

# Synthesis of micro-dispersed zirconium oxide for glass manufacturing

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**Abstract.** A rather simple and original method for processing of zirconium-containing raw material from Algoma deposit (Khabarovsk region, Russia) was suggested, which comprised fluorination of the initial sample with a diluted HF solution followed by the thermal treatment of fluorination products and pyrohydrolysis of zirconium tetrafluoride. Water vapors obtained by hydrogen and oxygen burning in a hydrogen torch as well as by simple evaporation were used for pyrohydrolysis. The feed rate of the water and its temperature were regulated. The temperature of water vapors reached 800–1200 °C. Zirconium dioxide with a purity of 99.97 % or more and a dispersity of 0.1 µm or less was synthesized.

## 1. Introduction

Zirconium dioxide exhibiting a number of important physicochemical properties such as optical, dielectric, high thermal (melting point is above 2700°C) and mechanical stability, chemical inertness is widely used in practice. It is used in glass manufacturing, constructive ceramic materials, fuel cells, catalyst systems, oxygen sensors, as well as in various areas of microelectronics. Optical properties of fianite single crystals based on zirconium dioxide are close to those of diamond. Recently, zirconium dioxide is widely used in prosthetic dentistry and cosmetology.

Zirconia, which is used in the modern technology, must have a high purity (at least 99.99 %) and dispersity (less 0.1 µm). Conventional methods of zirconium dioxide production from chloride, nitrate and oxalate zirconium solutions comprise the precipitation of its basic salts followed by their one-stage calcination [1]. A technology of alkaline sintering of zircon is based on the process of fusing zirconium-containing raw materials with NaOH and Na<sub>2</sub>CO<sub>3</sub> at 450–1050°C with subsequent treatment with water [2].

We use fluoride methods for the ZrO<sub>2</sub> production when the zirconium-containing raw material is processed with hydrofluoric acid and ammonium fluorides.

The HF using for zirconium dioxide obtaining was suggested in [3]. It comprised the treatment of zirconium-containing raw material with hydrofluoric acid, aqueous leaching of the reaction products, pulp filtration, neutralization by ammonia with simultaneous precipitation of zirconium hydroxide, separation of the precipitate and its treatment by the reagent with obtaining zirconium-containing solution, evaporation of solution, purification from impurities, and calcination of zirconium-containing

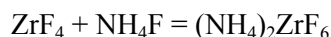


precipitate, characterized in that the zirconium-containing raw material was treated by hydrofluoric acid and ammonium fluoride in molar ratio 1-4: 3 per 1 mole of zirconium dioxide and solid ammonium bicarbonate was used as a reagent in an amount of 2.8–3.2 mol per 1 mole of zirconium dioxide. Separation of zirconium from impurities proceeded before evaporation by their successive deposition with the retention of zirconium in solution.

Ammonium hydrogen difluoride ( $\text{NH}_4\text{HF}_2$ ) was used for processing of zirconium concentrate consisted of a mixture of baddeleyite, zircon and quartz with the impurity of kaolin  $\text{Al}_2[\text{OH}]_4[\text{Si}_2\text{O}_5]$  and contained in mass. %:  $\text{ZrO}_2$  33–53;  $\text{SiO}_2$  40–50;  $\text{Al}_2\text{O}_3$  0.4–0.6; Fe 0.2–0.4. The method comprised fluorination with  $\text{NH}_4\text{HF}_2$  at 50–190°C for 3–72 h followed by heating of fluorination product at 330–650°C without the oxygen access for 0.5–3 h with simultaneous condensation of ammonium hexafluorosilicate at 230–270°C and ammonium fluoride at 25–150°C. The latter was returned to the fluorination stage. Desiliconized product was heated in inert atmosphere at 900–1100°C for 4–5 h followed by condensation of zirconium tetrafluoride at 250–850°C and its pyrohydrolysis at 900–920°C for 0.5–1 h with the formation of zirconium dioxide [4].

