COO-2712-1

STUDIES OF MECHANICAL PROPERTIES AND IRRADIATION DAMAGE NUCLEATION OF HTGR GRAPHITES

PROGRESS REPORT

FOR PERIOD JUNE 1, 1975 - JANUARY 31, 1976

P. A. THROWER

The Pennsylvania State University
University Park, Pennsylvania 16802

February 1976

PREPARED FOR

The U. S. Energy Research and Development Administration

Under Contract No. E(11-1)-2712

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed or represents that its use would not infringe privately owned rights.

DISCLAIMER

ABSTRACT

An apparatus has been constructed for the examination of the effect of compressive stress on the reaction of graphite with a gaseous mixture of helium, carbon monoxide, carbon dioxide, and water vapor. The system allows for the concentration of each constituent to be independently varied and continuously monitored. Concentrations of CO and CO_2 are measured using infrared gas analyzers and the H_2O content by means of a trace moisture analyzer. The graphite specimen is 1-1/2" long x 3/4" diameter and is stressed by dead weight loading between an alumina hammer and anvil. The load is applied by a simple lever arm arrangement through a metal bellows on top of a mullite lined furnace. The reaction rate is determined via the concentrations of CO and CO_2 in the effluent gas. Initial set up and testing of the apparatus is almost completed and initial experience is that the apparatus meets the requirements of the proposed research.

Samples of two pyrolytic graphites have been doped with boron to concentrations of 30 and 400 p.p.m. for irradiation at 1300°C later in the year in order to determine the possible effect of boron on vacancy nucleation at such high temperatures.

1. Irradiation Damage Studies

Because of delays in irradiation programs the samples required for the investigation outlined in the original proposal will not be required until June 1976 with irradiation commencing in the following August. During the past eight months effort has therefore been restricted to preparing samples for the reactor.

Crucibles of a high purity graphite have been doped with boron (B^{11}) to concentrations of 30 and 400 p.p.m. by weight. Specimens of two pyrolytic graphites with average basal plane crystallite sizes 1μm and 25μm have been impregnated with the B^{11} by heating for two hours at 3000°C in the doped crucibles. Earlier experiments (Mayer et. al., Phil. Mag. 19, 701, 1969) show that as a result of this procedure the graphite specimens have boron concentrations in the range ±50% of that of the crucible. Facilities are not available to accurately determine the exact boron concentrations in the samples, indeed they may vary from one sample to another, but for the purposes of nucleation experiments the above accuracy limits are acceptable.

In the remainder of the current contract period some effort will be made to characterize the samples to be irradiated so that any significant dimensional changes as a result of the irradiation may be subsequently measured.

2. Effect of Compressive Stress on Oxidation Rate

A. Apparatus

Since the project was initiated the major effort has been directed to designing and constructing a system for applying compressive loads to graphite samples while they are reacting, at temperatures up to 1000°C, with a gaseous mixture of helium with added small concentrations of CO, CO_2 and H_2O, and at the same time accurately determining the effect of this stress on reaction rate.

Major items purchased for the system were a six-point strip chart recorder, infrared gas analyzers to measure concentrations of CO and CO_2, and a trace moisture analyzer. A furnace has been custom-made to our design and requirements and a rig for applying the compressive load has been constructed in our engineering workshops. Failure of manufacturers to meet promised equipment delivery schedules by as much as three months has hindered the commissioning of the completely assembled apparatus until the time of writing.

A diagram of the apparatus is shown in Figure 1. Three gases are used; pure He, He + 1000 p.p.m. CO, He + 1000 p.p.m. CO_2, the latter two being slightly heated at the bottom of the cylinders to prevent separation. These are first passed through tubes of "Ridox" (Fisher Chemical Company) in order to remove any residual oxygen (manufacturers claim a 99% removal in conditions such as used here), and flow rates are measured using flowmeters in order to control the ultimate concentration of each gas. Thorough mixing is ensured by then passing the mixture through U-tubes filled with small glass beads. Water vapor is then added to the gas mixture by passing over ice at a controlled temperature.

The ice bath consists of a cylindrical copper vessel within which are a number of concentric slotted copper cylinders arranged such that slots in adjacent cylinders are diametrically situated. Each cylinder is sealed to the top of the vessel, which is filled with water to within 0.25 inches of the top thus leaving a tortuous path for the gas at the top. The partially filled cylinder is then placed in a refrigerant system composed of commercial automobile antifreeze and acetone. Using a Multi-cool refrigeration system (FTS Systems Inc.) the ice temperature may be controlled within the range -45°C to 0°C to ±0.1°C. By varying the ice temperature one varies the H_2O vapor pressure and hence the water vapor content of the reactant gas.

The gas mixture is then again stirred by passing through a bed of glass beads before a small fraction is bled off for analysis by a Beckman trace moisture analyzer which has a sensitivity of less than 1 p.p.m. and typically has an accuracy of 50 ± 2.5 p.p.m.

