

NOTE

Controlled Atmosphere Electron Microscopy Observation and Identification of Particles Responsible for the Catalytic Oxidation of Graphite

The behavior of many catalysts is understood inadequately because it is often difficult to identify the precise nature of the catalytic particles. For example, the role of trace elements as promoters or inhibitors may be deduced only indirectly, by a process of elimination. However, there are instances when one is faced with a serious catalytic behavior, perhaps an undesired one, caused by an element in trace quantities, in the presence of other trace impurities. Then it becomes important to identify the catalytic species unequivocally. Such a situation arose when it was found that a particular batch of graphite exhibited enhanced oxidation due, it was postulated, to the presence of a catalytic impurity. Total elemental analysis of the graphite (Table 1) revealed the presence of a considerable number of elements in

trace amounts, most of which appeared capable of causing the undesired catalysis. The problem then was to identify the catalyst positively, in the presence of the other trace impurities, so that steps could be taken to prevent its incorporation into the graphite in future.

The instrument chosen for the task was a controlled atmosphere electron microscope. Its construction and general performance have been described elsewhere (1) so for the present purpose it is sufficient to explain that it is a transmission electron microscope (Model JEM 7A; JEOL, Ltd) in which the specimen is mounted inside a cell, surrounded by a controlled gaseous environment. The resolution is ~ 2.5 nm and the specimen temperature may be controlled up to 1000°C , if necessary. The transmission image is displayed on a TV monitor, and recorded continuously on video tape. Its advantage in the present situation was that some of the contaminated graphite, having been powdered and prepared as an acetone slurry, could be transferred to the surface of a single crystal graphite slice which was transparent to the electron beam, (i.e., ~ 50 nm thick) then mounted in the microscope and observed as its temperature was raised in an oxygen environment.

When the temperature reached 600°C the powdered graphite started to oxidize, and small (~ 3 nm) particles became visible. These began to deposit onto the single

TABLE 1

Trace Element Composition of Graphite

Element	Elemental analysis (ppm by wt)
Al	0.5
Ba	1.5
Ca	8.0
Cu	0.3
Mo	0.8
Si	50
Sr	0.1
Ti	0.5
V	0.8

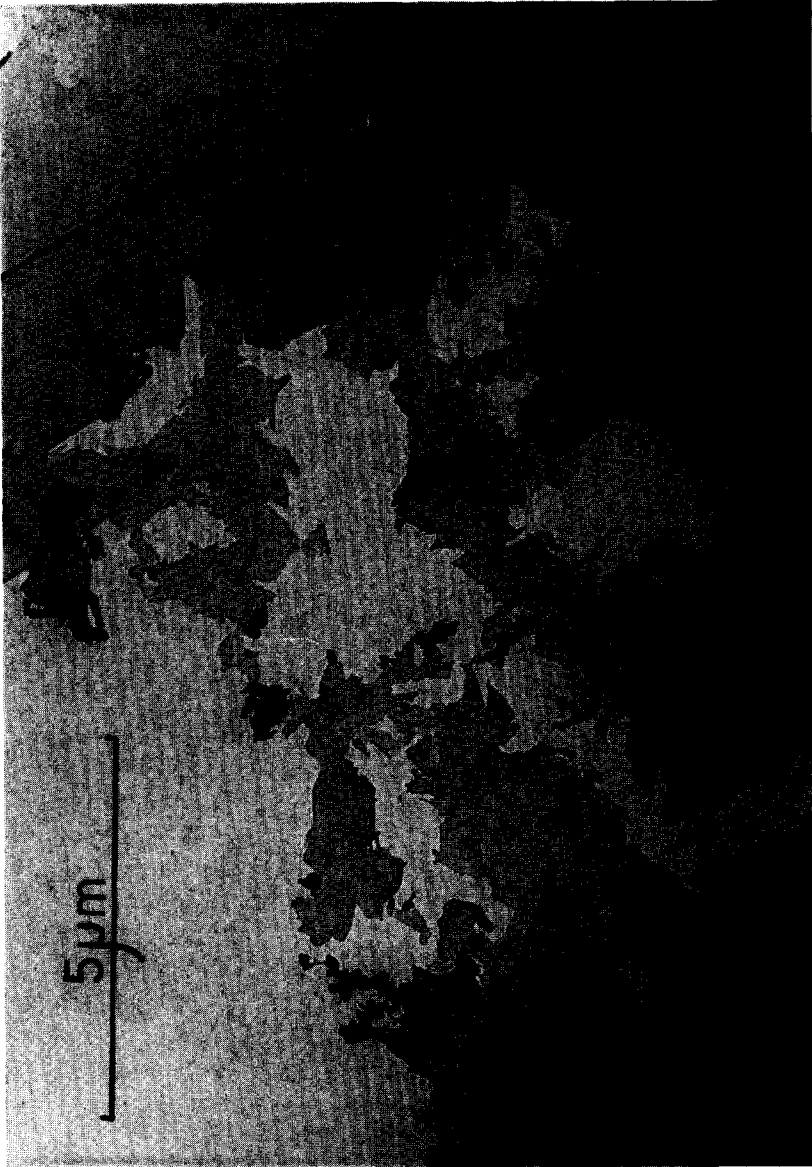


FIG. 1. A specimen of graphite, photographed in the controlled atmosphere electron microscope during oxidative attack by catalytic particles. One particular particle (arrowed) is seen leaving a fairly well defined channel in its wake.

