Manufacturing of anhydrous zirconium tetrafluoride in a batch reactor from plasma-dissociated zircon and ammonium bifluoride

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Synopsis

Anhydrous zirconium tetrafluoride can be used as a precursor for the manufacturing of nuclear-grade zirconium metal. This can be done by fluorinating plasma-dissociated zircon with ammonium bifluoride in a batch reactor. This paper describes the batch process. It was proved that anhydrous zirconium tetrafluoride can be manufactured by this route as confirmed by X-ray diffraction. The process shows potential for scaling up to the kilogram scale and possibly the tonnage scale.

Keywords
Zirconium tetrafluoride, zircon, plasma-dissociated zircon, PDZ.

Introduction

Anhydrous zirconium tetrafluoride can be used as a precursor for the production of nuclear-grade zirconium metal by reduction of the tetrafluoride with magnesium or calcium metal[1,2]. High-purity zirconium tetrafluoride is also one of the major constituents of the ZBLAN glass (ZrF_4-BaF_2-LaF_3-AlF_3-NaF) which is used in optical fibre applications[3].

Various methods are used for the production of zirconium tetrafluoride, including halogen exchange, where zirconium tetrachloride is reacted with hydrogen fluoride gas at 300°C to produce zirconium tetrafluoride[3–5]. Large quantities of zirconium tetrafluoride can be produced by adding concentrated (40 per cent) hydrofluoric acid to a concentrated (65 per cent) nitric acid solution of zirconium to precipitate zirconium tetrafluoride monohydrate. The precipitated monohydrate is dried and treated with hydrogen fluoride gas at 450°C to form anhydrous zirconium tetrafluoride[5]. Zirconium tetrafluoride can also be produced by hydrofluorination of zirconium dioxide at 25°C followed by sublimation in hydrogen fluoride gas[3] at 825°C. Zirconium dioxide or zirconium tetrachloride can also be reacted with ammonium bifluoride at 200°C to form ammonium heptafluorozirconate [$(NH_4)_3ZrF_7$], which is thermally decomposed to form zirconium tetrafluoride and ammonium fluoride[3,6,7] at approximately 450°C.

The prime objective of this work was to produce zirconium tetrafluoride on a kilogram scale that can be used for subsequent sublimation and plasma reduction to zirconium metal. Zirconium tetrafluoride was prepared in a batch reactor by reacting plasma-dissociated zircon (PDZ, $ZrO_2.SiO_2$) with ammonium bifluoride (NH_4HF_2) according to the method described by Nel *et al.*[8]. It was assumed that zirconium tetrafluoride was produced according to Equations [1] to [4]. Fluorination of PDZ occurs at approximately 180°C (Equation [1]). This is followed by a stepwise thermal decomposition of the ammonium fluorozirconate, at 300°C (Equation [2]), 350°C (Equation [3]), and 400°C (Equation [4])[6].

$$ZrO_2.SiO_2 + 8NH_4HF_2 \rightarrow (NH_4)_3ZrF_7 + (NH_4)_2SiF_6\uparrow + 3NH_4F\uparrow + 4H_2O\uparrow \quad [1]$$

$$(NH_4)_3ZrF_7 \rightarrow (NH_4)_2ZrF_6 + NH_4F\uparrow \quad [2]$$

$$(NH_4)_2ZrF_6 \rightarrow (NH_4)ZrF_5 + NH_4F\uparrow \quad [3]$$

$$(NH_4)ZrF_5 \rightarrow ZrF_4 + NH_4F\uparrow \quad [4]$$

Experimental

The batch reactor is schematically presented in Figure 1. This stainless steel reactor was 200 mm high and had a diameter of 100 mm. The reactor was externally heated by a 2 kW heating element. A thermocouple was used to monitor the internal temperature of the reactor, and the rate of heating and soaking time was electronically controlled. The reactor lid was fitted with a nitrogen inlet to purge the reactor

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Manufacturing of anhydrous zirconium tetrafluoride in a batch reactor

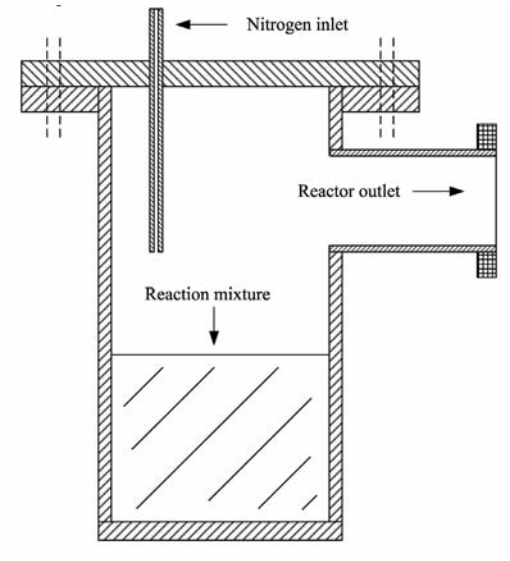

Figure 1—Schematic diagram of the batch reactor that was used for the preparation of ZrF_4

and the downstream system with nitrogen, which would act as a carrier gas for the gaseous reaction products as well as to maintain an inert atmosphere. The nitrogen purge rate was approximately 0.9 kg/h.

