PRELIMINARY REPORT

KINETICS OF THE REACTION OF ELEMENTAL FLUORINE WITH ZIRCONIUM CARBIDE AND ZIRCONIUM DIBORIDE AT HIGH TEMPERATURES

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INTRODUCTION:

Although there have been extensive studies of oxidation and nitridation rates for metals and compounds, there have been very few studies of reaction rates with fluorine. The kinetics of the reactions between fluorine and ZrC and ZrB_2 is complicated because of the variety of possible solid reaction products — a mixture of zirconium fluorides with the tetrafluoride being the most stable. The other products (carbon tetrafluoride or boron trifluoride) are both gases at normal temperatures and one predicts that these should leave a rather porous layer of ZrF_4 as the reaction takes place at the carbide-fluoride or the boride-fluoride interface. Thus, the reaction would obey a linear rate law and not be diffusion controlled. On the other hand, because of the large volume ratio of fluoride to carbide or fluoride to boride of zirconium, one might expect some degree of protection if the fluoride layer is adhesive. The actual state of affairs is complicated by the fact that ZrF_4 sublimes readily at moderately high temperatures and decomposes at higher temperatures. Volatilization and decomposition data for ZrF_4 are therefore required for a complete explanation of the fluorination kinetics of zirconium and its compounds.

EXPERIMENTAL:

A detailed description of the apparatus used has been given previously.[1] Slight modifications were effected for sending a slow

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[1] T. C. M. Pillay and J. L. Margrave, Technical Documentary Report No. ASD-TDR-62-204 Part I, April, 1962, pp. 77-79.

stream of dry nitrogen from the top of the helical spring chamber in order to exclude any fluorine from the spring-compartment. Proper changes were also made in the furnace windings for attaining high temperatures rapidly and in the flow meter systems for obtaining low fluorine partial pressures.

In order to check the variability of the apparatus for fluorination studies in general, observations were first made on the reaction between electrolytic copper foil and fluorine as a standard, since this is the only system for which the kinetics of reaction with fluorine have been worked out in any detail.[2,3]

Before commencing the reaction, the nickel furnace tube was passivated by reacting it with pure fluorine at 500°C. Nickel is known to form a protective coating of nickel fluoride at high temperature in fluorine.[4] The process was carried out during a period of three days, intermittently admitting fluorine for two or three hours each time. Also, before starting any run, a mixture of fluorine and helium was passed through the already passivated furnace tube, heated at the desired temperature for nearly half an hour to one hour as required, until fluorine was detected coming out of the exit from the combustion tube in large amounts, as indicated by use of KI paper. After passivation at the required temperature, the system was evacuated and flushed with helium several times and the sample to be fluorinated was

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2. P. M. O'Donnell and A. E. Spakowski, NASA Technical Note D-768, April, 1961.
3. P. E. Brown, J. M. Crabtree and J. F. Duncan, J. Inorg. and Nuclear Chem., 1, 202 (1955).

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4. M. J. Steindler and R. C. Vogel, ANL-5662, Argonne Nat. Lab., January, 1957.

suspended from the helical spring by means of a 0.007" nickel wire, in the atmosphere of flowing helium gas. After about 10 minutes, fluorine was also admitted, along with the helium and a timer started simultaneously. The partial pressure of fluorine was calculated from the individual flow rates of fluorine and helium at atmospheric pressure. Any reaction of the fluorine with the nickel suspension wire was neglected on the grounds that the surface area of the nickel wire exposed to the hot zone of the furnace was negligibly small compared to the relatively large area of the specimen. The change in extension of the spring was observed by means of a cathetometer and the smallest measurable weight change was 0.05 mg. Readings were taken at suitable intervals of time. The silica spring was protected from attack by fluorine by having a blanket of dry nitrogen in the form of a slow, steady stream sent from the top of the system. At the conclusion of the run, the fluorine was cut off and helium and nitrogen continued to flow until the exit gas was free from fluorine.

The copper foil was cleaned with dilute HNO_3 and washed with water and subsequently with acetone and benzene and dried. The ZrC and ZrB_2 samples in the form of small pellets weighing about 0.2 to 0.4 gm. were polished by grinding with abrasive powder. The ZrB_2 had a shining mirror-like appearance while the ZrC had a dark gray color. Surface areas of the specimens were determined to the nearest 0.01 $cm.^2$

RESULTS AND DISCUSSION:

Reaction between fluorine and copper:

The fluorination study on copper was carried out at 500°C under various fluorine partial pressures ranging from 23-740 mm. of Hg. Parabolic plots of the results indicated an initial fast reaction during the first five minutes followed by a slower reaction for a period of approximately an hour and a half until the runs were stopped. In a diffusion-controlled surface reaction, deviations from a parabolic law may be expected in the early stages of the reaction, when the thickness of the product layer is small, since other factors are operative. Parabolic rate constants for the reactions, shown in Table I were, therefore, computed taking into consideration only the values after the initial fast reactions. It is clear from Table I that the partial pressure of fluorine does not influence the rate of fluorination of copper to any great extent; the rate of increase of the rate constant is roughly proportional to the fourth root of fluorine partial pressure between 23 and 167 mm. and thereafter being almost independent of the same up to 1 atm. The reaction product in all the cases is an adherent layer of red cuprous fluoride beginning to darken on the outside possibly due to the formation of small amounts of cupric fluoride.