The remaining reactant gas then passes directly to the furnace, or may be diverted to the infrared gas analyzers in order to obtain an accurate determination of CO and CO_2 concentrations.

The furnace is custom built for this experiment. The interior is lined with Mullite with universal tube seals at the ends which have been modified for gas inlet and outlet and a bellows at the top to allow for strains introduced by the compression rig. The anvil and ram used to apply pressure to the sample are of 1" diameter alumina. Chromel-alumel thermocouples are used to monitor both specimen and furnace temperature and are sheathed in alumina. The design of the furnace is such that the risk of any surrounding materials or contaminants influencing the reaction is minimized. The furnace, and hence sample, temperature is controlled using a Eurotherm power supply control package.

After reacting with the graphite sample in the furnace the effluent gas is passed through the infrared gas analyzers and the CO and CO_2 concentrations measured.

During the experiment a six point recorder monitors the sample and furnace temperatures, the moisture content of the reactant gas and the CO and CO_2 concentrations of the effluent gas. At any time the reactant gas may be made to bypass the furnace so that its CO and CO_2 concentrations may be measured.

In addition the system as designed and set up contains four standard calibration gas mixtures of He + 200 p.p.m. CO, He + 800 p.p.m. CO, He + 80 p.p.m. CO_2 and He + 400 p.p.m. CO_2. These are used at the beginning and end of an experiment to check the calibration of the gas analyzers.

The apparatus described has been designed to allow the graphite reaction rate to be continuously monitored via the concentrations of CO and CO_2 in the effluent gas. This will allow any effects of stress on the reaction rate to be immediately discernable. In addition any effect of short or long term cycling can be observed without undue delay.

The apparatus for applying the load to the sample has been constructed from aluminum bar (2-1/2"x3/4" section) and is a simple arm lever device with dead weight loading, (Figure 2). The advantage of this system is its simplicity and associated economy, however it does not allow a load to be applied gradually and continuously. At present this does not appear to be a disadvantage. The immediate aim of this work is to investigate the effect of compressive stress on oxidation rate, but it should be possible to later modify the apparatus to allow the effect of tensile stresses to be investigated, such as used by Krefeld et. al. (ONRL-CONF-730601).

B. Materials

Samples to be investigated in the initial phases of this research are of Stackpole Carbon Company 2020 grade such as may be used for HTGR core support posts. The samples are 1-1/2" long x 3/4" diameter and fifty samples have been prepared. The relative positions of the samples in the original graphite log are accurately known so that samples may be paired for strength measurements indicative of strength before and after the reaction. Samples of the same size are also being prepared from Great Lakes Carbon Company H440 grade and in addition smaller samples of both grades are being prepared 1/2" long x 1/4" diameter.

C. Initial Results

At this stage of the research there are no results which may be reported with any certainty. We have just concluded the setting-up and testing of the apparatus and all indications are that we have a very effective system. There still remains some calibration of the loading apparatus to

be accomplished.

It is hoped to have an adequate set of preliminary data by the end of April for presentation at the Carbon '76 meeting in Baden-Baden, West Germany in July of this year. A copy of the Conference paper will be submitted to ERDA when prepared, assuming results at that time make such a paper possible.

3. Personnel

P. A. Thrower (principal investigator) has devoted 20% of his time to the project during the period reported here and is expected to do so during the remainder of the current contract period.

