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THE ROLE OF CARBON IN REACTIONS IN THE U-C-O-N SYSTEM

T. B. Lindemer, J. M. Leitnaker, and K. E. Spear

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THE ROLE OF CARBON IN REACTIONS IN THE U-C-O-N SYSTEM

T. B. Lindemer, J. M. Leitnaker, and K. E. Spear

ABSTRACT

Carbon plays a vital role in reactions in the U-C-O-N system. This has been demonstrated by extensive studies of the kinetics and thermodynamics of reactions in the system from 1400 to 2000°C, including those of UO_2 with carbon, UC with nitrogen, and UC_2 with nitrogen. Carbon can either act as a reductant or can control the reaction rate. It can control the rate of reactions either by diffusion processes, by the distribution of free carbon within the solid reactants, by the formation of compounds more rich in carbon, or by the formation of a nonequilibrium type of free carbon. In all cases, the role of carbon is dominant.

INTRODUCTION

The major component of future high-performance nuclear fuels will be one or more of the compounds or solid solutions in the U-C-O-N system. There are two major areas of technical interest in this system: the fuel cycle and the chemical stability. Several typical chemical reactions have been studied between 1400 and 2000°C to determine basic kinetic and thermodynamic properties: the reaction of UO_2 with carbon, UC with nitrogen, UN with graphite, and UC_2 with nitrogen.

Carbon plays an important role in the kinetics of these reactions. It acts as a reductant with UO_2. It controlled the reaction rate in

UC_2-N_2 reactions by a diffusion process and by its initial distribution as free carbon. Its rejection in the UC-N_2 reaction led to the formation of UC_2. Additionally, carbon can precipitate in a nonequilibrium form of free carbon. This discussion will review several studies that permit these conclusions.

EXPERIMENTAL TECHNIQUES

The general experimental methods used in the kinetic studies are described below, while techniques particular to a specific study are described in the discussion of that study. In many of the studies, the uranium compound was available as fully dense spheres with diameters of 500 μm. These were reacted for different times, and the outer diameters of the spherically symmetrical phases involved in the reaction were determined on equatorial cross sections of 25 spheres at each time by a metallographic method.[1] The principal data obtained were r_o, the radius of the sphere at zero time, and r, the radius of the reactant core at time t. These measurements were used in models that exist in the literature for reactions in solid spheres. The model for a reaction controlled by diffusion through the product layer is[2]

$$r_o^2 \left[1 - \left(\frac{r}{r_o}\right)^2 \left(3 - 2\,\frac{r}{r_o}\right)\right] = k_D t \ , \qquad (1)$$

in which k_D is in units of square centimeters per second. A model for control by a mechanism at the interface between the core and the product takes the form[3]

$$r_o - r = k_I t \ , \qquad (2)$$

in which k_I is in units of centimeters per second. A model for control at the surface is[4]

$$r_o \left[1 - \left(\frac{r}{r_o}\right)^3\right] = 3\ k_S t\ , \tag{3}$$

in which k_S is in units of centimeters per second. A plot of the left-hand side of Eqs. (1), (2), and (3) versus time for a series of experiments at a given temperature and incremental time intervals will often exhibit linearity for the left-hand-side function for one of the models; the plots for the other two models will be nonlinear. These characteristics provide one means for eliminating certain mechanisms from consideration as rate controlling.

Other techniques were used to obtain kinetic information from the thermodynamic studies. The intermediate stages of a reaction that eventually attained equilibrium were followed by the techniques of chemical analysis and Debye-Scherrer x-ray powder diffraction. In one case, the thermodynamic information developed from these studies could be used to show the existence of a nonequilibrium but kinetically stable form of carbon.

UO_2-C REACTION

The reaction of UO_2 spheres and graphite was studied between 1400 and 1750°C (ref. 5). This reaction is important because UO_2 is a starting material commonly used for making other nuclear fuels and because carbon is generally used as a reductant in the process. The UO_2 and graphite were reacted in a rotating tungsten crucible to maintain dynamic contact between graphite and the spheres. The reaction yielded

two quite different morphologies, depending on initial heating conditions. These results are illustrated in Fig. 1. The configuration in Fig. 1(b), in which the UO_2 maintained contact with the surface of the sphere until

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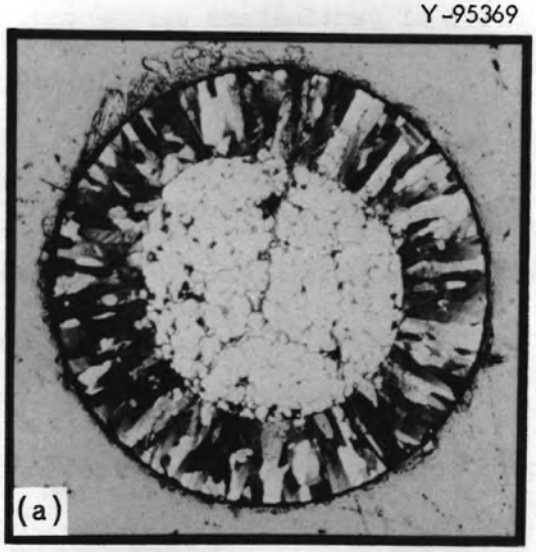

