INTRODUCTION

The NERVA nuclear rocket project involved a series of small, high-temperature, ultra-high-power reactors in which hydrogen was heated above 2000°C as it passed through small holes which ran the length of the reactor. The UC₂ was in the form of small spherical beads ~100 μm diameter and coated with 22 μm of pyrolytic carbon (PyC). The fuel matrix was polycrystalline graphite. Since the graphite was corrosively and erosively attacked by the hydrogen at these temperatures, a refractory carbide coating was applied to the inner surface of the hydrogen channels to protect them from attack. Since the fuel elements were very complex in shape and were extruded with coated fuel beads mixed into the plasticized mass, a certain percentage of fuel beads were broken in extrusion and in later machining operations. During storage before testing, moisture in the air caused these bead remnants to react causing the coating to crack from the resulting volume expansion. Since most previous hydrolysis work had involved reactions between UC₂ and liquid water and had produced only very limited kinetic data, this study was done. The study focused on determination of the rate of hydrolysis of UC₂ over a fairly wide range of temperature and water vapor partial pressures, and also included a rather thorough examination of the reaction products and nature of the reaction by optical and scanning electron microscopy.

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EXPERIMENTAL AND RESULTS

The first slide[1] shows the all-glass experimental apparatus. Pure He was bubbled through a carefully thermostatted trap containing distilled water. Following its humidification, the helium was flowed over the UC₂ sample which was held in a platinum-pan suspended from a Cahn RG recording balance. The UC₂ sample was held at a fixed temperature in the range 50-100°C by a constant-temperature bath. After its passage through the reaction chamber, the water vapor was removed from the He, which then flowed through a gas chromatograph where the major gaseous reaction products (H₂, C₂H₆, CH₄) were determined periodically.

Most of the work was done on bare UC₂ fuel bead cores containing depleted uranium. Some work was also done on artificially defected beads. All bare cores were kept in dry atmospheres until use to avoid premature hydrolysis.

A large number of experimental runs were made. The next slide[2] is a typical series of fractional weight gain curves. The corresponding rates are then shown in the next slide[3]. A typical series of gas production rates (for hydrogen) is shown in the next slide[4]. The maximum in gas production corresponded fairly well to those in weight gain rate. By using the maximum rate for a wide series of temperature and water vapor partial pressures, a set of Arrhenius plots were constructed. These are shown in the next slide[5]. The mean value of the activation energy is 6.07 kcal/mole ±0.70 kcal/mole.

Microstructural examination played an important role in the study. The original beads were characterized by optical and SEM techniques, and examinations continued throughout the study to improve our understanding of the hydrolysis process. The next slides[6,7] show some SEM photographs of as-received beads, while the following slides are optical micrographs of them[8,9]. Beads from various stages in the hydrolysis were collected and examined by both techniques. The next slide[10] shows a series of SEM photographs which show the reaction product UO₂ as growing in columns from the original core. Comparison optical work, shown in the next slide[11], helped to examine fine details of the columns as they grew from the core.
These microstructural studies revealed that the presence of flakes of graphite remaining on the bead surface played an important part in the nucleation of $\text{UO}_2$ columns, probably by acting as sites for water vapor adsorption. The next slide shows this very well[12]. The precipitated graphite was stripped in a fluidized bed of alumina. Hydrolysis runs on these stripped beads showed a longer induction period, probably due to the formation of a small amount of product to act as an adsorbent.

Since broken coated beads were the original source of difficulty, it was necessary to examine the microstructural aspects of this most relevant case. The controlled cracking of graphite coatings on beads only about 100 $\mu$m in diameter is rather difficult. The beads were finally damaged by allowing them to press against one another under hydrostatic pressure. In practice, 20,000 psi applied pressure produced cracked coatings in 60% of the beads sampled. The hydrolysis of cracked beads is shown graphically in the next two slides[13,14]. The first photo shows the defected bead, the second after 30 minutes hydrolysis at 100°C and 75.6 torr water vapor, corresponding to a weight gain of 15%. The third photo shows a bead hydrolyzed under the above conditions for 2 hours, corresponding to a 61% hydrolysis. It is seen that the porous $\text{UO}_2$ columns easily break the cracked shell in a manner similar to the way they crack their surrounding precipitated graphite when hydrolyzed. Hydrolysis of defected beads was similar in rate to the uncoated beads when a correction was applied for the fraction defected.

