

**MASTER**

C00-2712-6

STUDIES OF MECHANICAL PROPERTIES  
AND IRRADIATION DAMAGE NUCLEATION OF HTGR GRAPHITES

PROGRESS REPORT

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### ABSTRACT

Irradiation damage effects to highly oriented pyrolytic graphite by 1.5, 5.5 and 15 MeV neutrons are briefly described. A complete account is given in C00-2712-7.

Studies of the effects of oxidation on the structure and strength of Stackpole 2020, Great Lakes H440 and POCO AXF-5Q graphites have been continued using  $H_2O$  vapor as the oxidant. The effect of burn-off on compressive strength is similar to that of  $CO_2$ , but structural effects are quite different.

The kinetics of the  $C-CO_2$  reaction are being studied using low  $CO_2$  partial pressures in a total pressure of one atmosphere. The necessary modifications to existing apparatus have been made and experimental work is commencing.

A. Overall Project

1. Personnel and Tasks.

P. A. Thrower, principal investigator: electron microscopy of irradiated graphites; oxidation studies.

D. R. Marx, graduate student (anticipated completion of Ph.D., Summer 1979). Studies of the oxidation of graphite by  $\text{CO}_2$  at atmospheric pressure.

G. Mathew, graduate student (anticipated completion of M.S., Fall 1979). The effect of iron additions on graphite strength and oxidation effects.

2. Publications

A paper on "Annealing of Neutron Damage in Graphite Irradiated and Stored at Room Temperature" by P. A. Thrower and W. J. Gray (Pacific Northwest Lab) has been submitted to "Journal of Nuclear Materials."

A paper on "The Effect of Oxidation in Air  $\text{CO}_2$  and  $\text{H}_2\text{O}$  on the Compressive Strength of Graphite" by P. A. Thrower, J. C. Bognet and G. Mathew is in preparation.

A paper entitled "TEM Studies of Graphite Irradiated at Different Neutron Energies" (COO-2712-7) will be presented at the Fourteenth Biennial Conference on Carbon to be held at Penn State, June 25-29, 1979. Submission to 'Carbon' is anticipated after some further work.

B. Task Summaries

1. P. A. Thrower

Graphites irradiated at high temperatures were again not available during the period covered by this report. There is no certain date for their availability. Materials used in studies of Young's modulus changes at low

neutron fluences using different neutron spectra have been examined. Annealing studies of these materials are about to begin.

#### G. Mathew

Look at the effect of  $H_2O$  vapor oxidation on the three graphites used in earlier studies has been completed. Studies of the effects of iron ( $Fe_2O_3$ ) additions to the graphite binder/filler mix on the resultant material and its susceptibility to oxidation are just beginning.

#### D. R. Marx

Will finish work for Ph.D. thesis by studying the kinetics of the  $C-CO_2$  reaction at atmospheric pressure using a closed continuously recirculating system. During the past year the apparatus has been rebuilt and final testing is currently underway.

### 2. Previous Studies

Previous studies on the effect of oxidation on strength were concerned with the effects of air and  $CO_2$ . This report details results of studies using  $H_2O$  as the oxidizing agent. Studies of the possible enhancement of oxidation rate as a result of an applied stress have been terminated. Current efforts are aimed at obtaining reliable data for the  $C-CO_2$  reaction using small partial pressures of  $CO_2$  (50-400 ppm) in helium at atmospheric pressure.

### 3. New Tasks

New tasks for the completion of this project are :

- (I) to determine the effect of some impurity additions on the oxidation of graphite and accompanying strength loss.
- (II) to investigate the  $C-CO_2$  reaction at atmospheric pressures.

## C. Discussion of Results

### 1. Irradiation Damage Studies.

Complete accounts of the irradiation damage studies are given in the accompanying documents, "Annealing of Neutron Damage in Graphite Irradiated and Stored at Room Temperature", by W. J. Gray and P. A. Thrower (PNL-2676) and "TEM Studies of Graphite Irradiated at Different Neutron Energies" (COO-2712-7).

The effects of neutron damage using neutrons of energies 1.5, 5.5, and 15 MeV do not appear significantly different, but it is expected that any differences may be revealed by annealing and further electron microscope examination. The results of these studies will be available before the summer and it is expected to make an oral report on the results at the 14th Biennial Conference on Carbon.

### 2. Effect of Oxidation on Compressive Strength.

Earlier work on graphite oxidation involving oxygen (air) and carbon dioxide showed that the amount of oxidation weight loss required to produce a 50% strength reduction varied between 10-25% depending on the graphite and the oxidizing gas. In the case of the conventional binder-filler graphites (H440 and 2020) oxidation in air produced greater strength reduction than oxidation in CO<sub>2</sub>, whereas for POCO AXF-5Q the situation was reversed. The effect of water vapor attack has been studied in more recent experiments.