## 2. Experimental section

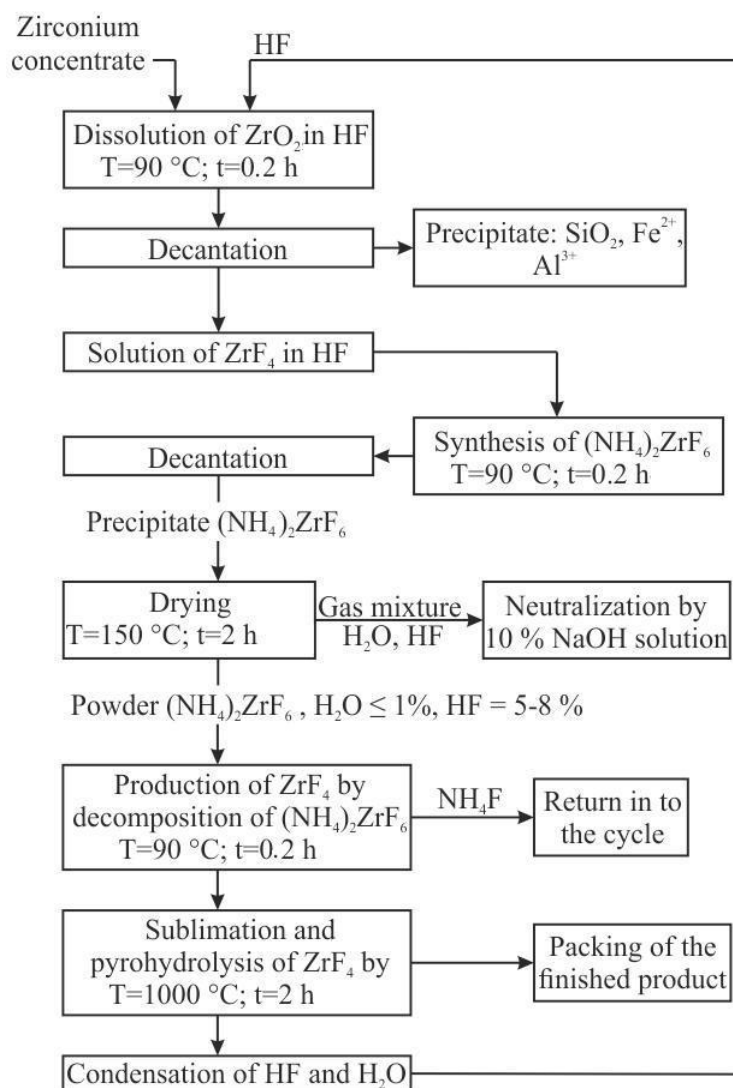
We suggested using the 10–20 % hydrofluoric acid solution for recovering of zirconium-containing raw material. There is no need to raise its concentration as the reaction proceeds exothermally with the isolation of a large heat amount. It is interesting that the quartz dissolution is not observed when a weak hydrofluoric acid solution is used (the dissolution degree is not more than 3% from the initial quantity of  $\text{SiO}_2$ ). The  $\text{SiO}_2$  precipitate is removed, and ammonia is added to the solution to separate the iron ions, which occurs at a pH higher than 5. Small excess of ammonium fluoride is needed relative to the reaction stoichiometry:



Ammonium hexafluorozirconate isolates together with a small amount of ammonium hexafluorosilicate. The precipitate is separated, dried and subjected to thermal decomposition at 600–650 °C with the formation of zirconium tetrafluoride and ammonium fluoride. Ammonium fluoride is distilled off in a condenser and recycled. The scheme of micro-dispersed  $\text{ZrO}_2$  synthesis is presented in figure 1.

Zirconium concentrate was presented by the Algoma deposit (Khabarovsk region), containing zirconium in the form of amorphous and fine-dispersive gel zircon. It contained in mass. %:  $\text{ZrO}_2$  52.1;  $\text{SiO}_2$  45.3; Fe 0.16; Al 0.45; W 1.88; Hf 0.95, and impurities Mn 0.5; Cs 0.005; Nb 0.04; Ba 0.028 and Pb, Sb, Sn, Sr 0.001–0.005. 200 g of the initial material were placed into glass-graphite vessel (1000 ml) and 450 ml of 20 % hydrofluoric acid were added. Exothermal reaction proceeded with a slight (40 °C) temperature rise of the solution. The solution was separated from the precipitate by filtration or decantation. Silicon dioxide, some amounts of iron, aluminum and tungsten remained in the precipitate. Zirconium and hafnium dioxides were dissolved quantitatively. Silicon dioxide was insignificantly dissolved (below 3 %). Concentration of the other impurities was 1–2 times lower than in the initial material. Their total content did not exceed 0.1%.