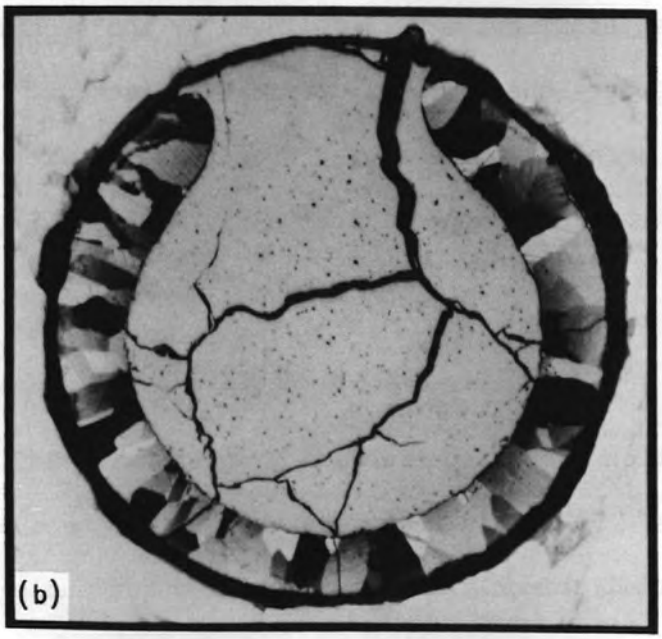

Fig. 1. Symmetrical (a) and Nonsymmetrical (b) Configurations Observed in the Reaction of UO_2 and Carbon. (a) 1700°C, 60 min, (b) 1750°C, 90 min. Cracks result from quenching at the end of the experiment. UO_2 is the core phase, UC_2 is the outer phase, and some graphite particles adhere to the outer surface. 150×. Etchant: 1:1:1 solution of water, acetic, and nitric acids.

the reaction was nearly complete, was obtained by heating the reactants to temperature at a rate greater than 50°C/min. The other configuration, which has a spherically symmetrical layer of UC_2, was obtained by a heating rate of 25°C/min or less. The initial heating rate apparently affects the initial nucleation and growth of the UC_2 on the surface of the sphere. The conversion rate for the nonuniform reaction was 2 to 5 times faster than that for the uniform reaction, a fact that has potential importance in the design of a process for the production of nuclear fuel.

The overall chemical conversion must occur by some sequences of mechanisms, all of which are either diffusion processes or interface reactions. There are illustrated schematically in Fig. 2. An example of an interface reaction at the surface of the sphere is the solution of graphite into UC_2. This is followed by diffusion of the carbon through the UC_2 to the interface between UC_2 and UO_2, where reaction produces UC_2 from UO_2. In the symmetrical reaction, the oxygen released by the reaction is postulated to go into solid solution in the UC_2, where it diffuses to the surface and reacts with graphite to form CO.

The mechanism controlling in the symmetrical configuration of Fig. 2 was deduced by comparing the results from the symmetrical and nonsymmetrical reactions. This comparison indicated that the diffusion of oxygen through the UC_2 was the rate-controlling step.[5]

The cause of the faster reaction in the nonsymmetrical configuration was also deduced.[5] The oxygen released at the interface between UO_2 and UC_2 diffuses through the UO_2 neck to the surface of the sphere, where it reacts with carbon to form CO. This process must be faster than the

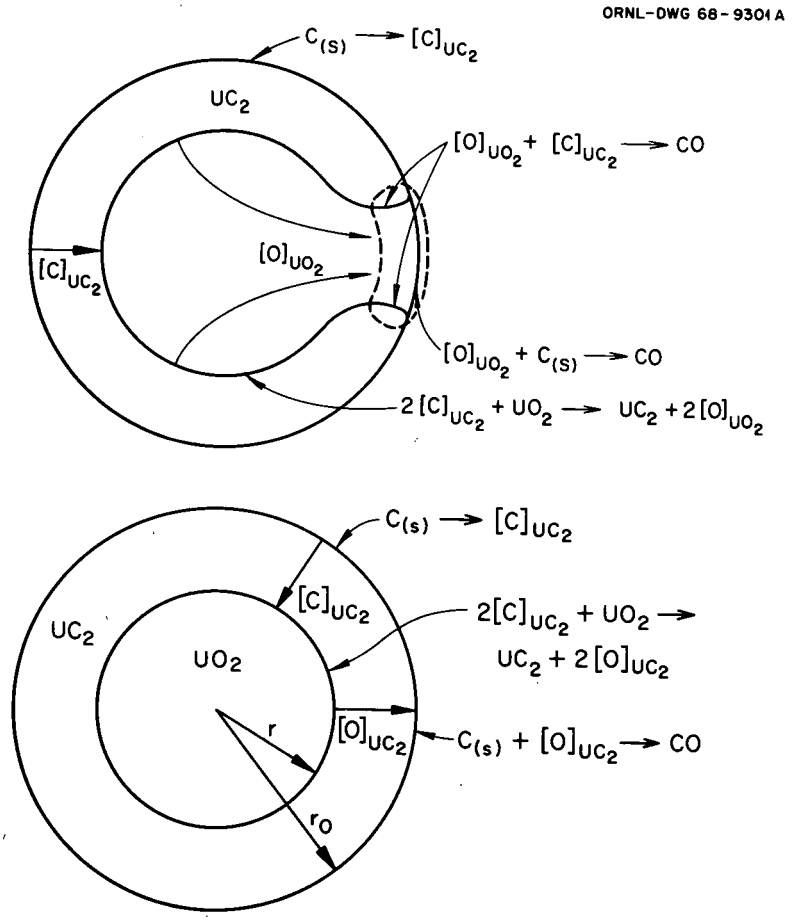

Fig. 2. Schematic Representation of Symmetrical (Lower) and Nonsymmetrical (Upper) Configurations Observed in the Reaction of the UO_2 and Carbon. The proposed mechanisms occurring during the reaction are shown.

diffusion of oxygen through the UC_2, and the conversion is therefore more rapid. The effect of grain size is not believed to change the rate-controlling steps observed under the conditions presented here.

Quantitative data was obtained for the uniform reaction by the metallographic technique described earlier. The average measurements for r and r_o at each time were used in the model for control by diffusion in spheres. The slope, k_D, of the plot at each temperature was fitted to the Arrhenius relation to obtain the activation energy, 90 kcal/mol.