Experimental conditions were maintained essentially the same as in earlier work. Samples 0.25" diameter x 0.50" long were held in pyrex tongs in a 1.75" internal diameter mullite furnace tube. Furnace

temperatures were maintained between 900°C and 1000°C. The oxidizing gas was obtained by passing helium through a fritted disc into a gas washing bottle filled with water. The water temperature was controlled by immersing the bottle in a constant temperature bath (Excal 300) at either 40°C or 60°C. Temperature control was better than  $\pm 0.5^\circ\text{C}$ . Resulting  $\text{H}_2\text{O}$  vapor pressures were 55 and 150 mmHg respectively. Gas flow rate past the sample was calculated to be 3.2 mm/sec.

The above conditions were chosen because they gave good uniform erosion throughout the samples, except for AXF-5Q. It was earlier found impossible to obtain uniform erosion of AXF-5Q using  $\text{CO}_2$  or air, presumably because of the much smaller pore size ( $0.45 \mu\text{m}$ ) in this material.

Plots of compressive strength versus burn-off for the three graphites are shown in Figures 1 to 3. In all cases the plots closely follow those obtained previously for  $\text{CO}_2$  oxidation.

The burn-offs required to produce a 50% strength loss may be compared with those given in Table I of last year's report (COO-2712-5). Again the similarity with  $\text{CO}_2$  is evident.

Burn-Off(%) Required to Produce a 50%  
Loss in Compressive Strength

	<u>Air</u>	<u><math>\text{CO}_2</math></u>	<u><math>\text{H}_2\text{O}</math></u>
H440	9	14	12
2020	10	13	13
AXF-5Q	25	15	13



Mercury porosimeter measurements showed that there are strong differences between  $H_2O$  and  $CO_2$  oxidation despite their similar effects on strength. For POCO AXF-5Q, there appears to be an enlargement of the whole pore spectrum, i.e., the curve (Figure 4) shifts over to the left, and there are some very large pores generated, presumably near the specimen surface. Scanning electron microscope observations reveal attack to be quite uniform across the sample but very localized.

Figure 5 shows a complete cross sectional view of a fractured 0.25" diameter specimen. The sizes of oxidized pores near the center are somewhat smaller than at the edges but oxidation has occurred very locally to create these pores. Sample burn-off in this instance is 16.5%, the great majority of which is accounted for by the opening of these macropores (<200  $\mu m$  diameter). It is interesting to note that the oxidation rate used here is the same order as that used in earlier studies (air and  $CO_2$ ), but that the burn-off is much more uniform here and that, unlike the earlier studies, there is no significant surface erosion, i.e., the sample diameter is not significantly changed.

It therefore appears that oxidative attack by  $H_2O$  vapor is more towards the chemical control region of reactivity and the influence of diffusion, or mass transport, phenomena is much less than for air and  $CO_2$ .

Higher magnification SEM studies show that several, although not all, of the macropores produced by oxidation have a small quantity of ash in them. Figures 6 and 6a are enlargements of pore A in Figure 4. There is obviously a channel leading from this pore, presumably to connect to another one, and some residue (bright contrast) which has not yet been identified because of difficulties with it being hidden in the hole. However, it looks very similar to Fe/Ca/Si ash seen on the surface

of oxidized graphites containing large amounts of impurity; (AXF-5Q contains, in ppm, 40 Fe, 50 Ca, 50 Ti, 100 Si, 300 V, 50 Ni, 100 Zn).

Comparison of particle morphology with AXF-5Q oxidized in air and  $\text{CO}_2$ , shows that all three are quite different. Particles here do not exhibit the ragged outline of those oxidized in  $\text{CO}_2$ , neither do they have the well defined, smooth outlines of particles oxidized in air. Obviously, the mode of attack is quite different for all three gases, while  $\text{CO}_2$  and  $\text{H}_2\text{O}$  produce similar effects of strength reduction versus burn-off.

Oxidation of H440 and 2020 obviously occurs preferentially at the binder leaving filler particles in sharp relief. The larger filler particles and pores are evident in H440 as compared to 2020 (Figures 7 and 8). Layer plane edges are smooth and not scalloped, as in earlier observations of  $\text{CO}_2$ -oxidized material.

It is therefore clear that there are marked microscopic structural differences between samples of the same graphite oxidized in air,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The reason for these differences is not yet clear.

### 3. Oxidation Kinetic Studies.

The studies of the effect of compressive loading on oxidation rate have been terminated, it having been concluded that there is no measurable effect.

