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MASTER

ZIRCALOY PICKLE BATH SALTS.
Chemical Nature and Thermal Decomposition of Hydrated Zirconium Fluoride

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The pickling of Zircaloy with 3.8 v/o HF - 39 v/o HNO_3 is a standard practice in the nuclear materials industry. This treatment provides an economical method for the preparation of lustrous Zircaloy surfaces before a passive black oxide film is applied by autoclaving the specimen in high temperature water and in steam. Although machined surfaces have also given acceptable black oxide corrosion films after autoclaving, this type of surface preparation is somewhat expensive. Furthermore, the pickling procedure can be applied to recessed surfaces which are otherwise inaccessible by machining techniques.

In spite of the apparent advantages of pickling vs. machining, there are still some disadvantages. One of these is the possibility of retaining residual etchant fluoride which produces white corrosion product during autoclaving. Any Zircaloy parts which produce a white surface oxide after autoclaving are rejected for further reactor application; the surface is then reworked until a satisfactory black oxide film is obtained. However, it has been shown (5) that acceptable corrosion specimens, with no traces of white oxide, still contain finite amounts of fluoride in the surface film.

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* Operated by the General Electric Company for the United States Atomic Energy Commission.

DISCLAIMER

In 1956 approximately 500 grams of white crystals were found in the bottom of a spent HF-HNO_3 solution which had been used to etch wrought pieces of Zircaloy prior to autoclaving testing in high temperature water and in steam. The crystals were characterized tentatively as a hydrated zirconium fluoride, but remained a laboratory curiosity. It is now believed that the traces of fluoride in the black oxide corrosion films and the macro amounts of fluoride in the spent pickle-bath crystals have a common genesis. Furthermore, it is believed that the fluoride found on the surfaces of the pickled, pre-autoclaved, Zircaloy is also complexed as an insoluble hydrated zirconium fluoride which decomposes only partially during autoclaving. As a result, the black oxide film still contains significant concentrations of fluoride.

In the case of Zircaloy clad nuclear fuel, it is postulated that the oxyfluoride in the black film on the fuel element in-pile would undergo further thermal decomposition as presented in the following discussion and in Table 3, Equation 4. The release of fluoride in the localized areas of the in-pile Zircaloy could cause a propagation-type hydrolysis of zirconium forming a white oxide. This effect could threaten the longevity of the reactor core.

Ideally, the thermal decomposition behavior of the fluoride in the in-situ black oxide corrosion films would more nearly approximate the actual changes which occur in-pile (except for any radiation damage). However, the zirconium fluoride in the black oxide constitutes a micro portion of the ~ $10^4 A^o$ corrosion film. As such, any changes due to the thermal decomposition of the fluoride complex, would be "swamped out" by the decomposition behavior of the larger mass of the black oxide film. Fortuitously, the macro amounts of the zirconium tetrafluoride trihydrate crystals found in the etchant solution provided ample material to study the possible mode of in-pile thermal decomposition using the Chevernard photo-recording thermobalance.

The existence and preparation of hydrated fluorides of zirconium have been reported previously. Haendler (1) reviewed the work of Chauvenet (2), of Prideaux and Roper (3) and of Von Hevesy and Wagner (4) in connection with these salts. Chauvenet (8) prepared $ZrF_4 \cdot 3H_2O$ (also written as $ZrOF_2 \cdot 2HF \cdot 2H_2O$) by evaporating a solution of $Zr(OH)_4$ in H_2F_2 to crystallization, and then by air-drying the residue. The crystals were stable in air, and even in vacuo. The crystals began to lose water at 100°C, and at 140°C $ZrOF_2 \cdot 2HF$ (or $ZrF_4 \cdot H_2O$) was formed. Above 140°, HF was evolved and the neutral fluoride ($ZrOF_2$) was obtained. Later on Haendler (1) also demonstrated that a fluoride of zirconium corresponding to $ZrF_4 \cdot 3H_2O$ could be prepared by repeatedly evaporating a solution of hydrofluoric acid until hydrolysis products began to precipitate.* The crystals were filtered, washed with ethanol and acetone, and then air dried. The crystals showed no weight loss after exposure to the laboratory atmosphere for one month. Haendler then determined the weight loss at 110°C, and reported that no HF vapor was evolved, but that a monohydrate was formed. Heating the sample at a higher, unspecified, temperature gave off HF

