Kinetics of Carbon Deposition in a Fluidized Bed

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Rate data have been obtained for the deposition of carbon films from methane and acetylene in fluidized beds of alumina, uranium dioxide, uranium monocarbide, uranium dicarbide, and a solid solution of uranium-thorium dicarbide powders. These carbon films have been shown to provide excellent protection for the powdered fertile material against attack by hot concentrated nitric-acid solutions. The coated uranium-thorium dicarbide particles were also shown to be stable in humid air.

One of the principal difficulties in the design and construction of a nuclear reactor employing uranium, thorium, and plutonium carbides as the fertile or fissile material is the reactivity of the fuel with moisture even at room temperature to form oxides. If this partially hydrolyzed fuel is embedded in a graphite-matrix fuel element, subsequent operation at high temperature may result in the generation of carbon monoxide gas and in dimensional changes.

It was therefore desirable to develop a process whereby the carbide fuel in powdered or granular form could be coated with a protective film. Such a coated fuel powder could then be readily shipped and fabricated into fuel elements without recourse to the use of protective atmospheres. In addition the coating may help to retain fission products within the fuel particle during operation of the nuclear reactor. Pyrolytic carbon is probably the least expensive coating for this purpose, and it was expected that pyrolytic carbon films would be relatively easy to prepare. The investigation described herein was designed to provide quantitative information on the kinetics of the deposition reactions and qualitative information on the effectiveness of the coating as a moisture barrier.

Techniques used to coat powders with protective films have been extensively investigated for a number of years. The first commercial process based on a fluidized bed accretion technique is the fluid coking process, whereby a heavy petroleum residue is converted into coke and volatile hydrocarbons (*1* to *5*). Other work suggested that the metals could also be deposited in a fluidized-bed system (*6*). Based on a strong background of experience in chemical vapor-deposition reactions (*7*) the original fluidized-bed studies at Battelle were directed toward deposition on seed particles as a low-cost method of producing metals (*8, 9*). However recent work has included the deposition of metallic and ceramic coatings on nuclear-fuel particles (*10* to *16*). In addition Argonne National Laboratory has recently used the fluidized-bed vapor-deposition technique to prepare granular uranium dioxide from the hexafluoride (*17*).

EXPERIMENTAL STUDIES

Description of Equipment

A schematic flow diagram of the apparatus used in deposition studies is shown in Figure 1. Helium was used as the principal fluidizing medium in the majority of runs, and acetylene and methane were used as the source of carbon. All of the gases were metered through rotameters.

The deposition reactor consisted of a 24 in. length of 26-mm. quartz tubing, at the top of which was a 6 in. length of 53-mm. quartz expanded section to minimize loss of particles from the reactor. The bottom of the reactor tapered to a 5-mm. O.D. by 1-mm I.D. quartz capillary over the span of 1¼ inch. The capillary tube had a reverse bend of 1½-in. diameter and was connected to the preheater through a 12/5 ball and socket joint. The capillary was used to increase the velocity of the gas entering the reactor and thus prevent plugging of the inlet line by the solids in the fluidized bed. The temperature of the fluidized bed was measured by means of a chromel-alumel thermocouple protected by a 7-mm. quartz tube. This tube extended from the top of the expanded section to midway in the bed.

A preheater, consisting of a 14 in. length of 57-mm. quartz tubing filled with small quartz helices ¼ in. in diameter, was used to heat the fluidizing gas to a temperature just below that at which deposition takes place.

A special deposition reactor used for runs at 1,400°C. consisted of a 24 in. length of 26-mm. I.D. mullite combustion tube with a 6 in. length of 53-mm. quartz expanded section mounted at the top of the reactor to minimize loss of product. The bottom of the reactor had a taper somewhat similar to that of the quartz reactor. An outside platinum-platinum 10 w/o rhodium thermocouple was used to measure temperature in the 1,400°C. deposition runs.

Electrical resistance heater furnaces were used to heat the various units of the apparatus and proper temperatures were maintained by means of controllers.