The methods and results of this investigation compare most closely with those of Ainsley et al.[6] They studied the reaction of pelletized powder mixtures of UO_2 and carbon under vacuum from 1300 to 1550°C and concluded that the diffusion of either carbon or oxygen was rate controlling. They obtained an activation energy of 92 kcal/mol for the first-order rate constant.

In summary, potentially useful information has been found in the study of the reaction of UO_2 and carbon. For example, the conversion process is 2 to 5 times faster if contact can be maintained between the UO_2 and carbon during the reaction. For microspheres, this could be accomplished by heating the reactants to temperatures at a minimum rate of 50°C/min. (Rapid heating to temperature seems to be a determining factor.) The reaction is faster under these conditions, apparently because the oxygen migrates more rapidly through the oxide than it does through the dicarbide.

UC_2-N_2 REACTION

The reaction between uranium dicarbide microspheres and nitrogen was studied from 1500 to 1700°C (ref. 7). This reaction was considered for several reasons. First, it belongs to a general class of reactions that involve the conversion of metal carbides with nitrogen to produce a carbonitride solid solution. This carbonitride, with plutonium carbonitride in solid solution, is a potential high-performance nuclear fuel. Second, this study complemented a concurrent study that was being performed on the thermodynamics of the U(C,N) system. Third, in the production of uranium carbonitride from oxides, control of the quantity of carbon used is not as critical as for either pure UN or pure UC.

The experimental procedure and typical results will be described briefly. The apparatus used for these experiments consisted basically of a small graphite fluidized bed in a system that allowed the preheating of the nitrogen and the maintenance of a constant nitrogen pressure of 380 torr. The UC_2 spheres were dropped into the bed at zero time; about 200 to 1000 spheres were removed with a carbon bucket after each of eight equal-time increments. These spheres were examined by the technique described earlier[1] to obtain the conversion as a function of time.

A representative particle observed for each of the different times is shown in Fig. 3. The core consists of uranium dicarbide, the intermediate layer is uranium carbonitride, and the outer layer and dark precipitates are free carbon. The precipitates formed on free carbon that was present in the original UC_2 microspheres to the extent of about 1 vol %.

A particle was occasionally observed that contained little or no internal free carbon, as shown in Fig. 4. This sphere was obtained from the same sample as that shown in Fig. 3 that was reacted for 1080 min. The carbon precipitates only on the outer surface of the sphere, apparently because no free carbon was present internally to provide precipitation sites. The reaction rate to form U(C,N) in this type of material is about half that of the normal particle, as can be seen by comparing the thickness of the U(C,N) layer in the two different spheres.

Each of the mechanisms postulated to occur in the conversion must be examined to determine if it is the one controlling the reaction. These are shown schematically in Fig. 5 and can be divided into two classes: diffusion processes and interface reactions, including those