The apparatus has now been modified to enable data on the kinetics of the carbon- $\text{CO}_2$  reaction to be obtained. The experimental method involves recirculating the reactant gas past a graphite specimen. An all-glass recirculating pump has been constructed to circulate the gas in the chamber through the gas analysis system and back through the reaction chamber. A record of the disappearance of reactant gases and the ap-

pearance of product gases is made on a stripchart recorder. This design allows continuous monitoring of the progress of the reaction in a completely enclosed system. The total gas pressure is one atmosphere and sample size can be as large as 0.75" diameter x 2" long, thus eliminating the restrictions imposed by the microbalance systems normally used for reactivity studies.

Experiments will involve highly purified graphite AXF-5Q which has a specified total impurity content of less than 5ppm. Reactant gases are passed through scrubbing systems for the removal of water vapor,  $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{CO}$ , and  $\text{H}_2$  as required, and are preheated before being introduced to the reaction vessel. A high vacuum system is used to remove adsorbed oxygen from the surfaces of the sample before the reaction commences.

Results from this work are beginning to be available and will be reported in detail in the final report.

#### D. Future Work.

Three graphites have been manufactured at the Oak Ridge National Laboratory using low sulfur A-240 Ashland pitch. The pitch was coked at  $495^\circ\text{C}$ ; calcined at  $1000^\circ\text{C}$  and ground to a particle size of  $<1000\ \mu\text{m}$ .

$\text{Fe}_2\text{O}_3$  was added to the binder (2.7% S A-240 pitch) to give 0, 1 and 2% final iron contents in the mix. The molded blocks were baked to  $850^\circ\text{C}$ , impregnated and rebaked twice using the same pitch as the impregnant, and then graphitized to  $2500^\circ\text{C}$ .

These graphites are already being used to investigate the effects of Fe on the oxidation behavior of graphite. Further similar blocks are being manufactured to study the catalytic effect of vanadium and calcium as added impurities.

In the manufacturing process it was found that the iron was lost from the graphite unless a significant amount of sulfur was present. For this reason a second set of iron-doped samples is being prepared. The ones presently being investigated have only 0.1% Fe retained in the material with the original highest Fe content (2%). The other materials have been lower iron contents.

During the final year of the project, these materials will be used to study catalytic effects on oxidation reaction rate and on the accompanying strength reduction.

Budget Balances on May 31, 1979

(estimated)

Salaries and Wages	\$13,334
Supplies and Materials	14,100
(\$8,000 to be paid to ORNL for graphites)	
Publications	200
Travel	2,100
Other	5,700

These funds should be adequate for completion of the work outlined earlier.