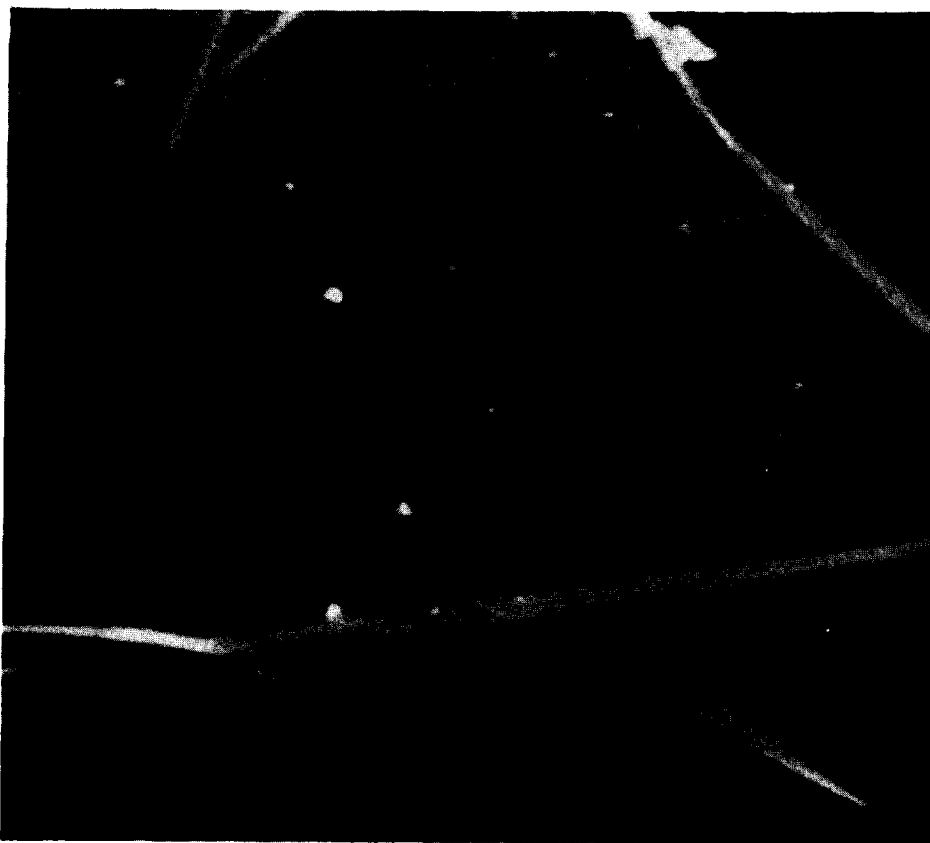


FIG. 2. Scanning Electron micrograph of pitted graphite. The particles in this case show up as white spots.

crystal graphite support as the powdered graphite finally disappeared. The particles then agglomerated into larger ($\sim 0.1 \mu\text{m}$) clumps, and began pitting into the single crystal graphite. At first the catalytic particles could be seen to produce well-defined pits and channels, but simultaneous noncatalytic oxidation caused the pits to become wider. The situation at this point is shown in Fig. 1, where small dark particles are seen associated with irregularly shaped pits in the graphite. In addition, there is indicated, by means of an arrow, a channel in its early stages of formation, with its associated catalytic particle.

In order to identify the elemental nature of these catalytic particles, the specimen was transferred to a combined electron probe X-ray microanalyzer/scanning electron microscope (Cameca Camebax), where

the area of interest could be re-located, admittedly with rather less resolution ($\sim 10 \text{ nm}$). However, the beam could be focused down onto the catalytic particles, from which characteristic X-rays were emitted. The X-rays were resolved by means of either a crystal spectrometer (for the lighter elements) or a Si (Li) solid state detector for elements above \sim sodium in atomic number.

Thus Fig. 2 shows a scanning electron micrograph of an area of pitted graphite using the normal secondary electron emission mode. (A more satisfactory image, giving contrast directly comparable with the transmission electron microscope image would have been obtained if a scanning transmission facility had been available on the instrument.) The catalytic particles were now visible as white spots near the

edge of the dark pit. On focusing the electron beam onto the particles and detecting their characteristic X-rays, they were found to contain predominantly calcium and oxygen (most likely in the form of calcium oxide).

Particles which were not associated with the pits, and which therefore did not appear to be contributing to the catalytic oxidative attack of the graphite, were found to contain silicon and aluminum, but little or no calcium. On the other hand, all pits had particles of calcium oxide associated with them.

As a check on the validity of this finding, a specimen of pure single crystal graphite was contaminated deliberately with calcium oxide, and examined in the controlled atmosphere microscope. It was found to exhibit catalytic oxidative attack which was very similar in behavior to that shown by the earlier specimen (Fig. 1). On the other hand, when similar single crystal graphite

specimens were contaminated with alumina and silica in separate experiments, they exhibited no such catalytic oxidation.

This work illustrates how the technique of controlled atmosphere electron microscopy, when coupled with a good analytical electron beam instrument, can constitute a powerful means of identifying positively the elements associated with a particular catalytic behavior.

REFERENCES

1. Baker, R. T. K., and Harris, P. S., *J. Sci. Instrum.* **5**, 793 (1972).

J. A. CAIRNS
C. W. KEEP
H. E. BISHOP
S. TERRY

*Atomic Energy Research Establishment
Harwell
Didcot, Oxfordshire, England*

Received April 8, 1976