The process flow diagram of the system is presented in Figure 2. The off-gases from the reactor were passed through a cold trap, where the gaseous reaction compounds solidified upon contact with the cold surfaces of the trap. The cold trap consisted of a water-cooled coil. The temperature of the water was at room temperature (approximately 18°C). Any fine particles that were carried further downstream, were removed by a cyclone. The off-gas was monitored in-line by Fourier Transform Infrared Spectrometry (FTIR). All the off-gases were further scrubbed by a HF scrubber and KOH scrubber before being released to the atmosphere.

ZrF_4 was prepared batchwise by loading a stoichiometric mixture of PDZ and ammonium bifluoride into the reactor. The PDZ was produced at Necsa and the ammonium bifluoride (purity >99 %) was obtained from Sigma Aldrich. The total mass of the mixture was about 400 g. The lid of the reactor was closed and the system was continuously purged

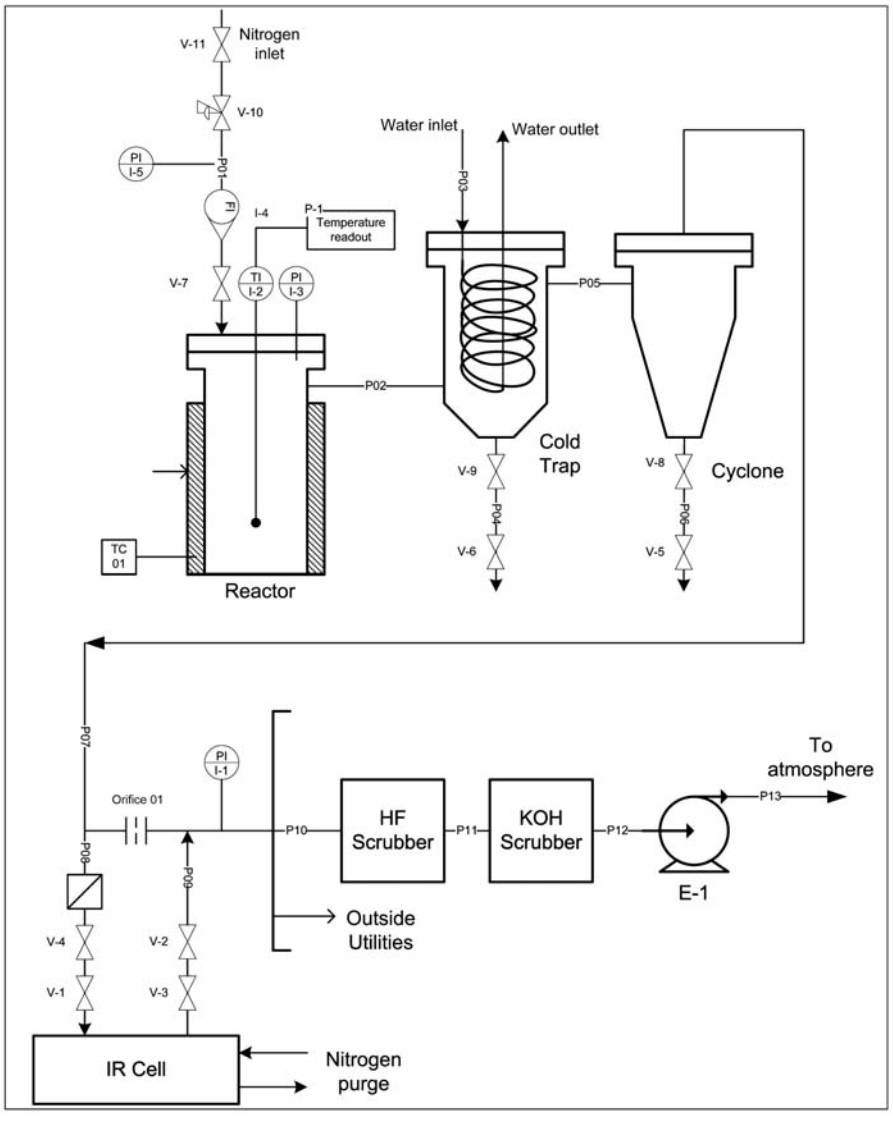

Figure 2—Process flow diagram of the zirconium tetrafluoride manufacturing system