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* More recently Buslaev, Gorbunova, and Gustyokova similarly prepared $ZrF_4 \cdot 3H_2O$ as a starting material for $ZrF_{2.5}(OH)_{1.5}$ 0.75 H_2O.

and water. The formula of the final product of decomposition was not reported.

In summary, Chauvenet (2,8) and Haendler (1) agreed that between 110 and 140°, $ZrF_4 \cdot 3H_2O$ decomposed to $ZrF_4 \cdot H_2O$. On the other hand, they disagreed on the decomposition products which were formed by heating the monohydrate to higher temperatures. Their descriptive reactions are summarized as follows:

Chauvenet:

$$ZrF_4 \cdot 3H_2O \xrightarrow{110-140^\circ} ZrF_4 \cdot H_2O + 2H_2O \xrightarrow{>140^\circ} ZrOF_2 + 2HF$$

Haendler:

$$ZrF_4 \cdot 3H_2O \xrightarrow{110^\circ} ZrF_4 \cdot H_2O + 2H_2O \xrightarrow{>110^\circ} ZrO_xF_y + HF + H_2O$$

The work reported in this paper verifies the thermal decomposition of $ZrF_4 \cdot 3H_2O$ in air, between 100 and 200°C, to $ZrF_4 \cdot H_2O$. However, new information is presented on the thermal decomposition of the monohydrate. For the first time, a graphic picture of the mode of thermolysis is given and suggests that a transient product, $Zr_2(OH)F_7$, is formed at 310-345°C. Above 845°C the final decomposition product of $ZrF_4 \cdot 3H_2O$ is ZrO_2.

X-ray diffraction patterns confirmed the identity of the trihydrate, the monohydrate, and of the zirconium oxide.

The "d" spacings for the newly identified compound, $Zr_2(OH)F_7$, are also given.

Experimental

The crystals obtained from the bottom of our $HF-HNO_3$ etch solution, were insoluble in hot and cold water, in hot conc. HCl,

HNO_3, and H_2SO_4. The crystals finally dissolved by prolonged heating in conc. sulfuric acid. After repeated fuming with H_2SO_4 to expel fluoride, the solution was diluted and ammonia was added to precipitate the zirconium. The precipitate was then ignited to ZrO_2 and weighed.

A separate sample of crystals was ground in a mortar and pestle to pass through a 40 mesh sieve. To analyze for fluorine, this sample was reacted with steam in a monel tube at 1000°C and the HF in condensate was titrated with standard alkali (6). The water in the sample was estimated by totaling the zirconium and fluorine and then subtracting from 100%. A spectrographic analysis was also made for the alloying and impurity constituents. Nitrogen in the salt was determined by the Kjeldahl method used for Zircaloy alloys. The complete analysis of the material is given in Table 1. The data indicate that the crystals are composed of zirconium, fluorine, and water in the following molar ratios, $Zr/4F/3H_2O$, with only traces of the alloying or other elements. The high purity of the hydrated zirconium tetrafluoride indicates that the crystal formation was selective and was initiated by exceeding the solubility product of the zirconium fluoride complex, rather than by causing a general crystallization of all elements through a concentration effect.

Two separate thermolysis curves were obtained at 4 month intervals for the <40 mesh material using a photographic-type Chevernard thermobalance. These thermolysis curves (Fig. 1 and 2) demonstrate the excellent reproduceability obtained and give a graphic picture of the mode of thermal decomposition of zirconium tetrafluoride trihydrate.

