

# THE COPPER-CATALYZED OXIDATION OF GRAPHITE

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**Abstract**—The role of copper as a catalyst in the oxidation of graphite has been studied by optical microscopy and thermogravimetric analysis. The presence of small amounts of copper salts was found to have a very marked effect on the rate of oxidation and ignition temperature of polycrystalline graphite in dry oxygen. Water vapor retarded the oxidation rate of both the catalyzed and uncatalyzed reactions, but had little effect on the ignition temperatures. During catalytic oxidation at 700–800°C, copper oxide particles in the 1–5  $\mu$  size range moved rapidly on the basal plane of natural graphite crystals, cutting irregular channels in the surface. The thermogravimetric results suggest that the catalytic effect involves the localized reduction of cupric oxide by graphite and subsequent re-oxidation of the resulting metal. Alloying of the copper with zinc, aluminum or tin inhibited the catalytic effect.

## 1. INTRODUCTION

The catalytic or inhibiting effects of small amounts of metals and oxides on the oxidation of graphite have often been reported and a large bulk of qualitative information has been obtained by the application of many different experimental techniques to graphite samples of various origins. In spite of much speculation concerning the mode of action of the catalytic phase, there is no general agreement on the mechanism involved. In fact, the wide range of materials which can catalyze the oxidation of graphite suggests that a single mechanism may not apply in all cases.

According to a recent review[1], theories of catalytic activity in connection with graphite oxidation can be divided into oxygen-transfer and electron-transfer mechanisms. In the former the catalyst is believed to undergo an oxidation–reduction cycle involving two oxidation states, whereas the latter mechanism proposes an electron transfer between the  $\pi$ -electrons of the graphite and vacant orbitals of the metallic catalyst.

In the case of iron, cobalt and nickel, which have probably received more attention than any other catalysts, evidence has been produced to support the electron-transfer mechanism[2]. Thus, recent optical work [3] has indicated that these elemental metals are intrinsically more active than the corresponding oxides, whereas other metals such as vanadium or molybdenum form oxides which exhibit very marked catalytic activity. On the other hand, Vastola and Walker[4] have proposed an oxidation–reduction cycle mechanism for the C–CO<sub>2</sub> reaction catalyzed by iron. In the case of the copper catalyzed graphite–O<sub>2</sub> reaction, cupric oxide appears to be the active entity, as discussed in the present paper.

Although the catalytic oxidation of graphite in the presence of copper salts has occasionally been studied in screening tests involving a number of metallic additives[5], no detailed investigation of this system appears to have been made. Estimates of the relative activities of various metals made by different authors often show wide

variations, due probably to subtle differences in the physical form of catalyst and graphite used. Thus, from measurements of the combustion of graphite containing 0.12 per cent of catalyst, Letort and Martin [6] obtained the activity sequence,  $\text{Au} > \text{Na} > \text{Ag} > \text{Cu}$  for combustion in air at 500°C. Using 110 ppm of catalyst, Amariglio and Duval[5] found the sequence,  $\text{Ag} > \text{Cu} > \text{Au} > \text{Na}$  for combustion in air below 600°C, whereas Heintz and Parker[7] have obtained the sequence,  $\text{Cu} > \text{Ag} > \text{Au}$  with 0.1 mole per cent of catalyst for combustion at 600°C and  $\text{Au} > \text{Cu} > \text{Ag}$  at 700°C.

The interaction of copper with graphite is of considerable practical importance in, for example, electric motor technology. In this case sliding contact between copper collector and graphite brush often occurs at elevated temperatures and in oxidizing environments. Oxidation of the graphite leading to accelerated brush wear can often be a limiting factor in the use of electric motors at operating temperatures above 100°C[8]. The present work was undertaken in the hope that an understanding of the catalytic behavior of copper might suggest means of inhibiting the deleterious action of this metal at elevated temperatures.

## 2. EXPERIMENTAL

### 2.1 Materials

The thermogravimetric experiments were carried out with highly purified polycrystalline graphite (Ultra Carbon Corp., Type UCP 2, 325 mesh). This material had a surface area of 2.9 m<sup>2</sup>/g, as determined by the BET method. The ash content was less than 5 ppm and the only detectable impurities were traces of magnesium and silicon.

For optical work natural crystals of graphite in a calcite matrix were obtained from the vicinity of Ticonderoga, New York. Selected graphite flakes were purified by alternate treatments with boiling hydrochloric and hydrofluoric acids (40% HF). Fresh graphite surfaces were obtained by cleavage, using

water-soluble adhesive tape (3M Co., Type 405).

The copper salts used in the catalytic studies were cupric acetate,  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$  (Matheson, Coleman and Bell, Reagent) and cupric formate,  $\text{Cu}(\text{COOH})_2 \cdot 4\text{H}_2\text{O}$  (Amend Drug and Chemical Co., Pure Grade).