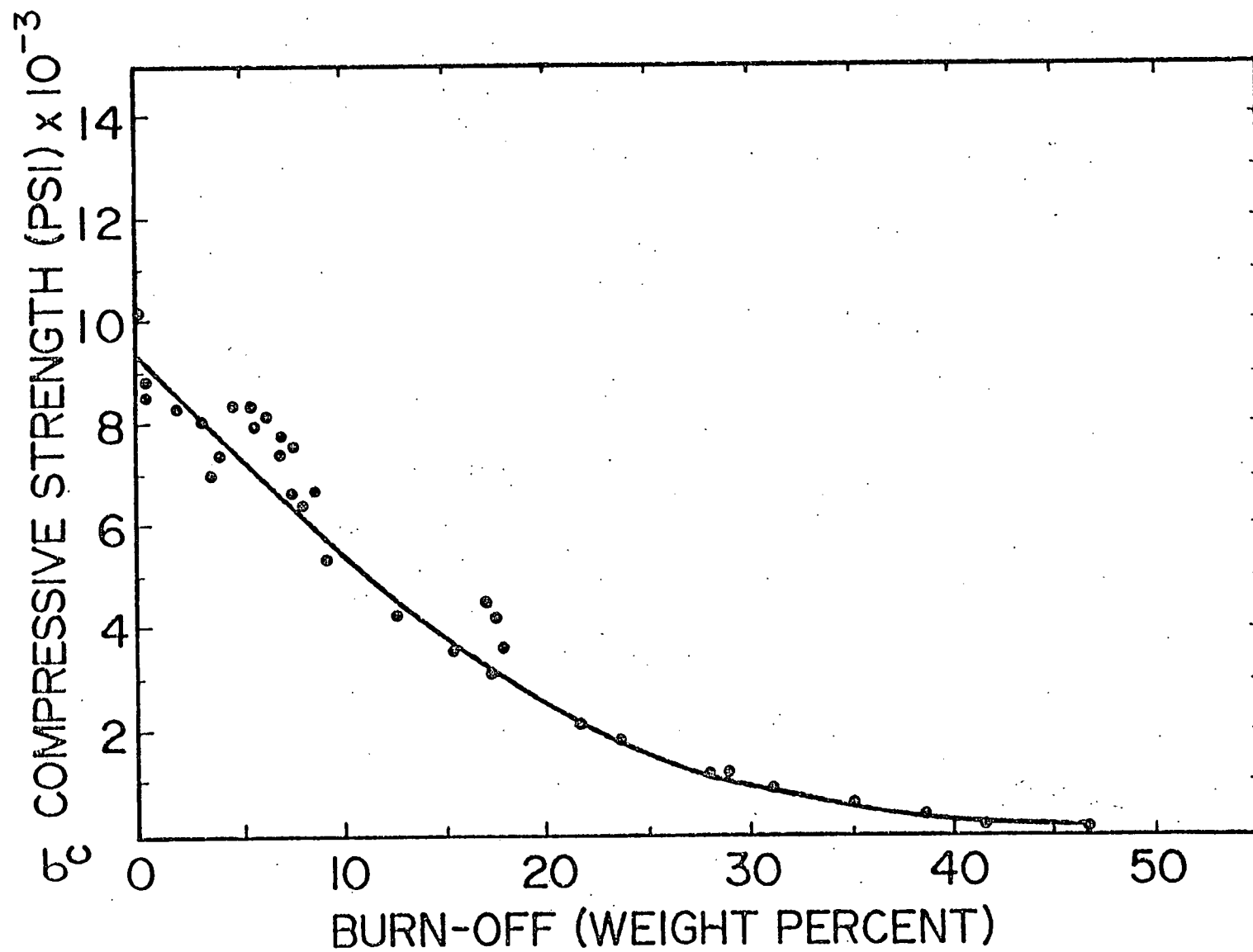


Figure 1. Compressive strength of H-440 as a function of burn-off in  $H_2O/He$ .