Table 1. Material Balance. $ZrF_4 \cdot 3H_2O$ Found in Depleted HF-HNO_3 Solution Used for Etching Zircaloy

Element	Theor.	Found			
	w/o	w/o		mol %	mol fraction
Zr	41.23	41.3[a], 40.7[b]		0.449 ± 0.007	1.00
F	34.35	33.29[c], 33.87[c]		1.767 ± 0.015	4.03
H_2O	24.41	25.50 ± 0.6[d]		1.417 ± 0.05	3.16
Spectrographic[e] and impurity analysis	-	Sn-20 ppm	Mo-<5 ppm		
		Al-35	Ni-45		
	-	Cr-15	Si-<15		
		Co-<2	Ti-<20		
	-	Cu-30	W-<20		
		Hf-93	N-<20		
	-	Fe-120			

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[a] The sample was dissolved in hot H_2SO_4, and fumed to remove HF. Zr was precipitated with NH_4OH, ignited to ZrO_2 and weighed.

[b] The sample was ignited in air at 1000°C to ZrO_2. The ZrO_2 was confirmed by X-ray diffraction.

[c] The sample was pyrohydrolyzed at 800°C. The HF in the condensate was titrated with standard NaOH (6).

[d] Water was estimated by difference.

[e] Performed by D.A. DelGrosso. The nitrogen analysis was performed by Mrs. L.K. Lolos.

To interpret the thermolysis curves, start at the top left-hand portion of the photograph. At the outset, the vertical distance on the photograph was calibrated by placing a 200 mg weight on the balance. The weight was then removed, and the furnace was turned on to obtain an automatic heating rate of $5.0 \pm 0.1^{\circ}C$/minute. The heating rate was continued, in one case to 105° (Fig. 1) and in the other case (Fig. 2) to $130^{\circ}C$. These temperatures were kept constant for 2.5 hrs., at which time the automatic heating rate was resumed and maintained uninterruptedly. With the programmed heating in operation, each vertical division on the thermolysis curve represents a 5° increase in temperature. The thermolysis curve is made on photosensitive paper which rotates on a steel drum. Therefore, the termination of the curve at the right hand edge is contiguous with the curve located at the opposite edge of the picture.

The thermolysis curve indicates that zirconium tetrafluoride trihydrate undergoes thermal decomposition in 3 steps between room temperature and $845^{\circ}C$. The final thermolysis product was identified by x-ray diffraction to be ZrO_2.

To identify the intermediate products, an attempt was made to determine the weight changes between the various plateaus, and to compare the loss-in-weight with the stochiometric evolution of volatile materials. However, because fluorine, oxygen, and water have approximately the same masses, the weight changes gave a somewhat ambiguous picture of the several possible modes of decomposition. Therefore, it was necessary to perform fluoride analyses on the intermediates as well as on the original and final product. The initial decomposition product, $ZrF_4 \cdot H_2O$, was stable over a broad temperature range (90-215°C). The fluoride analysis was performed on material dried at 110°C for 3 hrs. However, the transient product $Zr_2(OH)F_7$ was stable over a very narrow temperature range. Therefore, the thermolysis of $ZrF_4 \cdot 3H_2O$ was performed using a Chevernard pen-recording thermobalance, and the heating of the sample was stopped when the thermolysis curve indicated a slight plateau at 310-345°C. Again, a fluoride analysis was made on this material.

Using the change-in-weight data and the fluoride data (Table 2) it was possible to reconstruct the most probable mode of thermolysis (Table 3).