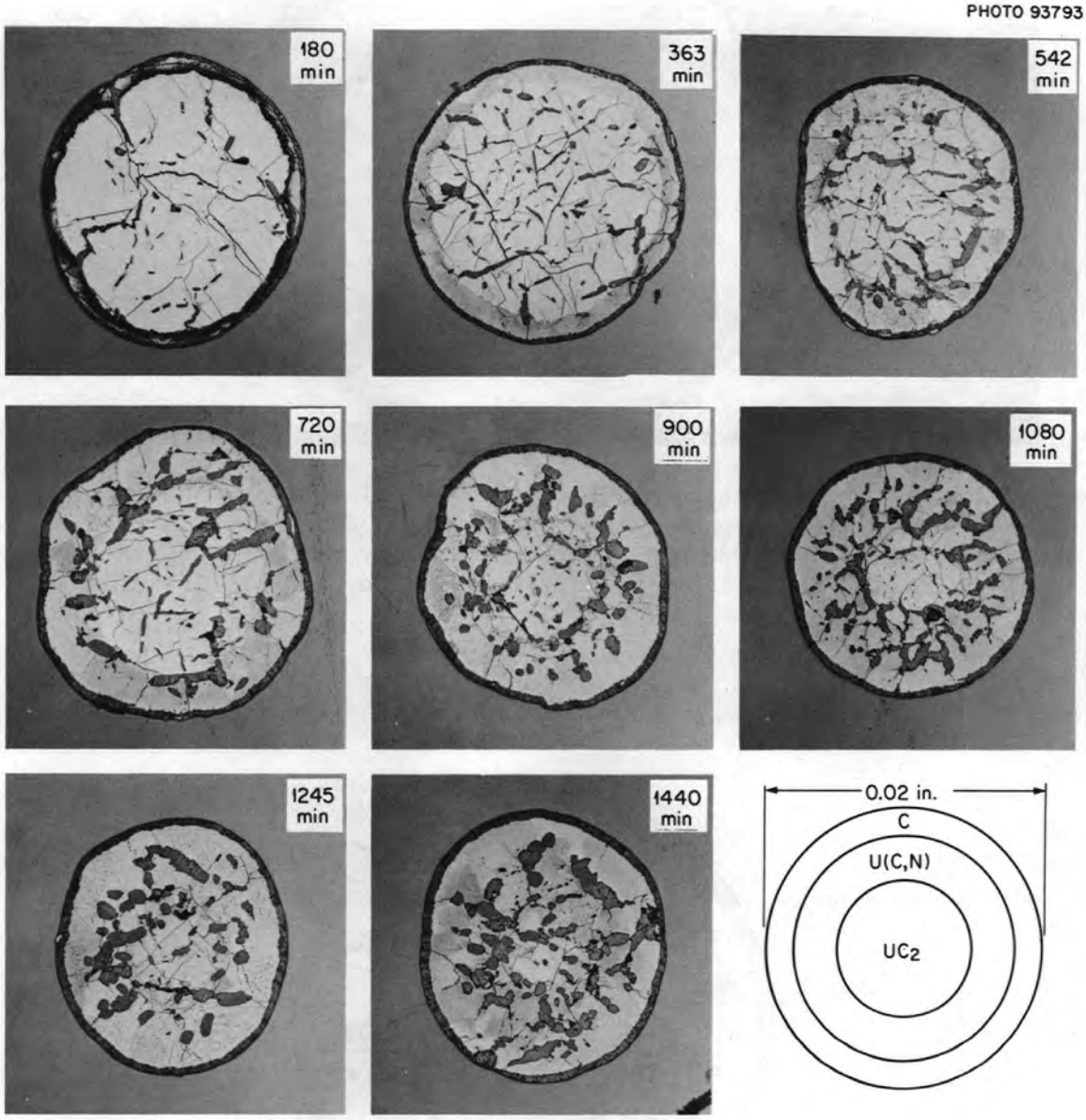

Fig. 3. Near-Equatorial Cross Sections of Approximately 500-μm-OD UC_2 Spheres Reacted with Nitrogen at 1700°C for the Indicated Times. The outer layer and internal precipitates are free carbon, the core is UC_2, and the intermediate layer is U(C,N). 150×. Etchant: 1:1:1 solution of water, acetic, and nitric acids.

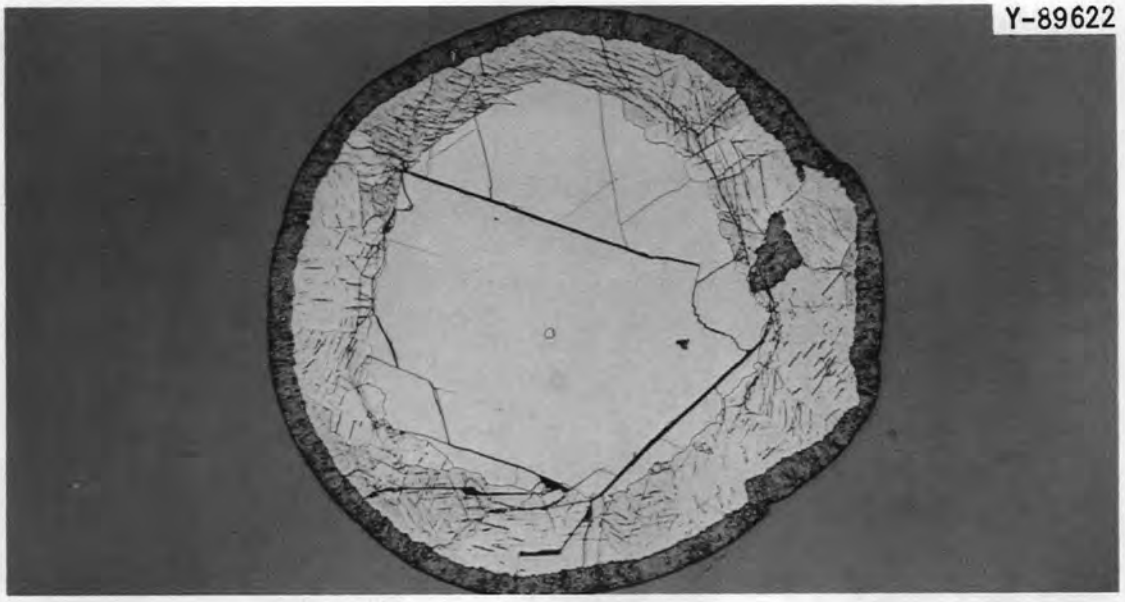

Fig. 4. Cross Section of UC_2 Sphere that Initially Contained Almost no Free Carbon. This sphere was from the same sample as that in Fig. 3 that was reacted for 1080 min. Note the smaller amount of U(C,N) present. 150X. Etchant: 1:1:1 solution of water, acetic, and nitric acids.

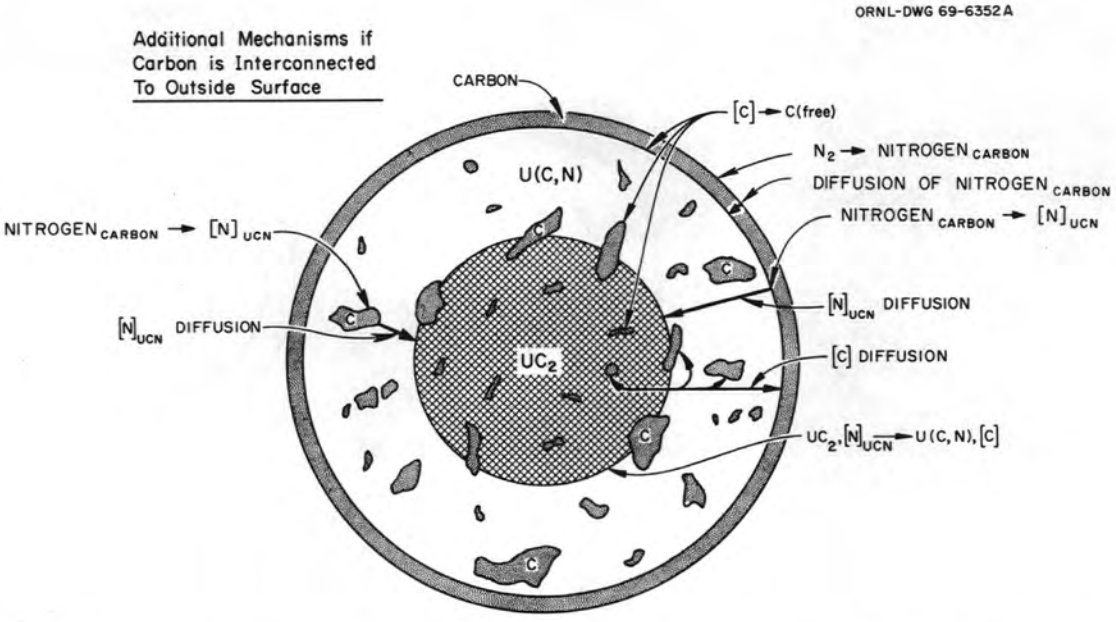

Fig. 5. Schematic Representation of the Phases Present in the Reaction of UC_2 and Nitrogen. The proposed mechanisms occurring during the reaction are also shown.

at the surface of the sphere. The interface reactions shown in Fig. 5 occur at two-phase interfaces, while the diffusion mechanisms involve the transport of carbon and nitrogen in the system. The interfacial mechanisms are proposed to be the following:*

A. N_2 to nitrogen in the outer layer of free carbon ($\text{nitrogen}_{\text{carbon}}$).

B. $\text{Nitrogen}_{\text{carbon}}$ to $[N]_{U(C,N)}$ at the interface between U(C,N) and the outer layer of free carbon.