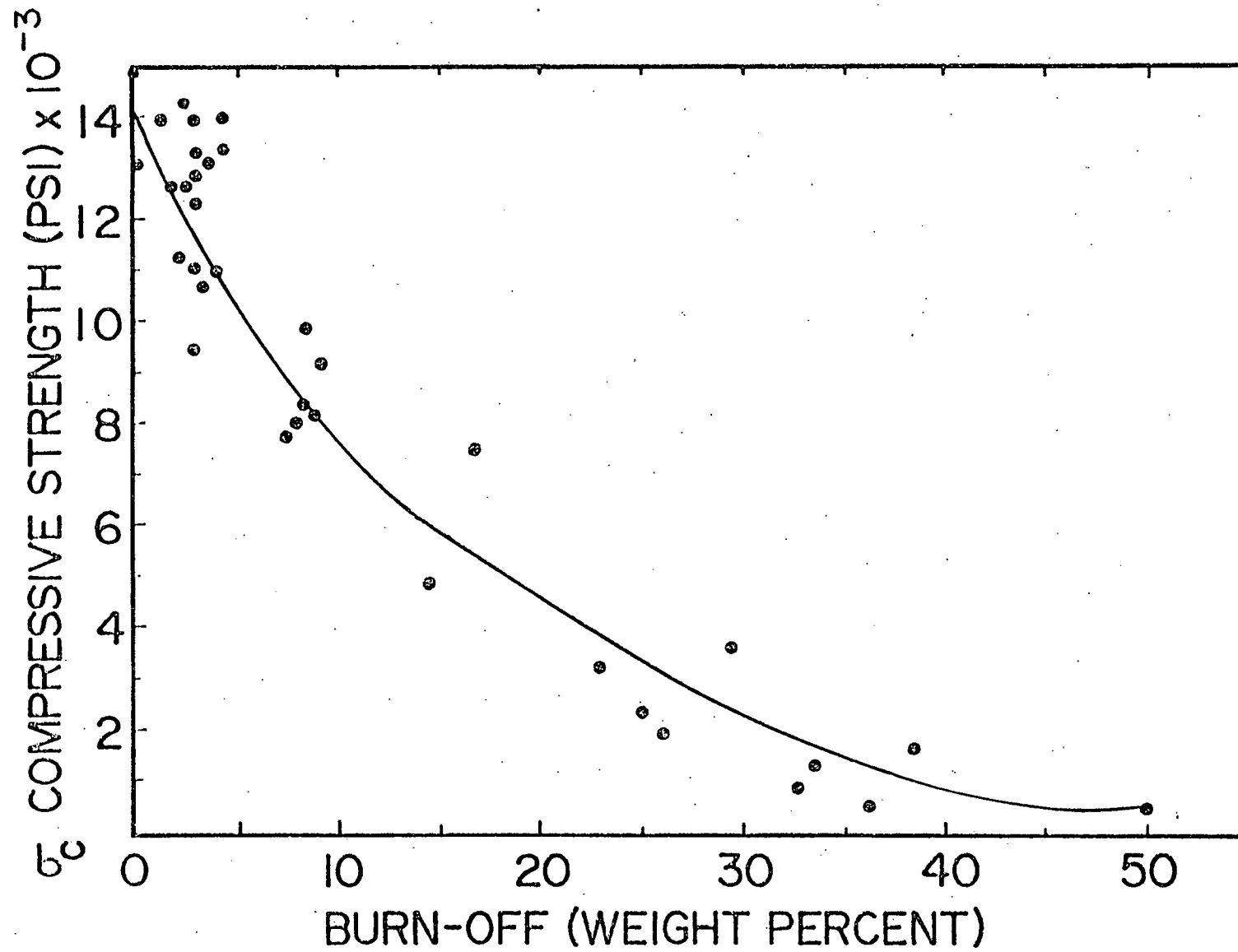


Figure 2. Compressive strength of 2020 as a function of burn-off in H<sub>2</sub>O/He.

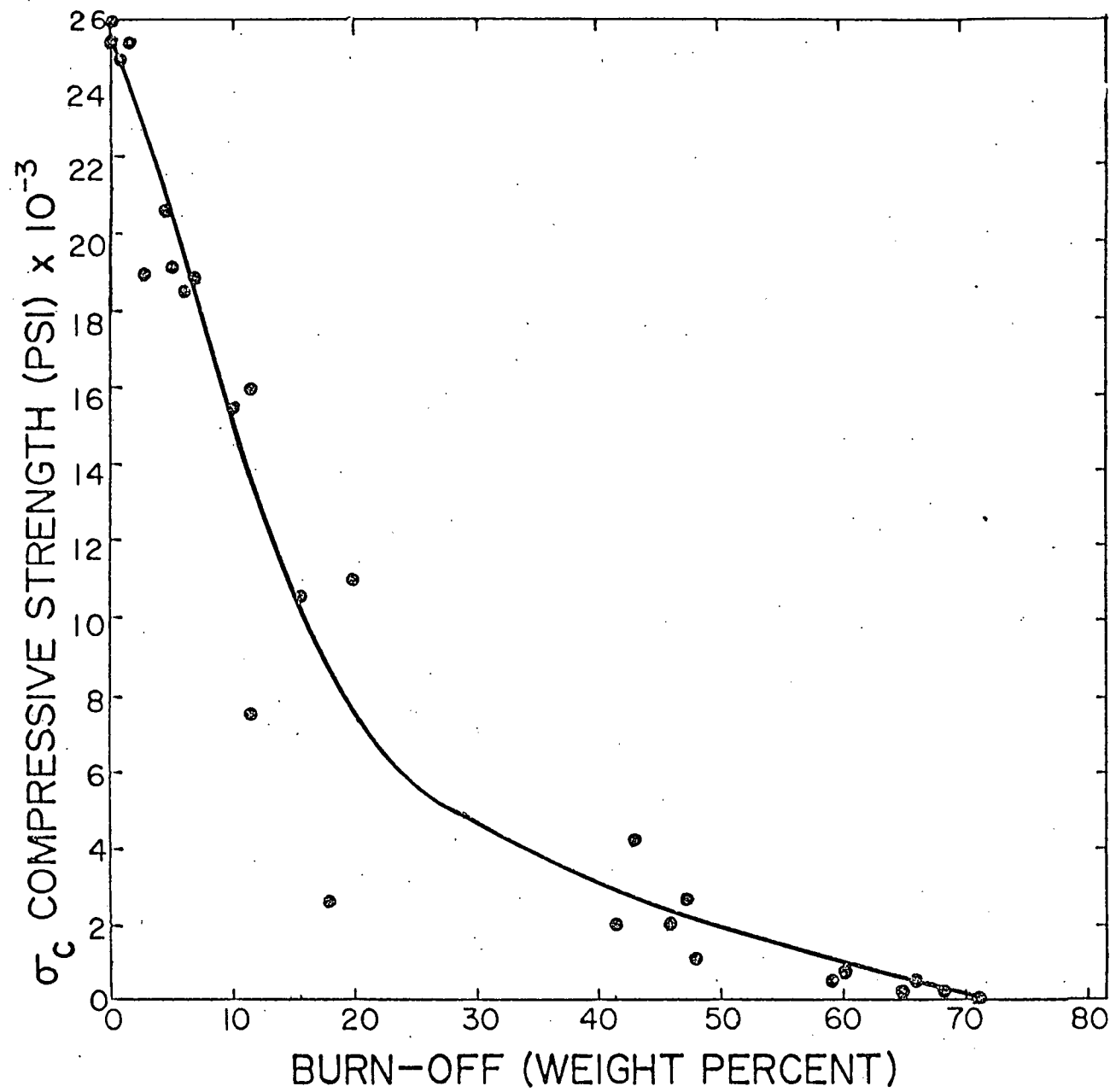


Figure 3. Compressive strength of AXF-5Q as a function of burn-off in  $H_2O/He$ .