### 2.2 Procedure

Thermogravimetric measurements were carried out in a Chevenard thermobalance, Model TH-59, the furnace of which had been fitted with a quartz sheath so that experiments could be carried out in flowing gas. Graphite samples, weighing 200 mg, were placed in a porcelain crucible resting on the top of a silica rod attached to the balance beam. The furnace temperature was measured by a Pt-Rh/Pt thermocouple positioned just above the sample. Weight changes of the sample with linearly increasing temperature were recorded automatically. Details of the operation of the balance are described by Duval[9]. Linear temperature rise rates of 150°C/hr and 300°C/hr were used with flow rates of oxygen or nitrogen of 250 ml/min. Provision was also made for injecting water vapor at controlled rates into the inlet gas stream by means of a constant speed syringe (Harvard Apparatus Co., Model 1101) and a stainless steel vaporizer. All thermograms were corrected for apparent weight gain.

Graphite powder was impregnated with known amounts of copper acetate or formate by evaporating aliquots of the salt solutions to dryness with weighed quantities of graphite under a heat lamp. The mixtures were then blended for several hours in a Fisher Mini-mill. The final copper content of the samples was determined by analysis.

A few measurements were made of the rate of oxidation of graphite samples at low pressures of oxygen in a static system. The apparatus, which consisted essentially of a volumetric adsorption system coupled

to a mass spectrometer, has been described previously [10]. Direct measurements of the rate of evolution of oxides of carbon could be made as a function of temperature and copper content of the sample.

Direct optical observations of the catalyzed oxidation of natural graphite crystals were carried out using a Leitz vacuum hot stage (Model 1750) mounted on the gliding stage of a Zeiss WL microscope. Graphite flakes mounted on the platinum specimen holder of the hot stage could be heated to over 1000°C in flowing oxygen. The temperature of the sample was measured directly by a Pt-Rh/Pt thermocouple in contact with the under surface of the specimen holder. To study the copper-catalyzed reaction, a tiny drop of 0.02% cupric acetate or formate solution was placed on the surface of the graphite flake by means of a micro-syringe and the solution evaporated slowly to dryness. The quartz cover glass was then mounted on the hot stage and the progress of the oxidation reaction was observed microscopically while the sample was heated to 700–800°C in flowing oxygen at atmospheric pressure. Linde 'Extra Dry' oxygen was generally used, although moist gas was sometimes used as described below.

For observing the formation of etch pits during the uncatalyzed oxidation of natural graphite, dark field illumination, using annular 45° incident light, was found to give the best contrast. However, for observing the behavior of small catalyst particles on the graphite surface, bright field illumination proved the most suitable. In some cases photomicrographs of the oxidized graphite surface were obtained by interference contrast (Nomarski) illumination, using a Reichert attachment fitted to a Bausch & Lomb inverted metallographic microscope.

### 3. EXPERIMENTAL RESULTS

#### 3.1 Effect of copper on the rate of oxidation of polycrystalline graphite

Thermograms for the oxidation of graphite

containing varying amounts of copper are shown in Fig. 1. In the case of pure graphite, very little loss in weight occurred in flowing oxygen on heating to 700°C. Above this temperature oxidation became increasingly

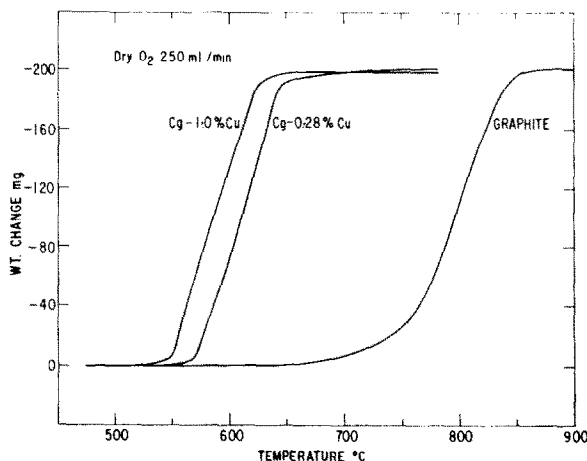


Fig. 1. Copper-catalyzed oxidation of graphite. Heating rate = 300°C/hr. Oxygen flow rate = 250 ml/min.

rapid, leading to ignition at about 740°C. In the presence of small amounts of copper, however, oxidation was initiated at much lower temperatures and, for the 1 wt.% Cu sample, the ignition temperature was reduced by about 200°C.

The effect of copper concentration on ignition temperature is shown in Fig. 2. The catalytic effect was most marked at very low copper levels and above 50 ppm the effectiveness of further increases in copper concentration became less. A similar relation between ignition temperature and catalyst concentration has been reported by Harker for alkali carbonates [11].