It may be mentioned that Brown et al.[3] observed no change in the rate of fluorination of copper with changes in the fluorine partial pressures over the range 6-60 mm. of Hg. and at temperatures below 250°C whereas the present investigation shows a slight enhancement of the reaction rate with increase of fluorine partial pressure. In general, the role of the partial pressure of the reacting gas in diffusion-controlled gas-solid reactions is not clearly understood in the sense that the pressure dependence of rates of reaction, changes from one system to another.

Fluorination of ZrC and ZrB_2:

Zirconium carbide is known to be readily decomposed by halogens and oxidizing agents,[5] in general, and hence a rather vigorous reaction

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[5] P. Schwarzkopf and R. Kieffer in "Refractory Hard Metals," MacMillan Company, New York, 1953, p. 95.

Table I

Parabolic Rate Constants for Fluorination of Copper Under Various Fluorine Partial Pressures at 500°C.

F_2 Partial Pressure (mm. of Hg.)	Parabolic Rate Constant, kp $(mg/cm^2)^2$/min. x 10^3
23.3	8.00
45.3	9.27
144.0	12.00
167.0	12.57
740.0	13.07

is to be expected with fluorine. A preliminary examination showed that ZrC would burn in fluorine or in an atmosphere rich in fluorine, at about 250-300°C. On the other hand, ZrB_2 did not catch fire in pure fluorine at a pressure of 1 atm., but broke into several bits at about the same temperature. The fluorination of these materials was examined at low fluorine partial pressures where the reactions could be effectively controlled.

Reaction between ZrC and Fluorine

Initial experiments with ZrC and F_2 under low partial pressure of F_2 (31 mm. of Hg.) indicated that the reaction was rather smooth at about 300°C with a regular increase in weight. The reproducibility of the results was checked at 300°C and found to be within 15-20%. With the same fluorine partial pressure, the reaction was conducted at various temperatures ranging from 278 to 410°C. Above 410° the reaction became too fast to be measured. The weight increase per unit area of ZrC with time at the various temperatures is illustrated in Figure I. There is no question regarding the linearity of the reaction with time. Abrupt breaks at and above 334°C indicate the crumbling of part of the fluoride layer formed on the ZrC. Thick scales of ash-gray zirconium tetrafluoride were observed on the surface of the ZrC after reaction. The adhesion of the scales was very poor and the material was soft and fluffy. The reacted samples had a sandwich appearance and their volumes had increased markedly because of the fluffiness of the ZrF_4 formed. The scales were apparently uniform and there were no visible cracks on them except at the edges, where the inner core was practically naked. Viewed under a microscope, the layers were made up of fine sugar-like crystals uniformly formed without any cracks. It is possible that the unreacted ZrC was in direct