D. Marx (graduate assistant) 50% time for 9 months (September 1975 - May 1976).

J. Bognet (graduate assistant) 50% time for 6 months (December 1975 - May 1976).

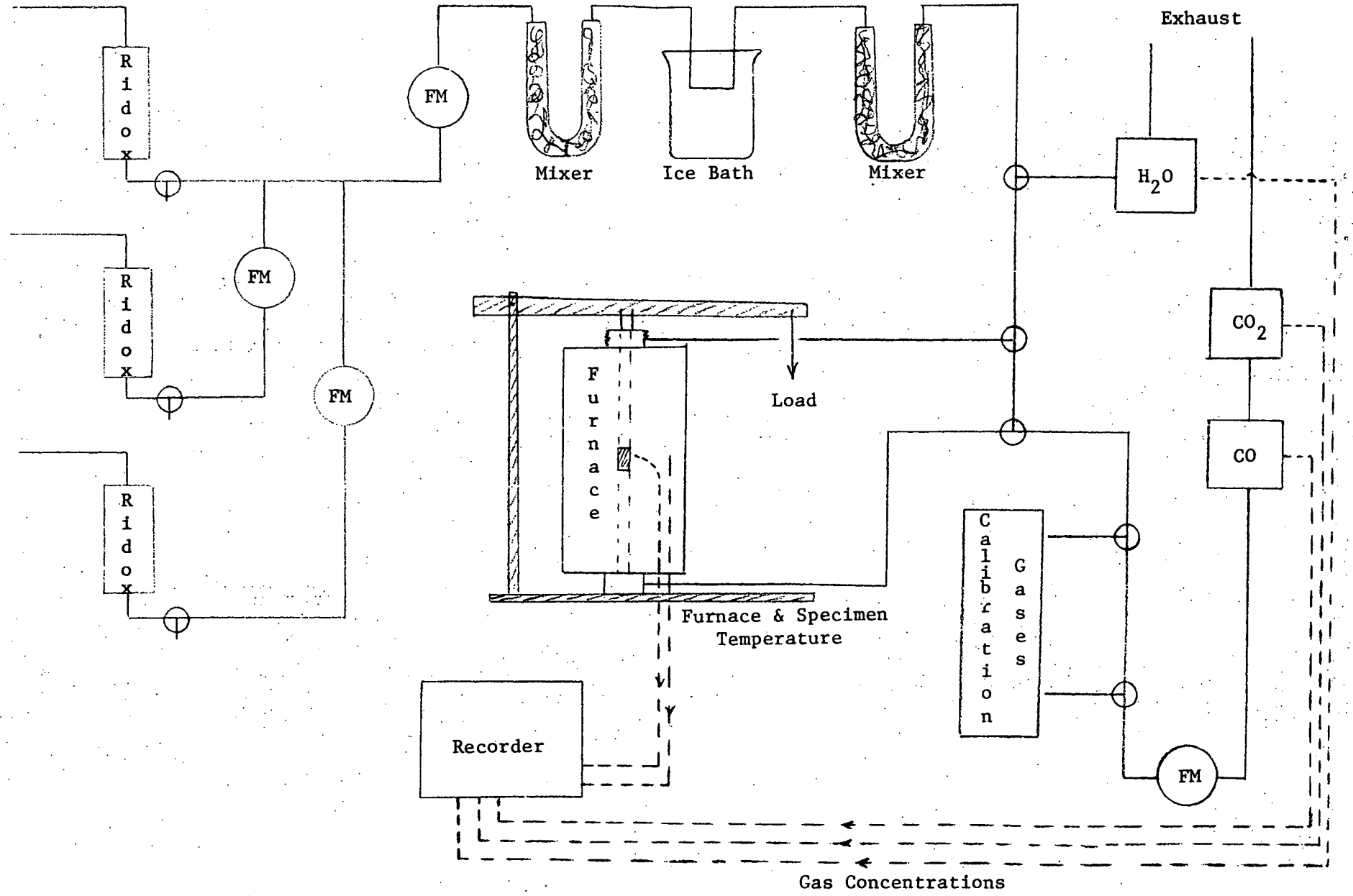

Figure 1. Diagram of Stress-Oxidizing Apparatus.

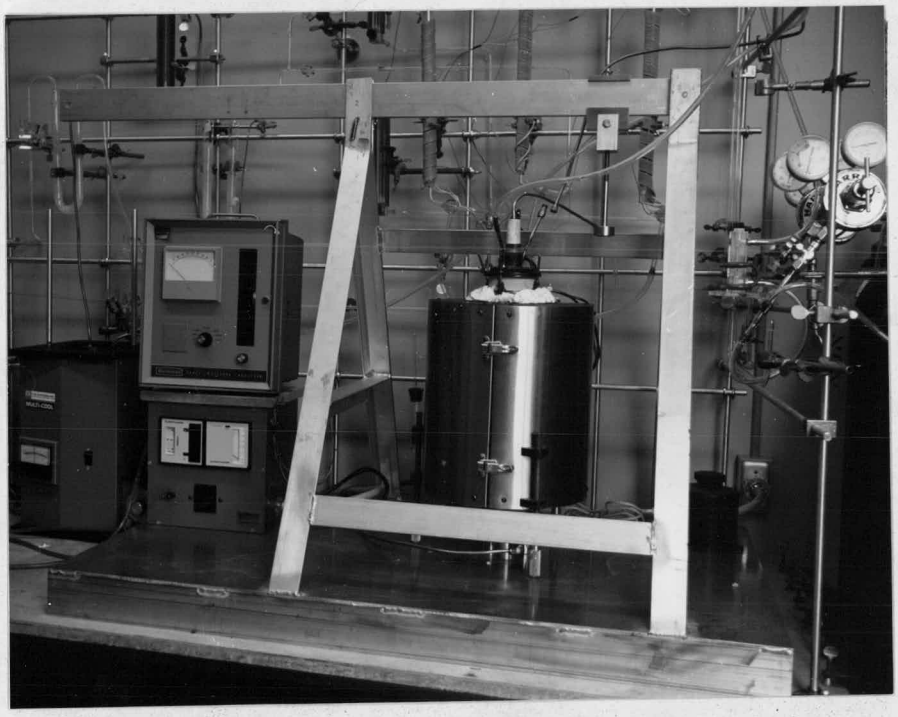

Figure 2. Dead Weight Loading Apparatus.