C. $\text{Nitrogen}_{\text{carbon}}$ to $[N]_{U(C,N)}$ at all interfaces between free carbon and both U(C,N) and UC_2.

D. [C] to $C_{(\text{free})}$ at all interfaces between free carbon and both U(C,N) and UC_2.

E. $[N]_{U(C,N)}$ reacting with UC_2 to form U(C,N) and [C] at the interface between U(C,N) and UC_2.

The diffusion mechanisms are postulated to be these:

F. [C] diffusing from the interface between UC_2 and U(C,N) through the U(C,N) or UC_2 to adjacent free carbon sites.

G. $[N]_{U(C,N)}$ diffusing from the sphere surface through the U(C,N) to the interface between UC_2 and U(C,N).

H. $[N]_{U(C,N)}$ diffusing to the interface between UC_2 and U(C,N) from adjacent interfaces of free carbon and U(C,N).

I. Nitrogen diffusing through the thin outer layer of free carbon.

Mechanisms C and H are rather unique in that one of them may be rate controlling if, and only if, the free carbon served as an interconnected path for N_2 to diffuse from the surface to the interior of the sphere.

The kinetic models used for the analysis of the results for conversion versus time permitted the elimination of many of these possible

*Brackets indicate a species in solid solution.

mechanisms as the ones controlling the conversion process. Plots of the functions of Eqs. (1), (2), and (3) are shown in Fig. 6, which indicates that the mechanism controlling the reaction occurs at the interface between U(C,N) and UC_2. Only mechanisms E, F, and H can occur in this region. It was concluded that mechanism F, the diffusion of [C] from the interface between UC_2 and U(C,N) to the free carbon sites closest to the UC_2-U(C,N) interface, was controlling during the conversion of UC_2 (ref. 7). For the spheres shown in Fig. 3, these sites are at or near the interface. For spheres lacking the internal sites, such as shown in Fig. 4, the nearest free carbon site is the surface of the sphere.

The uniform internal distribution of free carbon in the microsphere therefore affected the reaction rate.[7] This distribution maintains an approximately constant carbon-to-carbon separation during the entire conversion process. This permits an approximately constant flux of carbon via Fick's first law. The flux, in cubic centimeters of carbon per square centimeter of interface between U(C,N) and UC_2 per unit of time, limits the rate of conversion of UC_2 to the region near the interface of UC_2 and U(C,N). The reaction would, therefore, follow Eq. (2) even though the diffusion of carbon was controlling the reaction. The activation energy for the diffusion of carbon was obtained for this system from the Arrhenius relation and the least-square slope, k_I, of plots such as that shown in Fig. 6. The slopes at 1500, 1600, and 1700°C and a N_2 pressure of 380 torr were fitted to the Arrhenius equation to give

$$k_I = 95.6 \exp[-78{,}000/RT] \text{ cm/s} . \qquad (4)$$

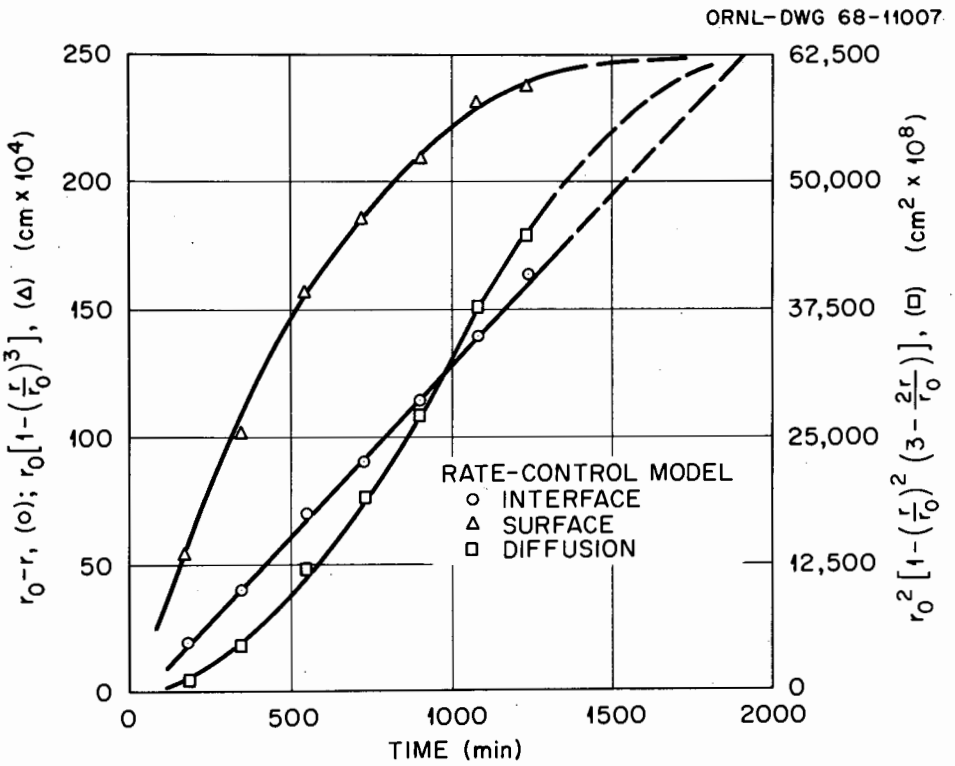

Fig. 6. The Time-Dependent Plots of the Functions in Eqs. (1), (2), and (3) for the Reaction at 1700°C of Nitrogen at 380 Torr with UC_2 Containing Free Carbon (Run A5164-54).