Experimental Procedure

The procedure for the deposition runs was relatively standardized. The reactor was placed in a furnace and coupled to the preheater, the expanded section, and the traps. The equipment was then leak tested. While the system was purged with helium, the reactor and preheater were heated to the desired operating temperatures. The reactor was then charged with bed material, and if the bed material was reactive with moist air, a glass transfer flask having a clamped exit line was used. With this arrangement the flask could be filled in a dry box and emptied into the reactor without exposing the materials to air. The hydrocarbon was introduced into the reactor in a predetermined ratio of hydrocarbon to helium. The total flow of both gases was adjusted to give somewhat

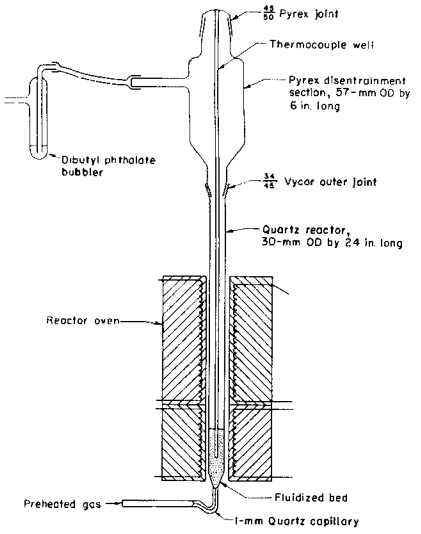

Fig. 1. Apparatus for coating powders with carbon.

more than the rate needed for incipient fluidization.

At the end of the coating period the hydrocarbon gas was turned off and the helium flow increased. The reactor and preheater were cooled to room temperature. After the coated material was screened and weighed, samples of the coated particles were analyzed for carbon content and examined metallographically. Conversion levels were calculated on the basis of the increase in carbon content of the bed material.

Experimental Results

A summary of a sample of the experimental data for the deposition experiments is presented in Table 1*. Photomicrographs of carbon coated uranium dicarbide and carbon coated thorium-uranium dicarbide particles are shown in Figures 2 and 3.

CORRELATION EQUATIONS

In order to satisfactorily correlate the experimental data it was necessary to derive linearized kinetic equations for both a differential and integral reactor system. These linearized equations were then solved by use of an IBM-650 computer and standard regression techniques.

It can readily be shown on the basis of kinetic theory that the rate of activated collisions of hydrocarbon on the surface of the bed material resulting in reaction can be expressed (*18*):

$$r_i = \frac{kP_i}{T_B} e^{-E_i/RT_B} \qquad (1)$$

Generalizing to include the possibility of a nonlinear proportionality between variables one gets

$$r_i = \frac{kP_i^{\,n}S_B^{\,a}}{T_B} e^{-E_i/RT_B} \qquad (2)$$

The weight rate of carbon deposition is therefore

$$W_c = m_j M_j S_B r_i = \frac{k'P_i^{\,n}S_B^{\,a+1}}{T_B} e^{-E_i/RT_B} \qquad (3)$$

For low conversions such as in the case of the methane data Equation (3) can be applied directly without regard to the actual flow mechanism through the reactor, changes in reactant partial pressure, or the possibility of reverse reaction. Taking logarithms of both sides of Equation (3) one obtains

$$\ln W_c T_B = \ln k' + n \ln P_i + (a+1) \ln S_B - E_i/RT_B \qquad (4)$$

This equation is in linear form, and the unknown coefficients (k', n, a, E_i) can be obtained from the data by regression techniques (*19*).

In the case of the acetylene data, where an appreciable conversion of the reactant occurred, Equation (3) must be used in conjunction with the general equation for flow over a differential element of reaction surface. Here an assumption must be made as to the flow pattern, and it has been assumed that piston flow of the gaseous stream is predominating. The relation between conversion level and the process variables for the case of no volume change upon reaction becomes (if $n \neq 1$) (*20*)

$$\frac{(1-x)^{1-n}-1}{n} = \frac{k(P_i^{\,o})^n S_B^{\,a+1}}{(a+1)Z_o F T_B} e^{-E_i/RT_B} \qquad (5)$$

Expanding one gets

$$(1-x)^{1-n} - 1 = \frac{-(1-n)x}{1!} + \frac{(1-n)(-n)}{2!}x^2 - \frac{(1-n)(-n)(-1-n)}{3!}x^3 + \ldots. \qquad (6)$$

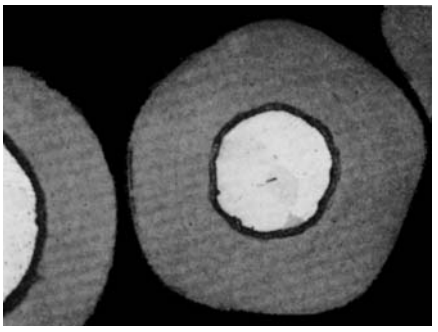

Fig. 2. Spherical uranium dicarbide coated with 80 μ of carbon. Sample is from Run 18.