X-ray diffraction analysis confirmed the identity of the trihydrate, the monohydrate, and zirconium oxide all in a highly purified state. The x-ray pattern of the material heated to 310-345°C also indicated that this zirconium salt was a mixture of $ZrF_4 \cdot H_2O$ plus some compound other than ZrO_2. The "d" spacings have not been previously reported and are listed as follows:

100% intensity - 6.4, 4.0, 3.3 - These lines are common to pure $ZrF_4 \cdot H_2O$

80% " - 5.8)
50% " - 3.7) new, unidentified, lines
30% " - 4.4)

Table 2. Quantitative Weight Changes in the Thermal Decomposition in Air of $ZrF_4 \cdot 3H_2O$

t	Δ w/o*				Fluoride Content of Residue
°C	10/1/56	10/10/57	10/6/62	Avg.	w/o
20-90	0	0	0	0	33.29 33.87
90-215	16.5	16.7	16.4	16.5	39.26
215-310	9.35	9.48	9.65	9.49	39.80
310-845	19.0	19.3	-**	19.2	0.0224

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* The percent change-in-weight is based on the weight of the starting material.

** This data was not obtained because the thermolysis was interrupted at 310-345°C so that the fluoride content of the transient product could be determined.

Table 3. Probable Chemical Changes in the Thermal Decomposition in Air of Zirconium Tetrafluoride Trihydrate

		Δ w/o		F in Residue	
		Exp.	Theor.	Exp.	Theor.
Eq. 1	$2ZrF_4 \cdot 3H_2O \xrightarrow{20-105^{\circ}C} 2ZrF_4 \cdot 3H_2O$	0.00	0.00	33.3 33.9	34.4
Eq. 2	$2ZrF_4 \cdot 3H_2O \xrightarrow{105-200} 2ZrF_4 \cdot H_2O + 4H_2O \uparrow$	16.6	16.3	39.26	41.0
Eq. 3	$2ZrF_4 \cdot H_2O \xrightarrow{200-345} Zr_2(OH)F_7 + HF \uparrow + H_2O \uparrow$	9.5	8.6	39.8	40.1
Eq. 4	$Zr_2(OH)F_7 + 3O_2 \xrightarrow{345-845} 2ZrO_2 + 3OF_2 \uparrow + HF \uparrow$	19.2	19.5	0.022	0.000

Discussion

The equations for the probable mode of thermal decomposition of $ZrF_4 \cdot 3H_2O$ in air have been developed from a knowledge of the gravimetric changes and from the fluoride content of the thermolysis residues. Direct identification or confirmation of the off-gas products is lacking. There is little doubt that the volatiles up to 200°C (eq. 1 and 2, Table 3) are mostly water. This was demonstrated by Haendler (1) who noted no HF vapors on heating to 110°C. On the other hand, we have identified acid vapors using a wet litmus paper test, but believe that these are only trace quantities of HF + HNO_3 left on the unwashed surfaces of the crystals. The quantitative estimation of volatile fluorine at the various temperatures of interest is possible by pyrolysis in air using the apparatus of Warf et al (6). However, the molecular configuration of the evolved fluorine is difficult to determine. The fluorine can come off as HF, HF-H_2O, or possibly oxygen-fluoride compounds.

Equations 1 through 3 represent the thermal decomposition which would take place in vacuum as well as in air. However, equation 4 demonstrates the oxidation type decomposition which is necessary for the complete liberation of fluorine and the formation of ZrO_2. The existence of oxygen-fluorine compounds O_2F_2 and OF_2 have been previously reported (9). However, it may be difficult to demonstrate the presence of oxy-fluorine compounds here because of the highly reactive nature of gases with the container walls and with the mass spectrometer tubes.

After completion of this investigation and the writing of this text, the work of the Russian scientists, Buslaev, et al (7), came to our attention. These workers concurred in our observations that a transition product is formed at 345°C by the thermal decomposition of $ZrF_4 \cdot 3H_2O$. However, they identified their product as $Zr_4F_{14}O$ or $Zr_2O_{0.25}F_7$.