Carbon is consequently involved in two important effects on the reaction of UC_2 and N_2. As has been shown, one is control of the reaction by the diffusion of carbon; the second effect results from the number and distribution of sites available for the precipitation of carbon. Increasing the number of sites was observed to result in an increase in the reaction rate.

UC-N_2 REACTION

Several observations were made about the kinetics of the reaction between UC and nitrogen during a thermodynamic study of the UC-UN solid solution from 1500 to 1900°C (ref. 8). The −325 mesh, arc-melted UC was exposed to a given pressure of nitrogen in a graphite furnace and then

analyzed by chemical and Debye-Scherrer techniques. The results of this study are understood more readily by reference to the U-C-N quasi-equilibrium diagram of Fig. 7. (U_2C_3 is not shown because the kinetics for its formation are unfavorable in these experimental situations.)

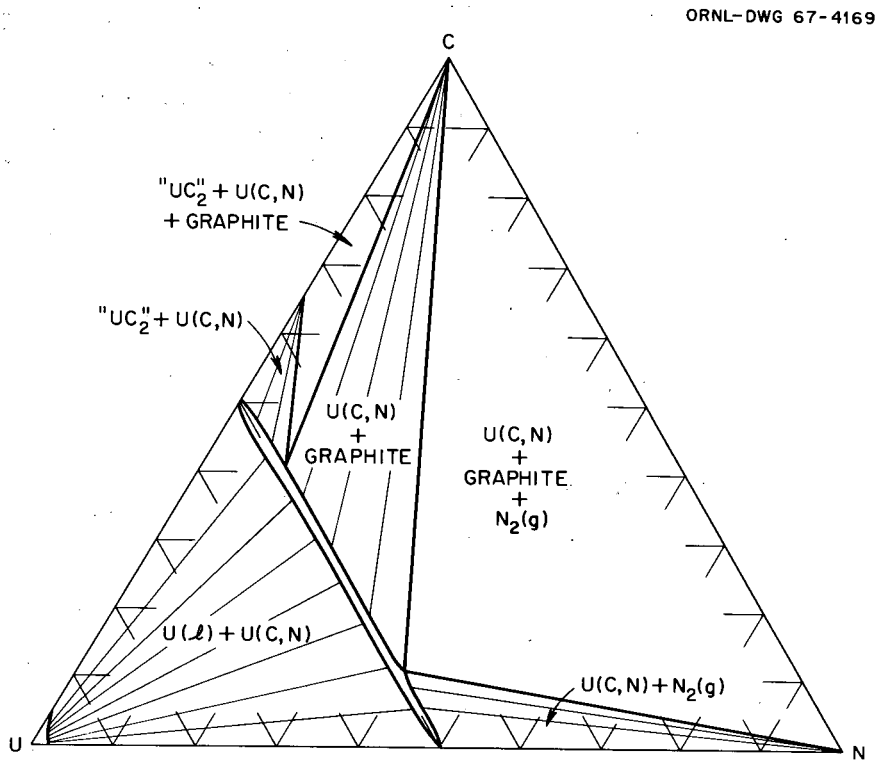

Fig. 7. The U-C-N Quasi-Equilibrium Diagram at 1700°C and a Pressure of 0.5 atm. U_2C_3 is not shown because its formation is kinetically difficult in the present experiments.

The reaction proceeded in at least three stages. In the first and most rapid stage, the UC reacted to form the high-carbon U(C,N) solution that is in equilibrium with UC_2. The carbon rejected when the U(C,N) was formed from UC reacted with the adjacent UC to form UC_2, as shown in Fig. 8, but formed little or no free carbon. The second stage began after the UC had reacted to form the U(C,N) and UC_2. The UC_2 then reacted with nitrogen to form additional high-carbon U(C,N) and free