Retaining the first two terms of Equation (6) substituting into Equation (5) and taking logarithms one obtains

$$\ln Z_o F T_B x + \ln\left(1 + \frac{nx}{2}\right) = \ln\frac{k}{a+1} + n \ln P_i^{\,o} + (a+1) \ln S_B - E_i/RT_B \qquad (7)$$

since

$$\ln\left(1 + \frac{nx}{2}\right) = \frac{nx}{2} - \frac{1}{4}\left(\frac{nx}{2}\right) + \ldots. \qquad (8)$$

Retaining the first term in Equation (8), and substituting into Equation (7) one gets

$$\ln Z_o F T_B x = \ln\frac{k}{a+1} + n(\ln P_i^{\,o} - x/2) + (a+1) \ln S_B - E_i/RT_B \qquad (9)$$

Equation (9) is in linear form and can be solved by standard techniques.

DISCUSSION

Process Variables

The effects of the process variables, that is partial pressure of reactant, surface area of the bed, and deposition temperature, were determined by a regression analysis of the experimental data and the linearized kinetic expressions for the rate of carbon deposition. The rate constants for carbon deposition were found to be as follows:

Summary of Regression Analyses for Carbon Deposition in a Fluidized Bed

	Methane Avg.	Methane Std. dev.	Acetylene Avg.	Acetylene Std. dev.
Activation energy	90.4	± 3.7	51.0	± 1.8
Partial pressure dependence	1.30	± 0.25	1.45	± 0.10
Surface area dependence, $a+1$	1.39	± 0.16	0.92	± 0.10
Logarithm of rate constant, $\ln k'$ or $k/a+1$	21.537	± 0.723	11.173	± 0.543

* Tabular material has been deposited as document 6752 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or for 35-mm. microfilm.

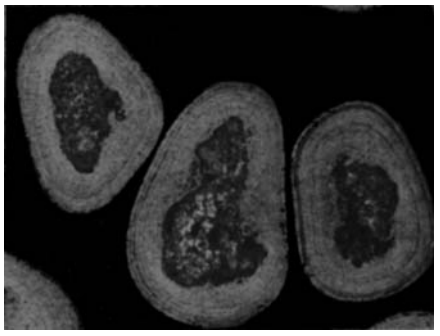

Fig. 3. Thorium carbide-uranium carbide solid-solution carbide coated with 30 μ of carbon. Sample is from Run 12. Structure of carbide is not clearly discernible because of the rapid hydrolysis of the core after sectioning for examination.

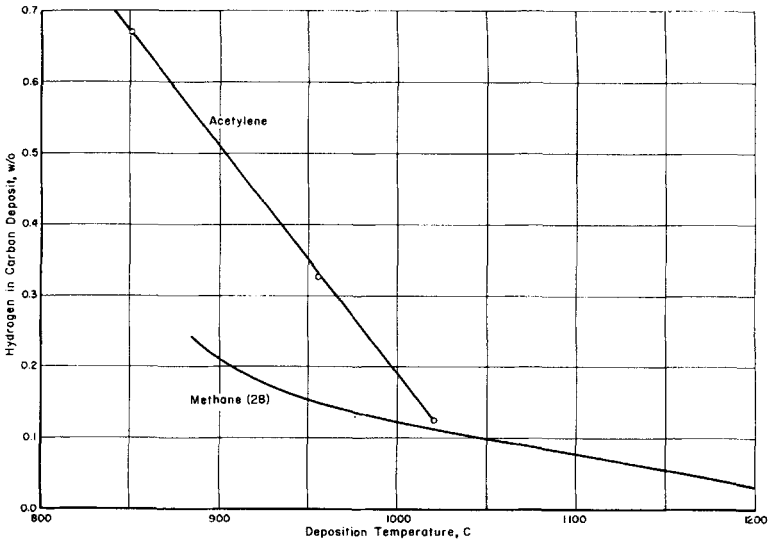

Fig. 4. Hydrogen content of deposited carbon as a function of deposition temperature.