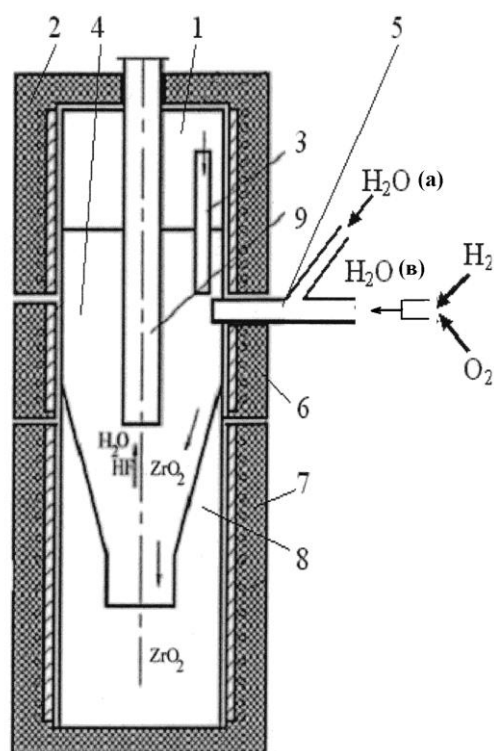
70 g of ammonium fluoride were added to the solution in the second stage. There was a release of a precipitate which was separated from the solution by decantation and dried. As a result, 216 g of the product were obtained, which means virtually full dissolution of zirconium dioxide. All taken  $\text{NH}_4\text{F}$  were spent virtually on the formation of  $(\text{NH}_4)_2\text{ZrF}_6$ , and only its part on the dissolved silica.



**Figure 2.** Scheme of micro-dispersed  $\text{ZrO}_2$  synthesis

Powdery product was lilac-pink and consisted of  $(\text{NH}_4)_3\text{ZrF}_7$ ,  $(\text{NH}_4)_3\text{SiF}_7$  and  $(\text{NH}_4)_2\text{SiF}_6$  mixture in accordance with the XRD data. 120 g of the product were heated to 650 °C in a glass-graphite reactor until complete removal of  $(\text{NH}_4)_2\text{SiF}_6$  and  $\text{NH}_4\text{F}$ . The residue mass after 1 h of heating was 36.5 g containing 0.2 % of silicon.

Ammonium fluoride (72.5 g) was condensed at 150 °C and returned in to the cycle. The residue was gray. It consisted of  $\text{ZrF}_4$  (98–99 %) and Al, Fe, Hf, Mn, Pb fluoride impurities (1–2 %). This product was placed into a nickel evaporator for  $\text{ZrF}_4$  sublimation. Isolated zirconium tetrafluoride was pyrohydrolyzed in a special device, the scheme of which is given in figure 2.



**Figure 2.** Device for pyrohydrolysis of  $\text{ZrF}_4$ .

- 1— vessel for solid  $\text{ZrF}_4$ ,
- 2— furnace 1,  $T=900-950^\circ\text{C}$ ,
- 3— pipe for  $\text{ZrF}_4$  vapors,
- 4— reactor,
- 5— pipes for introduction of water vapors,
- 6— furnace 2,
- 7— furnace 3,
- 8— vessel for storage of  $\text{ZrO}_2$ ,
- 9— pipe for removing of HF and  $\text{H}_2\text{O}$  vapors.

Conventional water vapors (a) and water vapors obtained from hydrogen burning in oxygen (b) heated to  $800-1200^\circ\text{C}$  came in to the reactor 4 through the connecting pipes 5. Temperature of water vapors was regulated by hydrogen burning rate and by the  $\text{H}_2\text{O(a)}:\text{H}_2\text{O(b)}$  ratio. Reactor was heated to  $900-950^\circ\text{C}$ . During pyrohydrolysis, HF was formed, which came through the pipe 9 in to the apparatus for its trapping and regeneration. The obtained  $\text{ZrO}_2$  was gathered in the vessel 8 for their storage. Powder of zirconium dioxide with the particle diameter less than  $0,1\ \mu\text{m}$  ( $100\ \text{nm}$ ) was produced. Its purity was 99.97 % and the yield was 89.4 %.

### 3. Conclusion

Using natural zirconium-containing raw material of Algoma deposit (Khabarovsk region, Russia) consisting mainly from amorphous fine-dispersive gel zircon enabled to propose the fluoride method (including dilute solutions of HF and ammonium fluorides) for production of micro-dispersed high purity zirconium dioxide. It provides decreasing number of the stages and operating time and increasing of processing efficiency of raw material.

### Acknowledgments

This work was supported by the Ministry of Education and Sciences of the Russian Federation, Agreement # 14.578.21.0024, RFMEFI57814X0024.

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