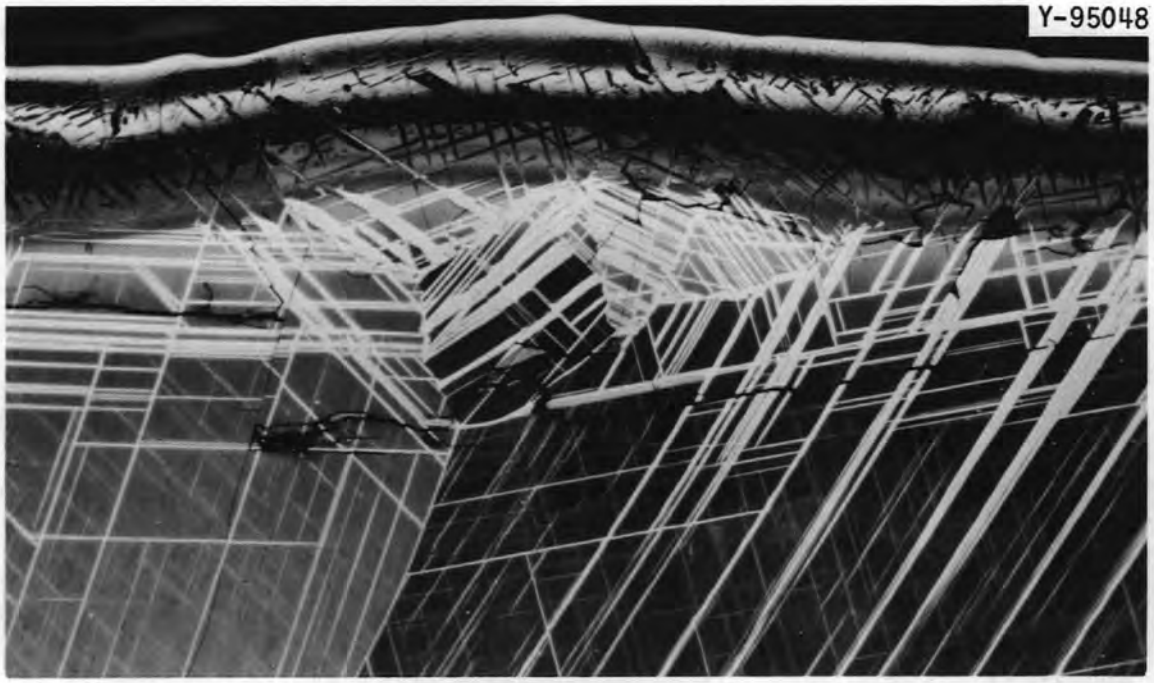

Fig. 8. The Microstructure Observed During the First Stage of the Reaction of UC and Nitrogen. The outer phase is U(C,N), the irregular phase layer is a UC_2–U(C,N) mixture, and the inner phase is essentially UC. Etchant: 1:1:1 solution of water, acetic, and nitric acids. 200×.

carbon. The third stage of the reaction began after the UC_2 had been converted. The U(C,N) reacted with nitrogen to reject more free carbon and slowly formed the nitrogen-rich U(C,N) composition in equilibrium with carbon and nitrogen. This third stage appeared to be controlled by the diffusion of the nonmetal atoms, for the x-ray results, which are representative of the surface of the material, always indicated more combined nitrogen in the U(C,N) than did the results of chemical analysis.

These results seem to fit the pattern established in the previous experiments. Again, a primary factor in the reaction appears to be the precipitation of free carbon. It is considerably slower than the formation of the UC_2 in the first stage of the reaction. The stepwise nature of the reaction is also revealing. It is apparent that the usual practice

of writing a chemical equation for the overall reaction, $UC + x/2\ N_2 \rightarrow U(C_{1-x}N_x) + xC$, reveals little about the way the reaction actually takes place or about the intermediate phases that may form.

ACTIVE CARBON

Another interesting phenomenon is the form of the free carbon that precipitates in some of these reactions between the carbide and nitrogen. The carbon can appear in a form that is chemically more active than graphite. Whether it does or not depends on the reactants and the reaction conditions. Active carbon has been observed in both the U-C-N and V-C-N systems.

The existence of active carbon was postulated from the results of a thermodynamic study of two reactions in the U-C-N system.[9] The starting materials in the first reaction were UC and N_2. These reacted to produce the U(C,N) solid solution and free carbon. The second reaction involved UN and graphite and produced U(C,N) and N_2. The reactions were performed under identical conditions of temperature and nitrogen pressure and, therefore, would be expected to give the same thermodynamic information at equilibrium.

The results of the two reactions were not always identical, however. The data for the equilibrium reaction

$$UC_{(s)} + 0.5\ N_{2(g)} \rightleftharpoons UN_{(s)} + C_{(s)}\ , \tag{5}$$

were used to evaluate the function J^{o}_{298}, where

$$J^{o}_{298} = T\left[-\ R\ \ell n\left(\frac{X_{UN}}{X_{UC}\ P^{0.5}_{N_2}}\right) - \Delta\left(\frac{G^{o}_{T} - H^{o}_{o}}{T}\right)\right]\ . \tag{6}$$

This function* is plotted in Fig. 9 versus the mole fraction of UN.

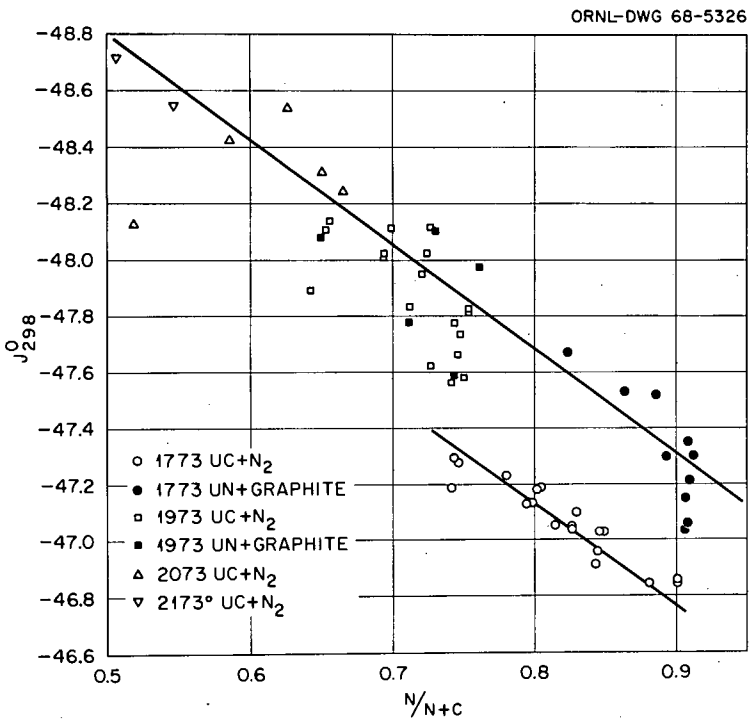

Fig. 9. The Quantity J^{o}_{298} [Eq. (6)] as a Function of the Ratio of of N:(C+N) for the Specified Reactions in the U-C-N System.

The results at 1700, 1800, and 1900°C for the reactions UC plus N_2 and UN plus graphite all give statistically the same results for the equilibrium reaction. However, a deviation was observed at 1500°C.

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*If the UC-UN solid solution were ideal and if the activity of carbon were unity, the quantity J^{o}_{298} would be identical to the heat of reaction, ΔH^{o}_{298}, for Reaction (5). Such a quantity serves as a useful means of comparing results at different temperatures since $RT\ell n\gamma$ at a particular composition will change slowly with temperature and will not change at all for an ideal or regular solution.