At a bed temperature of 1,000°C. a hydrocarbon partial pressure of 760 mm. of mercury, and a bed surface area of 7,000 sq. cm., the rate of carbon deposition from acetylene is 182 times the rate of deposition from methane. However at 1,600°C. the rates of carbon deposition from both methane and acetylene become equal under these same conditions.

The experimental activation energies for the pyrolysis of the hydrocarbons, as determined on the basis of carbon-deposition rates, are in rather good agreement with the literature values. The activation energy for carbon deposition from methane was found to be 90,400 cal./g.mole, which is in excellent agreement with the most recent values of 93,000 by Kervorkian, Heath, and Boudart (*21*) and Shantorovich and Pavlov (*22*) and compares favorably with most of the previously reported data, that is 78,000 to 102,200 (*23* to *26*). In contrast Brown and Watt have reported a value of 21,600 (*27*) and have calculated a value of 39,000 from the data of Grisdale, Pfister, and Von Roosbroeck (*28*). However failure to correct for depletion of reactants may be the reason for these latter low values.

The activation energy for the deposition of carbon from acetylene was found to be only 51,000 cal./g.-mole, which is somewhat higher than the values of about 30,000 which have been reported previously (*29*, *30*). Since the acetylene activation energy is so much lower than that of the methane system, it would appear that a step by step reduction scheme (*26*, *31*), wherein the decomposition of methane is slow with respect to the subsequent steps, is correct in principle at low temperatures, although the mechanism involved in each step has yet to be clearly defined.

The fact that the rate of carbon deposition is roughly proportional to the surface area of the bed, since the exponent on the surface-area term in the rate equations varies from 0.92 to 1.39, indicates that at least the reactions leading to the deposition of carbon are heterogeneous. However this does not necessarily mean that the entire pyrolysis reaction is so dependent. Gordon (*32*) reported that there is a large catalytic effect of surface in the early stages of the pyrolysis of methane. Tesner and Refal'kes (*33*) reasoned that the process of carbon formation is an example of a purely surface reaction and is in no way bound up with simultaneous changes in the hydrocarbons which take place in the volume of gas. It is also noteworthy that they reported that the rate of deposition of carbon on a carbon surface was greater than any other surface studied. The data obtained in the current study support the conclusion that surface area does have a very significant effect on the rate of deposition.

In both the methane and acetylene pyrolysis studies the exponents of the partial-pressure term were greater than unity, that is, 1.30 and 1.45. Although good data concerning the order of these reactions are scarce, most observers have assumed a first-order reaction for methane decomposition. Kevorkian, Heath, and Boudart (*21*) have shown that the methane decomposition is closer to a first-order reaction than it is to a second-order reaction. Kassel (*26*) showed that at low concentrations of hydrogen, and hence in a differential reactor system, his theory leads to a linear proportionality between rate and methane partial pressure. Tesner and Refal'kes (*33*) found a linear relationship between the rate of carbon deposition and concentration for both methane and acetylene pyrolysis, while others have reported a second-order reaction for acetylene pyrolysis (*29*, *30*).

It is believed that the disagreement between the fluidized-bed studies and prior work concerning the order of the reactions is theoretically significant and may be due to hydrogen inhibition as a result of chain termination, although from a practical viewpoint the general