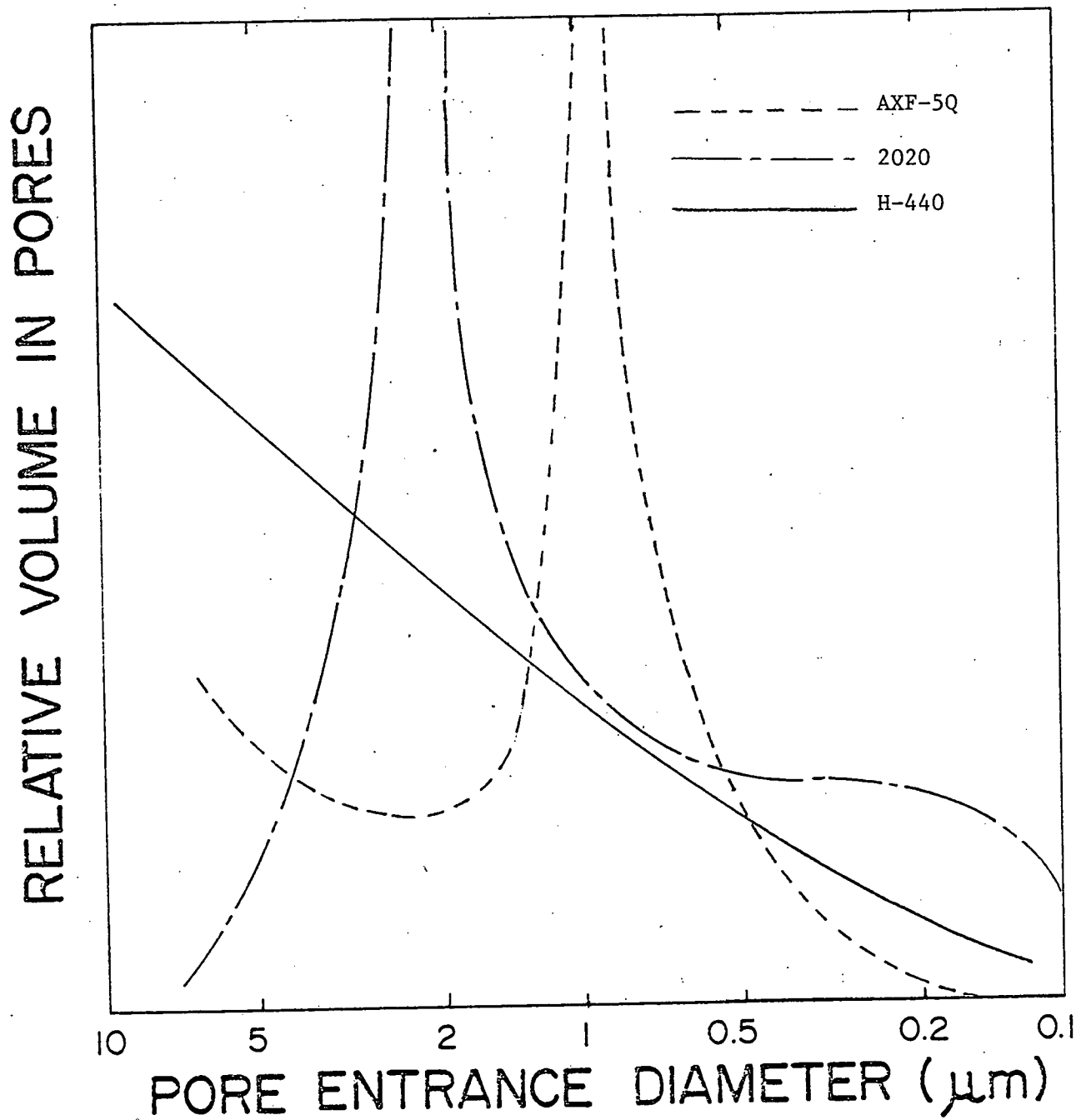


Figure 4. Pore size distributions for graphites oxidized in  $\text{H}_2\text{O}/\text{He}$ .