with nitrogen for the full duration of the experiment. The reactor was heated to 150°C and kept at this temperature for 30 minutes. It was then heated to 280°C and kept there for 30 minutes. The temperature was then increased to 380°C and kept there for 30 minutes. These temperature steps correspond more or less to the temperatures of the reactions in Equations [1] – [4]. After the experiment, the reactor cooled to room temperature and was opened. The product was collected from the bottom of the reactor. The cold trap was also opened and a white fluffy type of product was collected from the cold finger and the cyclone. The product from the reactor and the cold trap were analysed by X-ray diffraction (XRD). No attempt was made to do an accurate mass balance or to analyse the product for impurities. This will be the purpose of further optimization experiments.

Results and discussions

Qualitative analysis of the off-gas during the experiment by FTIR showed that hydrogen fluoride gas and ammonia were detected. A typical FTIR spectrum of the off-gas is presented in Figure 3. The spectrum clearly indicates the presence of hydrogen fluoride and ammonia, which are formed by the thermal decomposition of ammonium fluoride according to Equation [5]:

$$NH_4F \rightarrow NH_3 \uparrow + HF \uparrow \quad [5]$$

XRD analysis of the product that was collected at the bottom of the reactor showed that the reaction product was indeed anhydrous zirconium tetrafluoride, as expected (Figure 4). The white fluffy product collected from the cold finger was identified by XRD as a mixture of NH_4F (Figure 5) and $(NH_4)_2SiF_6.NH_4F$ (Figure 6).

Conclusion

Anhydrous zirconium tetrafluoride can be manufactured successfully in a batch reactor from a mixture of plasma-dissociated zircon and ammonium bifluoride. This was achieved on a scale of several hundred grams, and the