TABLE 1. SUMMARY OF SELECTED EXPERIMENTAL DATA ON DEPOSITION OF CARBON

Run	Bed material	Avg. part. diam., μ	Bed weight, g. Init.	Bed weight, g. Gain	Coating thickness, μ	Run time, hr	Bed temp., °C	Helium flow rate, cc./min. STP	Conv. to deposited carbon, %	Reactant	Reactant flow rate, cc./min. STP	Deposition rate, μ/hr.	Uranium leached in porosity test during time indicated, % 0-1 Hr.	1-7 Hr.	1-8 Hr.	0-8 Hr.	7-19 Hr.	8-15 Hr.
1	Al_2O_3	266	53.0	—0.1	0.2	3.0	955	1,075	0.05	CH_4	2,140	0.07	—	—	—	—	—	—
5	UO_2	166	193.8	2.6	1.0	4.0	1,015	—	0.94	CH_4	3,200	0.25	88.8	4.47	—	—	0.07	—
6	UO_2	173	193.8	11.3	7.0	0.5	1,015	2,150	36.4	C_2H_2	1,050	14.0	0.28	0.006	—	—	<0.001	—
8	Al_2O_3	139	45.7	1.0	4.0	2.0	850	2,150	2.26	C_2H_2	1,050	2.0	—	—	—	—	—	—
14	UC_2	318	107.8	11.4	40	3.0	1,095	2,950	40.3	C_2H_2	333	13.3	—	—	—	0.004	—	<0.001
15	UC_2	240	98.6	7.6	17	0.8	1,015	2,150	22.1	C_2H_2	1,050	21.2	—	—	—	0.004	—	<0.001

effect is the same, that is, higher partial pressures of hydrocarbons yield higher rates of deposition.

Product Evaluation

The hydrogen contents of the carbon films deposited from acetylene were measured and found to decrease at higher temperatures, which is similar to the trend reported by Grisdale, Pfister, and on Roosbroeck for carbons deposited from methane (28). However in all cases the hydrogen contents of the films deposited from acetylene were greater than those reported for carbons deposited from methane, as can be seen from the data in Figure 4. Nevertheless it would appear that the curves for the two sets of data might interact at a temperature of about 1,030°C., which is about the highest temperature at which the hydrogen content of the deposited carbon was measured in the present study.

The evaluation of the properties of the carbon coatings was primarily based on the ability of the coatings to protect the fertile material against attack by hot concentrated nitric acid for periods of about 8 hr. As can be seen from the data in Table 1 the carbon coatings provide excellent protection for the powdered fertile materials. Although the data are somewhat spotty, since the major emphasis was placed on evaluation of the process, it would appear that a 7-μ coating deposited from acetylene at a temperature of 1,015°C. on uranium dioxide powder provides good protection. Surprisingly a 7-μ coating deposited from methane at 1,125°C. on uranium dicarbide powder did not provide good protection. It is suspected that difference in behavior is a result of the difference in coating conditions and not the difference in base material, although further information on this point should be established. It was determined that a 9-μ coating on uranium monocarbide, a 17-μ coating on uranium dicarbide, and a 30-μ coating on thorium-uranium dicarbide are within the safe coating-thickness region.

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NOTATION

a = exponent on surface-area term
E_i = activation energy for a chemical reaction, kcal./g.-mole
e = a constant, 2.718
F = feed rate of inert gases, g.-mole/hr.
k = a rate constant, $\beta_i/\pi R\sqrt{2E_i/M_i}$
k' = a rate constant, m_jM_jk
M_i = molecular weight of the i component in a gas mixture, g./g.-mole
M_j = molecular or atomic weight of solid deposit, g./g.-mole
m_j = number of moles of deposit per mole of converted reactant feed
n = exponent on partial-pressure term
P_i = partial pressure of reactant gas, mm. of mercury
P_i° = partial pressure of reactant gas in feed stream, mm. of mercury
R = ideal gas constant, 1.987 cal./(g.-mole)(K°) or its equivalent
r_i = activated collision rate, mole/(hr.)(sq. cm.)
S_B = surface area of the bed, sq. cm.
T_B = bed temperature, °K.
W_c = weight rate of carbon deposition, g./hr.
x = fractional conversion of reactant
Z_o = g.-mole of reactants/g.-mole of inerts in feed stream
β_i = fraction of activated collisions resulting in reaction
π = a constant, 3.14