References

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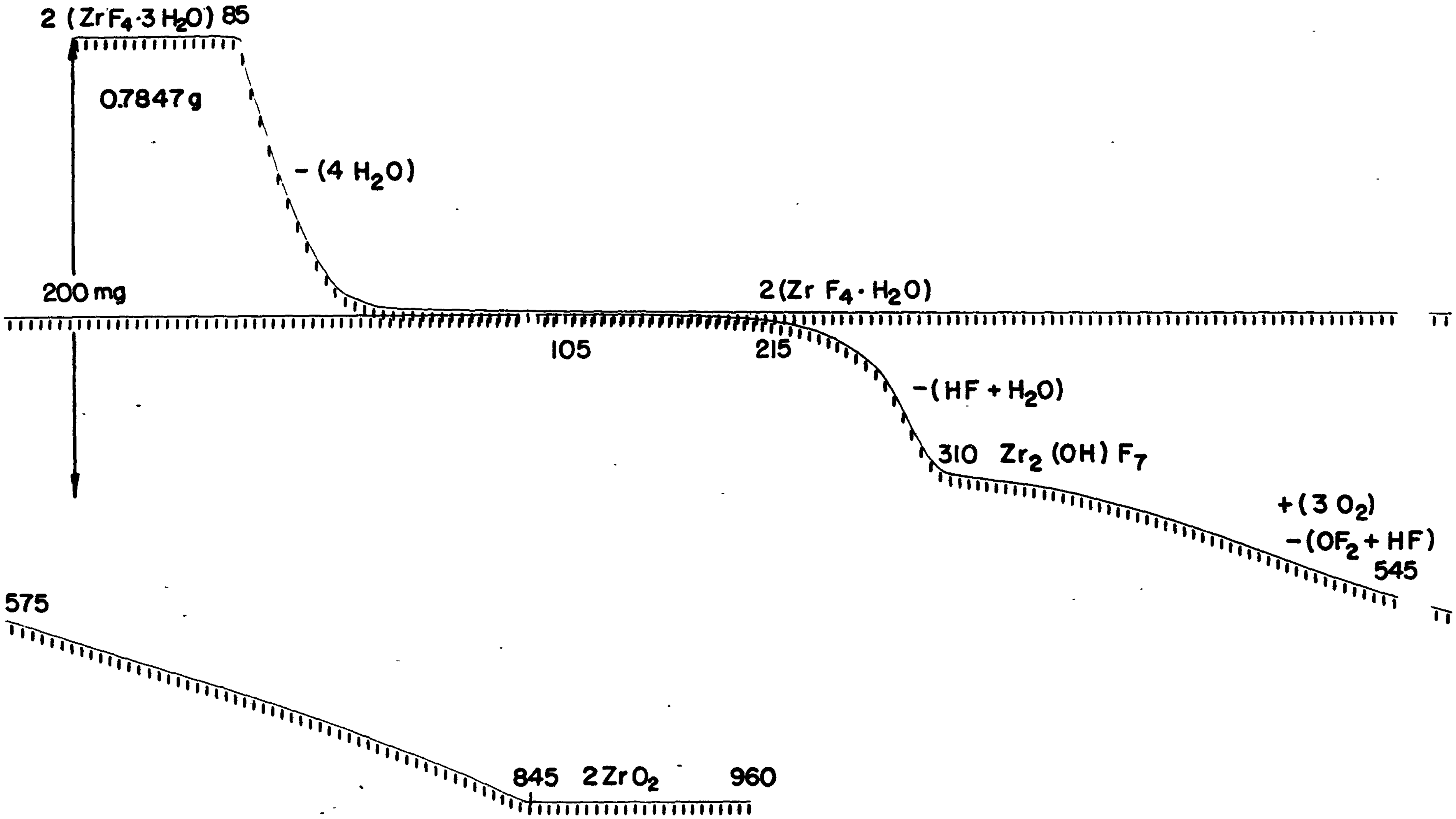

Fig. 1. Photograph - Thermolysis of Zirconium Tetrafluoride Trihydrate in Air.
Chevernard Photographing Thermobalance

