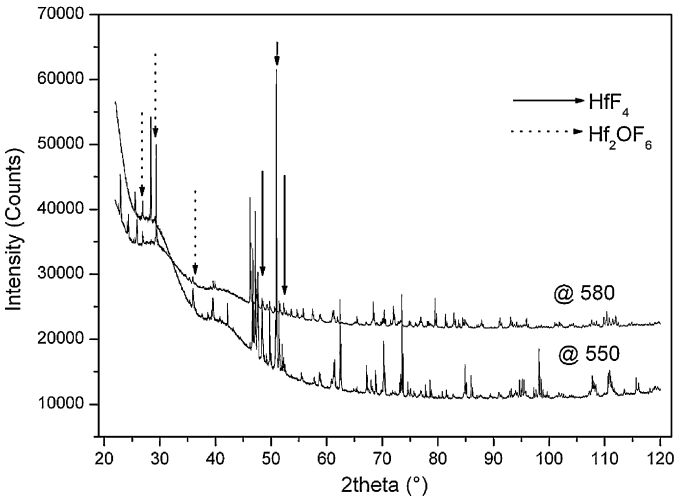

Fig. 8. XRD results of the fluorinated HfO_2 at 550 and 580 °C, showing the presence of Hf_2OF_6 and HfF_4.

rate. The rapid change in mass is often typical of a reaction that is rate controlled by a chemical reaction. This is, in our experience [21], also typical for reactions with fluorine, and usually accompanied with a large reaction enthalpy.

In the cases where the curves level off a stable intermediate is probably formed, whereas in the cases where the reaction proceeds at a much lower rate the logical conclusion is that the reaction mechanism changes, possibly to one that is rate controlled by diffusion through a product layer. Once an intermediate is formed, the reaction of this intermediate to form another intermediate or the final product could have a completely different reaction mechanism. Due to the number of different intermediates that formed it was not possible to do a complete kinetic analysis on the data, but this might be a useful subject for further study.

3. Conclusion

Thermogravimetric investigations were used to illustrate that fluorination of zirconium and hafnium oxides to the respective tetrafluorides can be achieved with fluorine gas at 525 and 580 °C respectively. The formation of ZrF_4 and HfF_4 was confirmed by XRD. The dynamic thermogravimetric runs showed plateaus indicating the possible formation of stable intermediates. Isothermal runs confirmed that stable intermediates are formed, with the mass changes indicating that the specific intermediate formed is dependent on the temperature. XRD confirmed in some cases that the intermediates are oxyfluorides.

At an isothermal temperature of 300 °C, XRD results indicated that zirconium oxide is partially fluorinated, but not hafnium oxide and thus the oxyfluoride (for zirconium) and starting compound (for hafnium) were mainly identified. A mixture of diffraction patterns, possibly due to starting material, oxyfluoro intermediates and the product, were observed from 400 °C upwards for both zirconium and hafnium. At 525 °C (for zirconium) and 580 °C (for hafnium) it is accepted (by considering mass change) that the fluorination reactions are essentially complete, although traces of the oxides and oxyfluorides are still detectable by XRD.

The possibility exists that the difference in the fluorination temperatures for ZrO_2 and HfO_2 can be exploited to effect separation of Zr and Hf. Sublimation of the fluorides can also be used for separation. The next step would be to exploit the volatility of ZrF_4 and HfF_4 at elevated temperature to separate Zr and Hf by sublimation. The high temperatures involved and the closeness of the sublimation temperatures of ZrF_4 and HfF_4 make this a difficult task, and it is the subject of ongoing research.

4. Experimental

4.1. Materials

The metal oxides (ZrO_2 pure) and (HfO_2 98%) were purchased from Sigma–Aldrich. Compounds were used as received without any further purification. Pelchem, the chemical manufacturing division of Necsa, supplied the F_2 (>99.4%).

4.2. Techniques

A commercial thermogravimetric analyzer (Perkin-Elmer TGS2) was used to perform dynamic and isothermal runs. To enable the use of corrosive fluorine gas the thermogravimetric analyzer was modified as described by Rampersard [22].

Dynamic thermogravimetric experiments were conducted by placing the sample (approximately 20 mg) in a nickel sample pan, introducing the reactive gas (10% F_2 in N_2) at the start of the experiment and increasing the temperature at a steady rate (normally 10 °C/min) while the thermogravimetric curve was recorded.

Isothermal thermogravimetric experiments were conducted by placing the sample (approximately 20 mg) in a nickel sample pan, heating it to the desired temperature under nitrogen. Keeping the temperature constant, a mixture of 10% F_2 in N_2 was introduced and allowed to react with the sample while the mass was recorded as a function of time to obtain a thermogravimetric curve.

4.3. X-ray powder diffraction

X-ray diffractometry was employed for chemical phase identification. The measurements were carried out using a BRUKER D8 Advance powder diffractometer. To avoid contamination and hydrolysis, special sealed sample holders were used for the analysis. Loading of the samples into the holders was done in a glovebox filled with dry N_2. The instrument was operated in parallel beam geometry with a Goebel mirror and fixed divergent slit on the primary side. Cu-K_α radiations were used and the diffracted beam was collected using a 1D Lynx eye detector. Analysis of data for phase identification was done with BRUKER's Eva software.

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