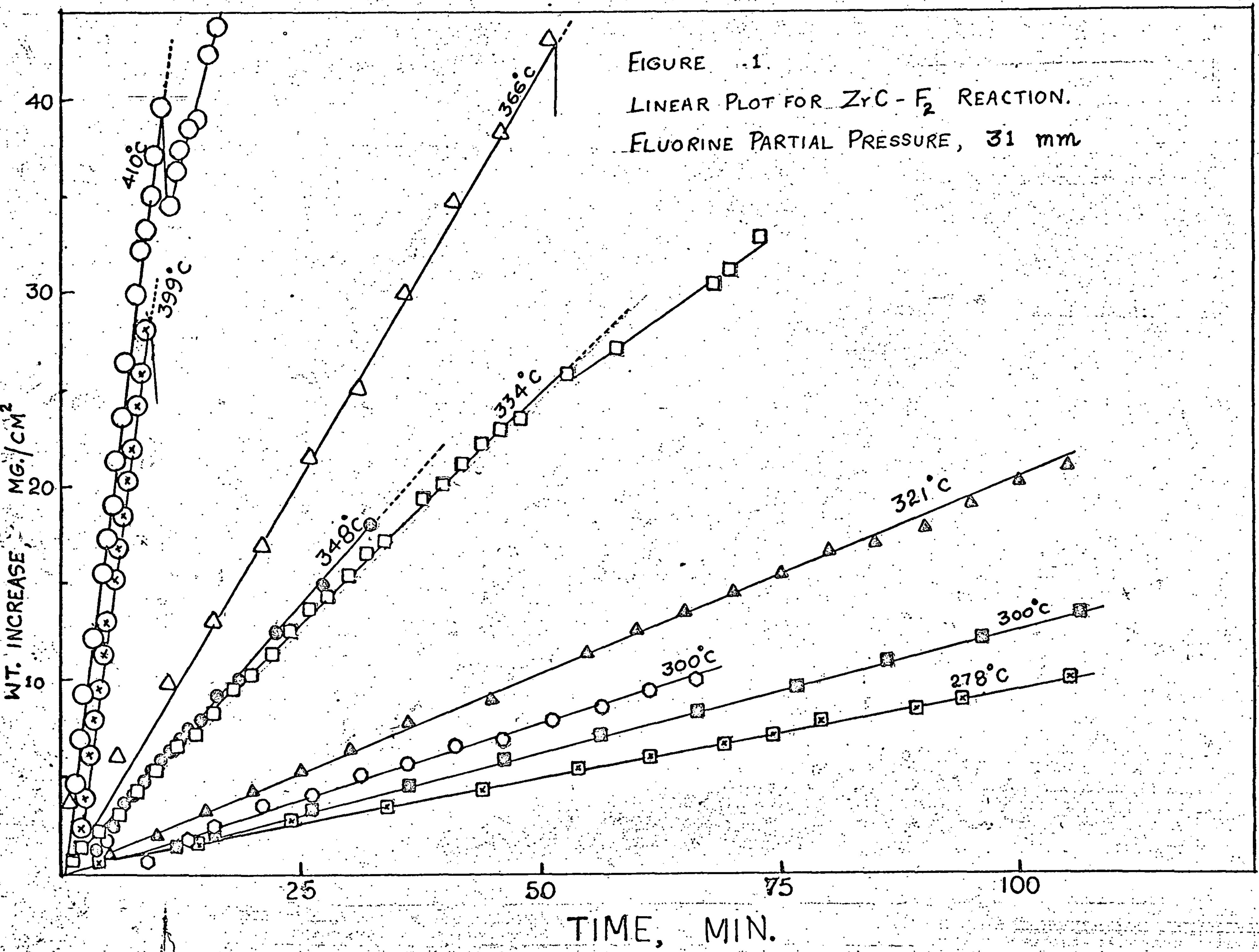

FIGURE 1.

LINEAR PLOT FOR ZrC - F_2 REACTION.

FLUORINE PARTIAL PRESSURE, 31 mm

contact with the fluorine atmosphere outside the fluoride coating through the corners and thus could show a linear rate of reaction. It is intended to study the fluorination of ZrC in the form of a sphere or a piece with rounded edges in order to check this possibility.

It is not possible to say whether zirconium or carbon in the system is preferentially attacked by fluorine, since the gaseous products were not analyzed. X-ray analysis of the inner core and the outer layer might show some evidence regarding this question. The fact that the inner core is rough when once the fluoride scales are removed, indicates that possibly one of the elements is reacted faster than the other.

From the slopes of the straight lines in Figure I, the linear rate constants for the reactions were estimated, not taking into account the volatile products. The values obtained are displayed in Table II. The activation energy computed by a least square method is 22.1 ± 1.6 kcal/mole.

Further work is in progress with regard to the effect of variation of the fluorine partial pressure on the reaction and the possibility of studying the reaction at higher temperatures with very low fluorine partial pressures.

Fluorination of ZrB_2:

For the conditions in which the fluorination kinetics of ZrC were investigated, ZrB_2 does not react with fluorine to any measurable extent. At 500°C, however, a gain in weight is observed as ZrB_2 reacts with F_2 at a partial pressure of 3-4 mm. of Hg. At about 600°C, it begins to lose weight in presence of F_2. Specimen removed after fluorination above 600° have practically no coating of fluoride on the outside and the ZrB_2 had lost its lustre. This indicates that the fluorides formed were all volatilized, especially when the system was

Table II

Linear Rate Constants for the $ZrC-F_2$ Reaction at Various Temperatures (Fluorine Partial Pressure: 31 mm. of Hg.)

Temperature (°C)	Linear Rate Constant, k_1 ($mg/cm^2/min.$)
278	0.0995
300	0.1282
300	0.1515
321	0.2010
334	0.5069
348	0.5526
366	0.8450
399	3.4545
410	3.6786

$\Delta E_a = 22.1 \pm 1.6$ kcal/mole

continuously flushed with about 600 ml. of gas every minute. However, the loss in weight could be measured reproducibly for calculating the rate of the reactions. The reaction was studied at 600, 700, 800, and 900°C and in all the cases the ZrB_2 was losing weight. An interesting point observed was that, out of these four temperatures, the corrosion rate was a maximum at 800°C. At 900°, the rate of the reaction was nearly equal to that at 700°C. This abnormal behaviour apparently shows that above 800°C, the ZrB_2-F_2 reaction has a negative temperature coefficient which means that the reaction rate could be still slower at higher temperatures. This phenomenon might be explained as being due to the onset of the decomposition of ZrF_4 above 800°, into its elements. However, these few experiments are not decisive and further work is needed before making any conclusions. The detailed values are, therefore, not reported herein.

It should also be mentioned that the ZrB_2-F_2 reaction obeys a linear rate law, except for a slight apparent decrease in the rate of reaction with time, due to the decrease in the surface area of the ZrB_2 with increasing extent of corrosion.