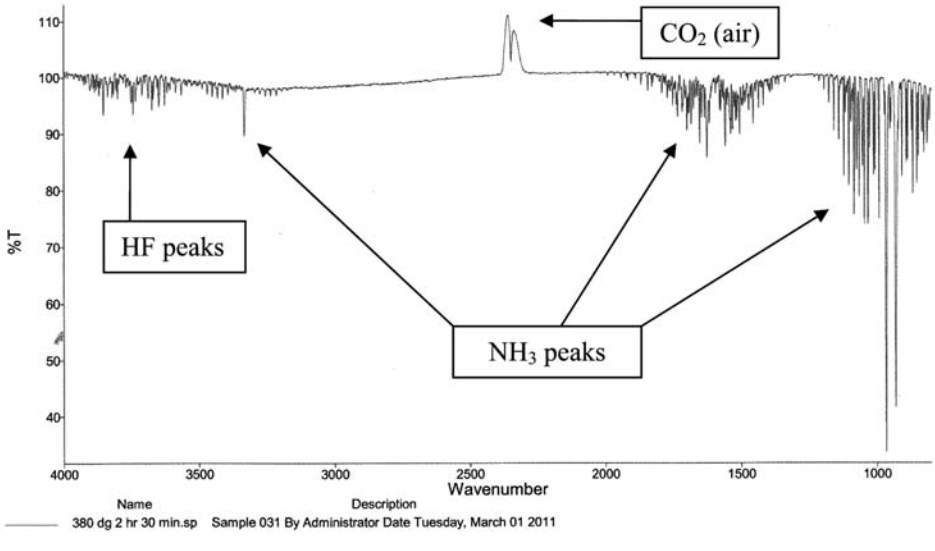

Figure 3—FTIR spectrum of the off-gas

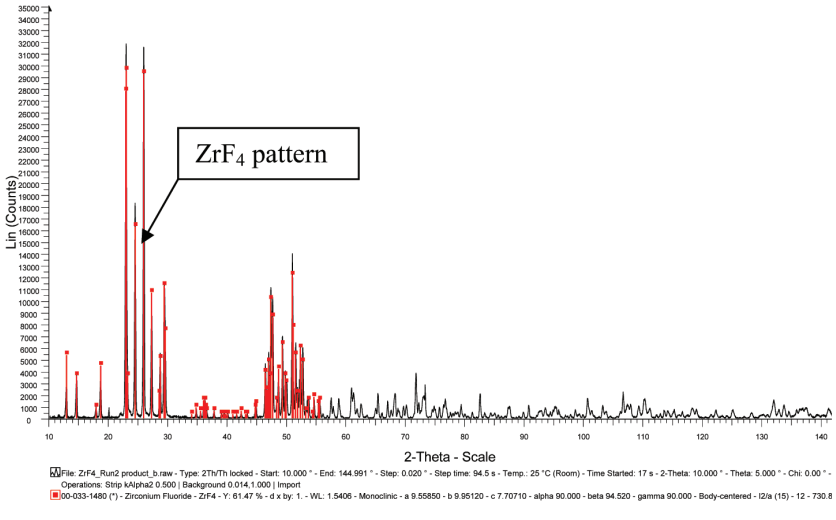

Figure 4—XRD powder diffraction pattern of the reactor product overlaid with ZrF_4 pattern from the database

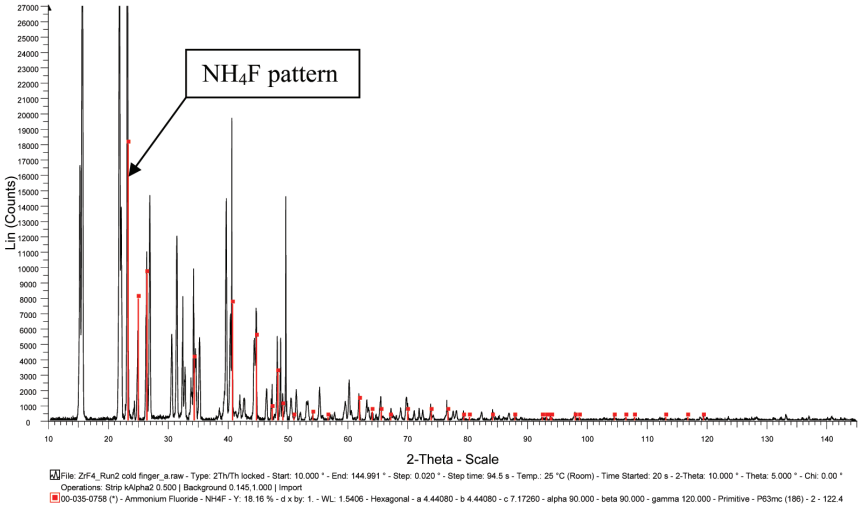

Figure 5—XRD powder diffraction pattern of cold trap product overlaid with NH_4F pattern from the database

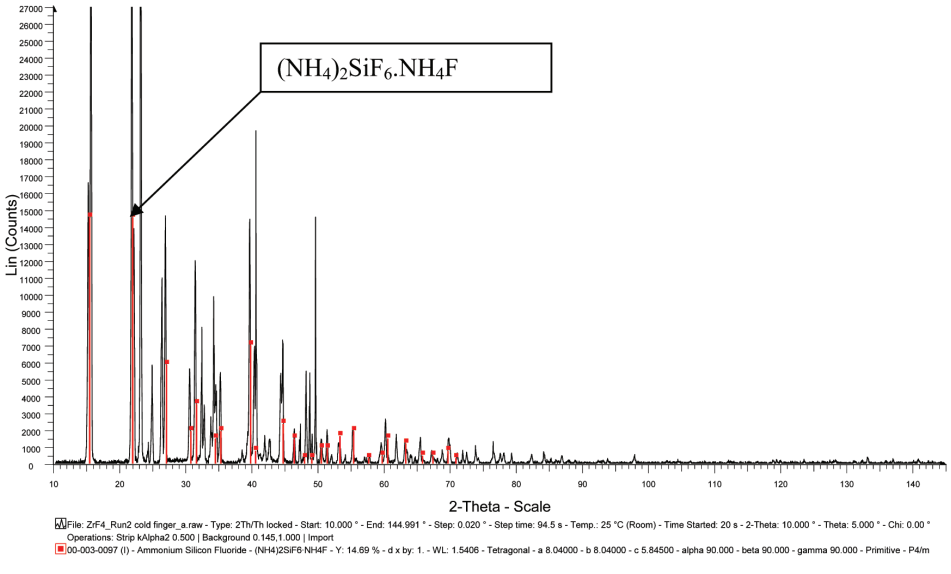

Figure 6—XRD powder diffraction pattern of product overlaid with $(NH_4)_2SiF_6.NH_4F$ pattern from the database

process promises to be scalable to several kilograms or maybe even to tonnage scale. Several optimization experiments are planned for the future, including an accurate mass balance, the yield of the reaction, energy consumption, and purity of the reaction product.

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