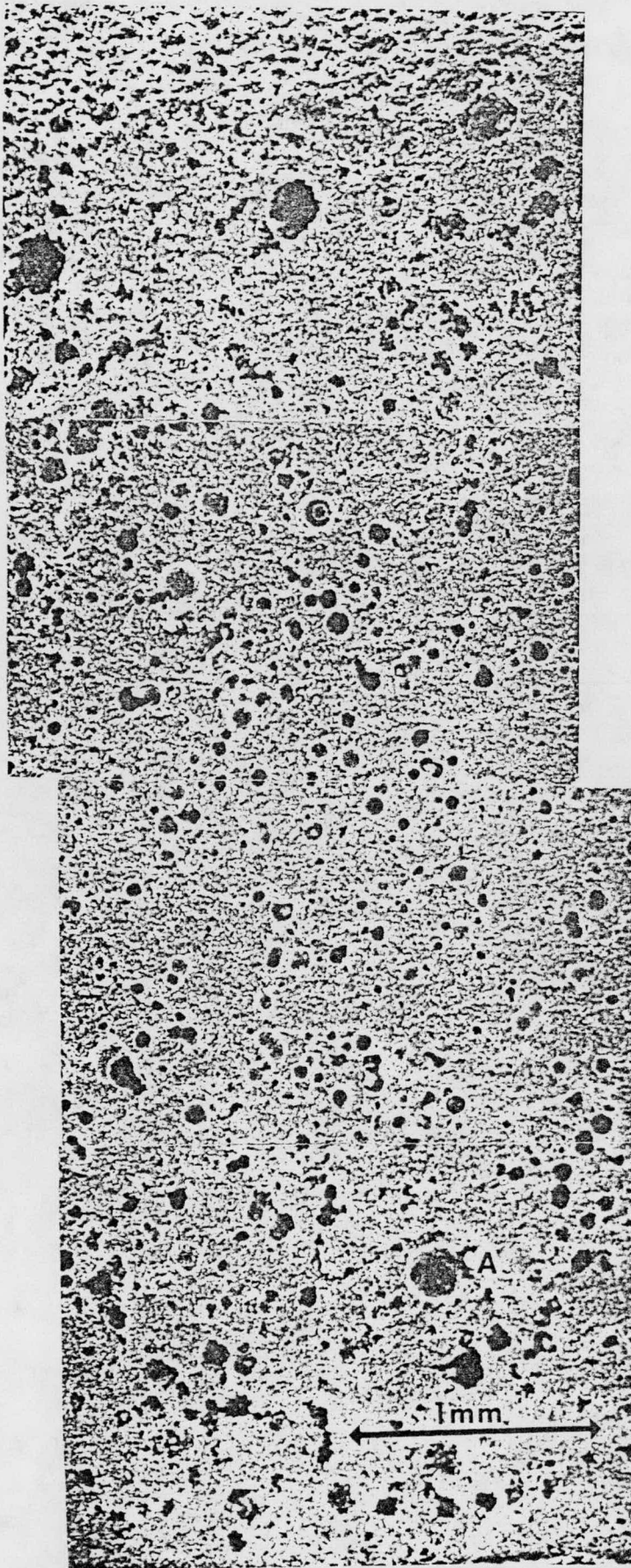
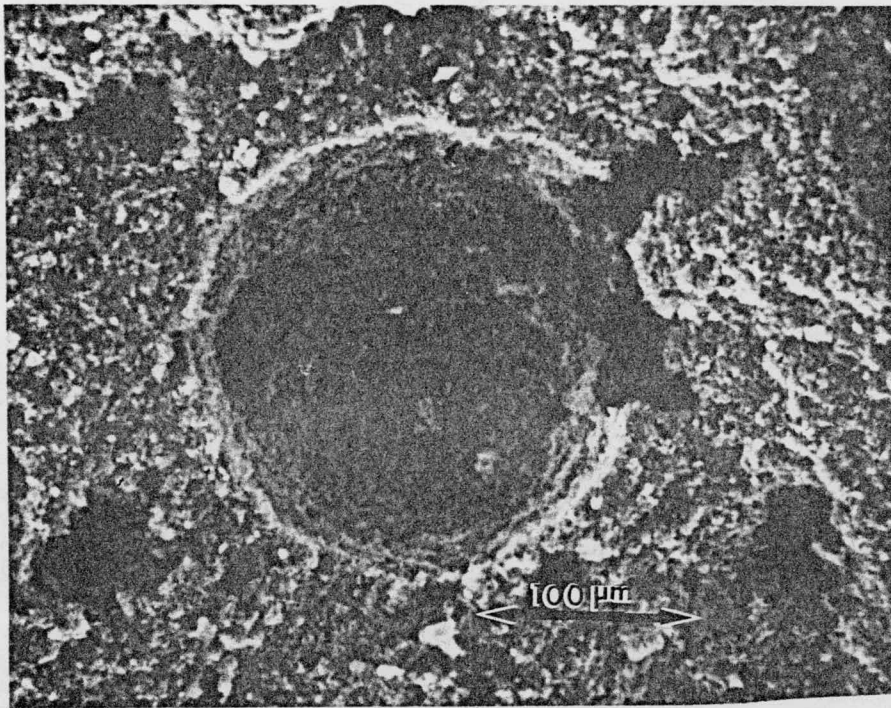


Figure 5. SEM view of cross section of 0.25" AXF-5Q specimen oxidized to 16% burn-off in  $H_2O/He$ .