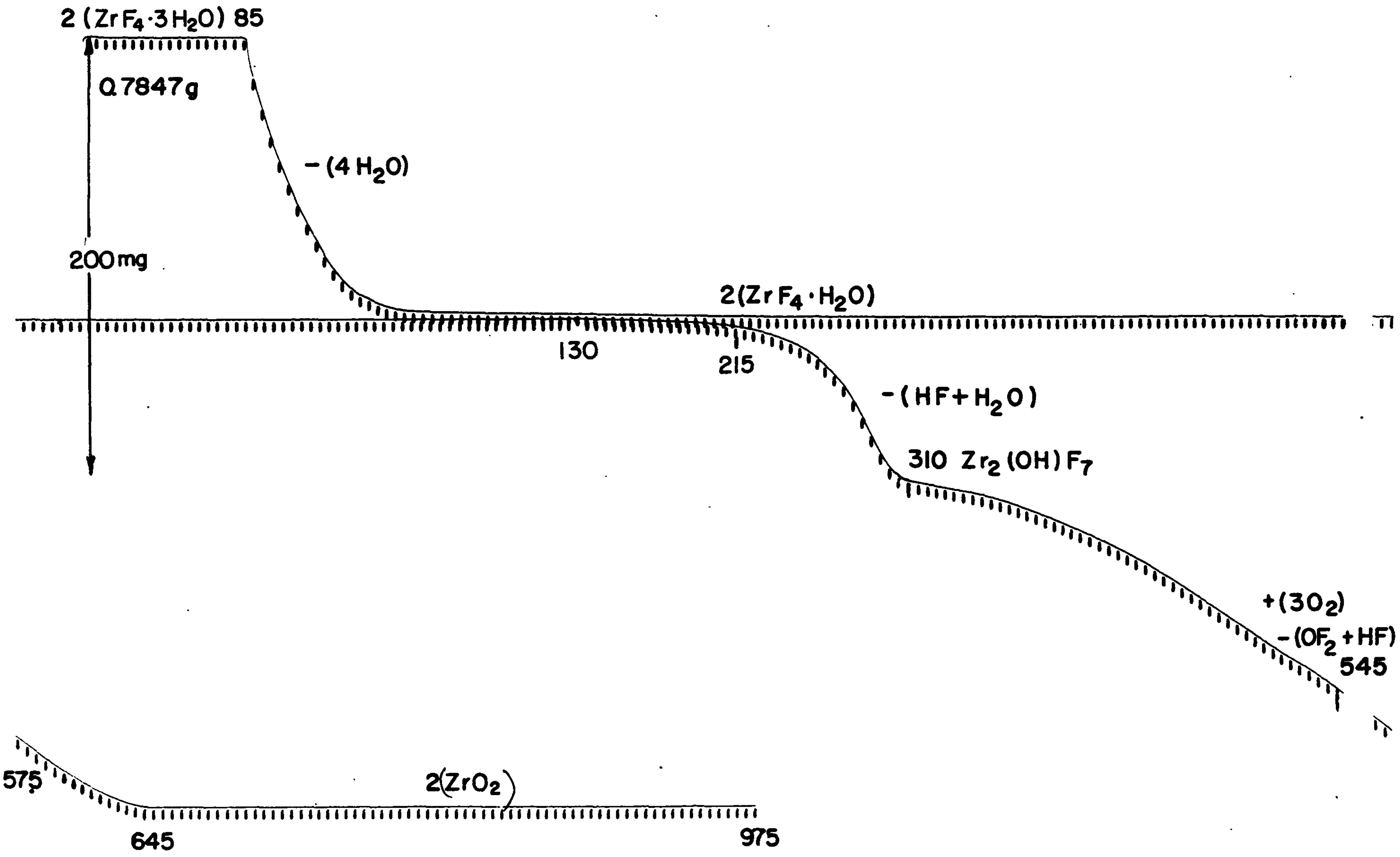

Fig. 2 - Photograph - Thermolysis of Zirconium Tetrafluoride Trihydrate in Air.
Chevernard Photographing Thermobalance