LITERATURE CITED

1. Voorhies, Alexis, Jr., and H. Z. Martin, *Oil Gas J.*, **52**, No. 28, p. 1204 (November 16, 1953).
2. Martin, H. Z., F. T. Bass, and R. W. Krebs, *ibid.*, **53**, No. 1, p. 166 (May 10, 1943).
3. Johnson, F. B., and R. E. Wood, *Petrol. Refiner*, **33**, No. 11, p. 157 (November, 1954).
4. Voorhies, Alexis, Jr., *Proc. Fourth World Petroleum Congr.*, Section III/F (1955).
5. Dunlop, D. D., L. I. Griffin, Jr., and J. F. Moser, Jr., *Chem. Eng. Progr.*, **54**, No. 8, p. 39 (August, 1958).
6. Cline, J. E. and John Wulff, *J. Electrochem. Soc.*, **98**, 385 (1951).
7. Powell, C. F., I. E. Campbell, and B. W. Gonser, "Vapor Plating," p. 158, Wiley, New York (1955).
8. Oxley, J. H., and I. E. Campbell, *J. Metals*, **11**, 135 (1959).
9. ———, and G. H. Kesler, *Chem. Eng. Progr. Symposium Ser.*, to be published.
10. Kates, L. W., "Quarterly Technical Progress Report for Period Ending June 30, 1958," SCNC-279, Classified (September, 1958).
11. Oxley, J. H., J. F. Hannah, J. M. Blocher, Jr., and I. E. Campbell, *Ind. Eng. Chem.*, **51**, 1391 (1959), and *Battelle Memorial Institute-1297* (October, 1958).
12. Goslee, David, *U.S. Atomic Energy Commission Rept. MND-AC-1755-1* (April, 1959).
13. Oxley, J. H., and J. M. Blocher, *Battelle Tech. Rev.*, **8**, (7), p. 9 (July, 1959).
14. Linquist, C. G., *U. S. Atomic Energy Commission Rept. KAPL-M-CGL-2* (October, 1959).
15. Nuclear Materials and Equipment Corporation, *NUMEC-NYO-2801* (November, 1959).
16. Blocher, J. M., Jr., N. D. Veigel, J. H. Oxley, V. M. Secrest, and E. E. Rose, *Battelle Memorial Institute-1440* (June, 1960).
17. Knudsen, I. E., N. M. Levitz, and Stephen Lawroski, *U.S. Atomic Energy Commission Rept.* ANL-6023 (August, 1959).
18. Kennard, E. H., "Kinetic Theory of Gases," 1 ed., McGraw-Hill, New York (1838).
19. Mood, A. M., "Introduction to the Theory of Statistics," McGraw-Hill, New York (1950).
20. Hougen, O. A., and K. M. Watson, "Chemical Process Principles," Part III, pp. 805-1107, Wiley, New York (1949).
21. Kevorkian, V., C. E. Heath, and Michael Boudart, *J. Phys. Chem.*, **64**, 964 (1960).
22. Shantorovich, P. S., and B. V. Pavlov, *Zhur. Fiz. Khim*, **30**, 811 (1956).
23. Skinner, G. B., and R. A. Ruehrwein, *J. Phys. Chem.*, **63**, 1736 (1959).
24. Tesner, P. A., and A. I. Echeistova, *Doklady Akad. Nauk SSSR*, **87**, 1029 (1952).
25. Murphy, D. P., H. B. Palmer, and C. R. Kinney, *Industrial Carbon and Graphite*, Soc. Chem. Ind. (London), **77** (1958).
26. Kassel, L. S., *J. Am. Chem. Soc.*, **54**, 3949 (1932).
27. Brown, A. R. G., and W. Watt, *Industrial Carbon and Graphite*, Soc. Chem. Ind. (London), **86** (1958).
28. Grisdale, R. E., A. A. Pfister, and Willy van Roosbroeck, *Bell System Tech. J.*, **30**, 271 (1951).
29. Greene, E. F., R. L. Taylor, and W. L. Patterson, Jr., *J. Phys. Chem.*, **62**, 238 (1958).
30. Blumberg, E. A., and D. A. Frank-Kamenetskii, *Zhur. Fiz. Khim.*, **20**, 1301 (1946).
31. Holliday, G. C., and W. J. Gooderham, *J. Chem. Soc.*, **134**, 1594 (1931).
32. Gordon, A. S., *J. Am. Chem. Soc.*, **70**, 395 (1948).
33. Tesner, P. A., and I. S. Rafal'kes, *Doklady Akad. Nauk SSSR*, **87**, 821 (1952).

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