(a)



(b)

Figure 6. Higher magnification views of Pore A in Figure 5.



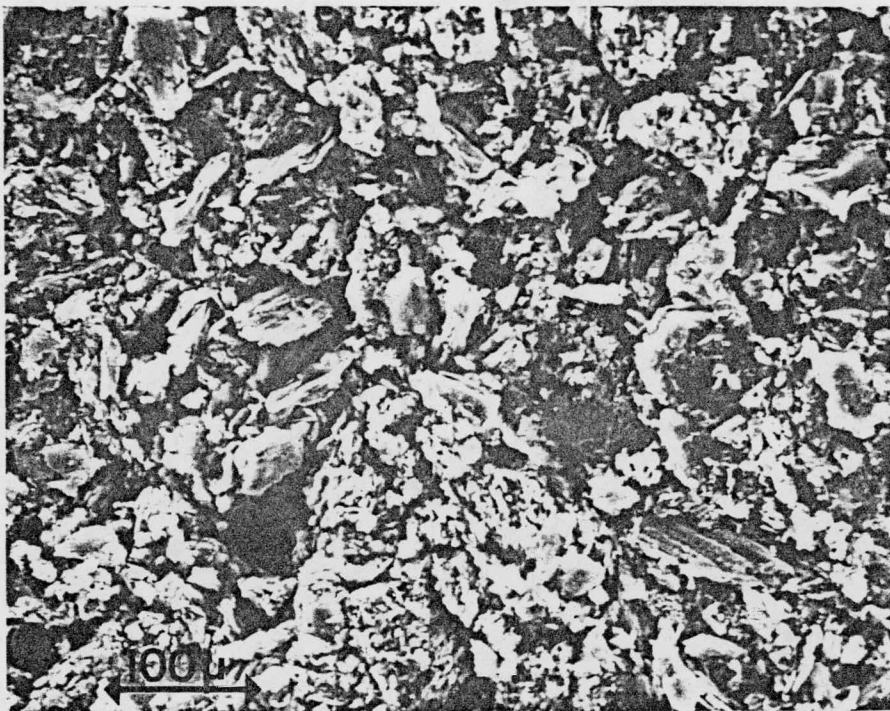


Figure 7. H440 oxidized to 13.6% burn-off in  $H_2O/He$ .

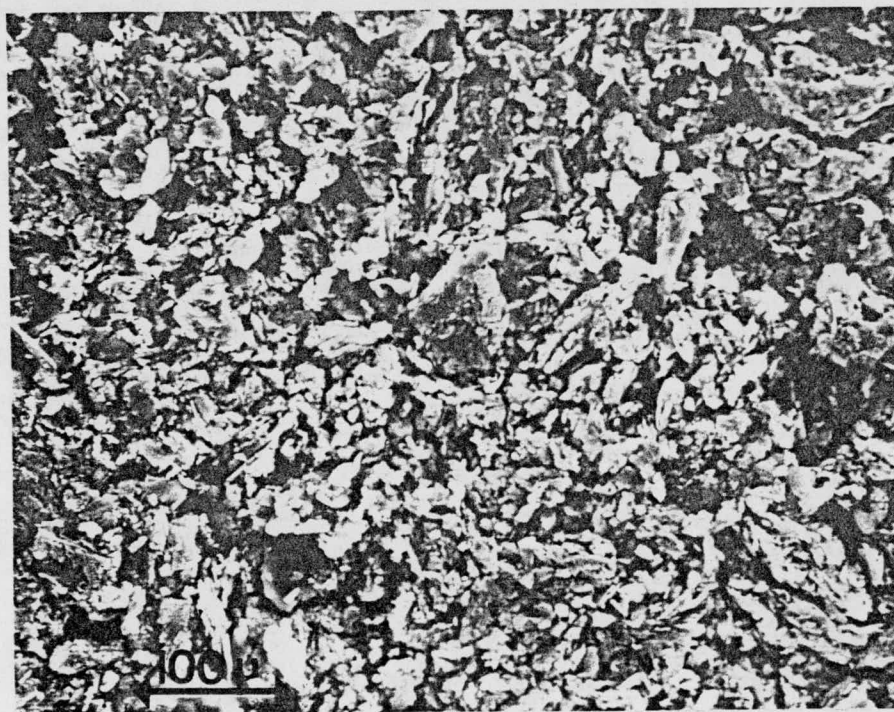


Figure 8. 2020 oxidized to 15.1% burn-off in  $H_2O/He$ .