**CONCLUSIONS**

1. The dependence of the rate of hydrolysis of uranium dicarbide fuel cores on temperature and water vapor pressure has been determined. The fractional weight change accompanying hydrolysis, even though complicated by the formation of a complex hydrocarbon wax, can be used to describe the true rate of reaction.

2. A plot of the maximum rate of hydrolysis versus reciprocal temperature is linear for the four water vapor partial pressures investigated. The activation energy for the hydrolysis reaction is $6.07 \pm 0.70$ kcal/mole.

3. The major gaseous reaction products accompanying hydrolysis have been identified as $\text{C}_2\text{H}_6$, $\text{CH}_4$, and $\text{H}_2$. 
4. The stages in the hydrolysis of uncoated UC$_2$ cores and the same cores after stripping of precipitated graphite have been defined by thermo-gravimetric means and by microscopy. In the as-received beads, hydrolysis products form under the precipitated graphite and lift it away as the process becomes more general. In stripped beads, there is an induction period associated with the development of sufficient reaction product to act as an adsorbent. The reaction then continues in a manner essentially identical to unstripped cores.

5. PyC-coated beads were successfully defected by hydrostatic pressing. These beads hydrolyzed in a manner similar to uncoated beads except for PyC coating, which was apparently easily broken and pushed away as the reaction proceeded.
FIGURE 1

System Used for Hydrolysis Runs in This Work.
FIGURE 3. Fractional Weight Gain in the Hydrolysis of UC₂ with pH₂O = 55.3 Torr.
FIGURE 4. Rate of Hydrolysis of UC$_2$ with p$_{H_2O}$ = 55.3 Torr.
FIGURE 5. Hydrolysis of UC₂ with $p_{H_2O} = 55.3$ Torr, $H_2$ Production.
FIGURE 17. Hydrolysis of UC$_2$. Effect of Temperature and Water Vapor Pressure.

$P_{H_2O}$ (Torr)

- $\square$ 23.8
- $\triangle$ 32.5
- $\bigcirc$ 55.3
- $\bigtriangleup$ 75.6

$\ln$ [max. rate (hr$^{-1}$) $\times 10^2$] vs. $10^3/T$ (°K)
FIGURE 33. Scanning Electron Micrographs of Coated UC₂ Particles.
FIGURE 35. Optical Micrographs of an Uncoated UC₂ Particle. Stain-Etched, Bright Field Views of the Same Particle. Arrow in (b) shows particulates on the surface.
FIGURE 38. Representative Low-Magnification (210X) Scanning Electron Micrographs from the First Five Hydrolysis Runs, Respectively.
FIGURE 39. Representative Optical Micrographs (252X) of Hydrolyzed Fuel Beads from the First Five Hydrolysis Runs, Respectively.
(a) 40°C, 60 min., Initial Lifting of Precipitated Graphite Coating (arrow), 1000X

(b) 40°C, 60 min., Profile View of Reaction Product Columns. 10,000X

FIGURE 43. Scanning Electron Micrographs Showing Stages of Hydrolysis.
FIGURE 59a. Optical Micrograph of 3M-N-15 Coated Beads Defected at 20,000 psi.

FIGURE 59b. Scanning Micrograph of 3M-N-15 Coated Bead Defected at 20,000 psi.
FIGURE 60.  Scanning Electron Micrograph of Coated, Defected Bead Hydrolyzed 30 Minutes.

FIGURE 61.  Scanning Electron Micrograph of Coated, Defected Bead Hydrolyzed 2 hours.