While the reaction of UN and graphite gives the same results as those at higher temperatures, the results for UC and N_2 give a statistically significant, lower value. At 1500°C, the carbon produced from the reaction of UC and N_2 appears to be in a state that is more active than graphite. This more active form of carbon causes the observed difference of about 500 cal in J^{o}_{298}. This difference is approximately the enthalpy of the reaction of graphite to form active carbon.

The evidence for active carbon has been substantiated by studies of vanadium carbonitride solutions.[10] The reactions studied here were the same as in the U-C-N system, except that vanadium was substituted for uranium. The reactions were carried out simultaneously in a twin crucible made from graphite. The principal analytical result obtained was the lattice parameter of the carbonitride solid solution, as shown in Fig. 10. Note that if the carbon that precipitates from the reaction of VC and N_2 is more active than graphite, then thermodynamic considerations predict that the carbonitride produced will be richer in carbon than the carbonitride from the reaction of VN and graphite. Figure 10 shows that the reaction of VC plus N_2 always resulted in a lattice parameter for the carbonitride higher than that of the reaction of VN plus graphite. The observed difference in the lattice parameter was experimentally shown not to result from errors in determinations of the lattice parameter, the kinetics of the addition or removal of carbon or nitrogen, differences in impurity levels, or temperature gradients across the twin crucible. The conclusion is that the precipitated free carbon is in a more active state than graphite.

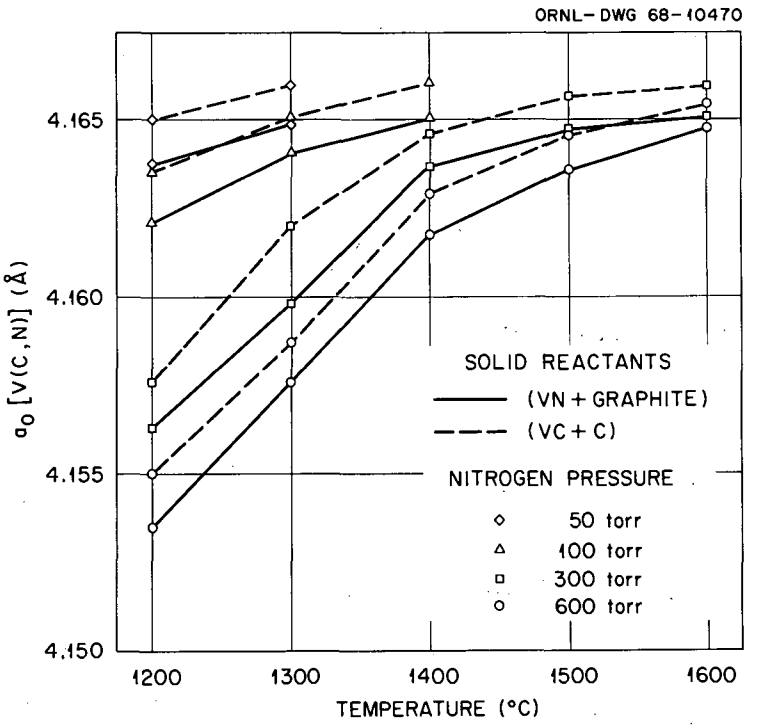

Fig. 10. The Lattice Parameter of V(C,N) Obtained by Reacting Either VN and Graphite or VC and Nitrogen at the Indicated Temperatures and Pressures.

These observations are supported by other experiments. Lewis, Frisch, and Margrave[11] observed a difference of 220 cal/mol in the combustion of pyrolytic carbon annealed at 2200 and 3600°C. Browning and Emmett[12] made equilibrium measurements in the system carbon-methane-hydrogen and found that carbon obtained from the decomposition of Fe_3C had a free energy about 300 cal/mol higher than that of graphite.

The effect of active carbon could be important in other systems. In the study of metal carbide vaporization reactions that produce free carbon, the enthalpy of formation calculated by assuming the free carbon to be graphite may be as much as 0.5 kcal/mol of carbon too negative unless the carbon could precipitate on preexisting graphite particles. In a peritectoid decomposition of solids that gives free carbon as a

product, the decomposition temperature would be lowered if active carbon were precipitated.

CONCLUSIONS

The results of the studies reviewed in this paper permit the following general conclusions about specific reactions in the U-C-O-N system between 1400 and 2000°C:

1. The primary rate-controlling mechanism in the reaction of UO_2 with graphite, UC with N_2, and UC_2 with N_2 was the diffusion of a nonmetal atom through one of the uranium compounds in the system.

2. Carbon has a significant role in these reactions. The observed effects are listed below.

   (a) Diffusion of carbon controls during the conversion of UC_2 by N_2 to U(C,N).

   (b) An initial distribution of free carbon in the UC_2 increased the rate of the reaction of UC_2 with N_2.

   (c) Carbon rejected in the first stage of the reaction of UC and N_2 combines with unreacted UC to form UC_2; free carbon appears only in the later stages of this reaction.

   (d) Below about 1600°C, the free carbon produced by these reactions can be thermodynamically more active than graphite. This behavior was shown to affect the results of thermodynamic and lattice parameter studies.

3. The physical configuration of the components in a system can have significant effects on the reaction rate. The following effects were noted:

(a) In the reaction of graphite with UO_2 spheres, the reaction rate was 2 to 5 times faster when the UO_2 maintained contact with the surface of the sphere.

(b) In the reaction of UC_2 with N_2, the initial distribution of free carbon in the UC_2 was observed to affect the rate by as much as a factor of 20.

4. The reaction to the final equilibrium product may occur in several stages, as was observed in the reaction of UC with N_2. In this reaction, these stages involved the appearance and subsequent reaction of intermediate phases or compositions.

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