The rate of formation of CO<sub>2</sub> from an oxidizing sample of pure graphite powder is shown in Fig. 3 at three different temperatures. These data were obtained in the volumetric apparatus with initial pressures of 20 Torr. of dry oxygen. Under these conditions the CO content of the product was very small. The apparent activation energy

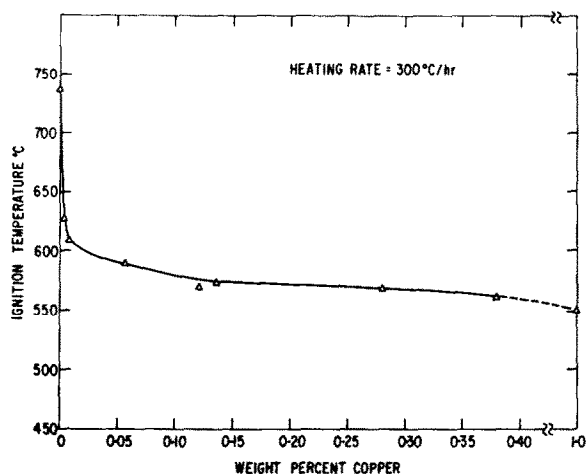


Fig. 2. Effect of copper concentration on ignition temperature of graphite.

obtained from the initial slopes of the curves in Fig. 3 was 54 kcal/mole, in reasonable agreement with the value of 58 kcal/mole obtained by Wicke[12]. Similar data for the graphite-0.28 wt. % Cu sample are shown in Fig. 4, the reaction in this case occurring at much lower temperatures. The apparent activation energy for this sample was 34 kcal/

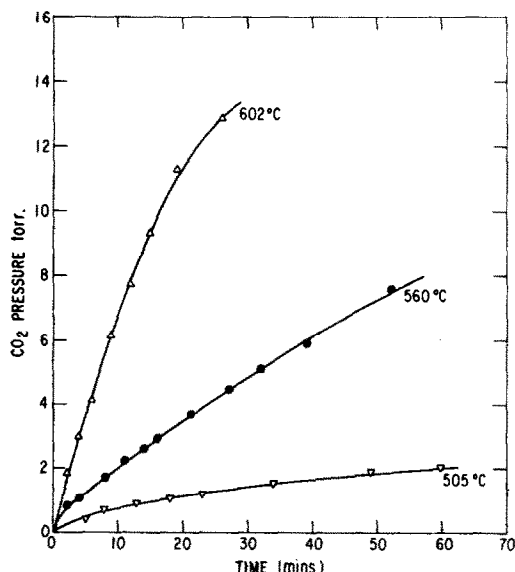


Fig. 3. Rate of oxidation of pure graphite (200 mg). Gas volume = 15 ml. Initial O<sub>2</sub> pressure = 20 Torr.

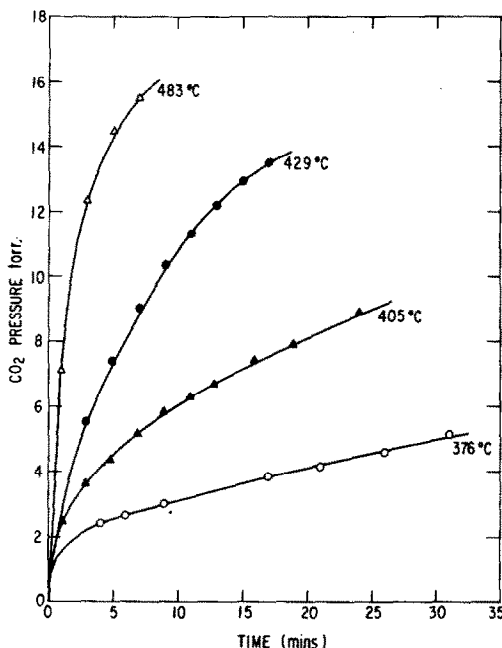


Fig. 4. Rate of oxidation of graphite-0.28 wt. % Cu (200 mg). Gas volume = 15 ml. Initial O<sub>2</sub> pressure = 20 Torr.

mole, based on initial rates. Thus copper, in common with most other active catalysts [1] appears to give rise to a decrease in activation energy for graphite oxidation. The magnitude of the change probably has no fundamental significance as the effective concentration of catalyst on the graphite surface increases rapidly during the oxidation process.

The effect of water vapor on the oxidation of graphite powder in flowing oxygen is shown by the thermograms of Fig. 5 for both pure graphite and graphite containing added copper. In both cases, increasing concentrations of water in the oxygen led to retardation of the rate of oxidation, although the ignition temperatures did not appear to be effected.

### 3.2 Oxidation of natural graphite crystals

The uncatalyzed oxidation of Ticonderoga graphite flakes by dry flowing oxygen at 700°–800°C resulted in the appearance of arrays of etch pits on the basal planes. The

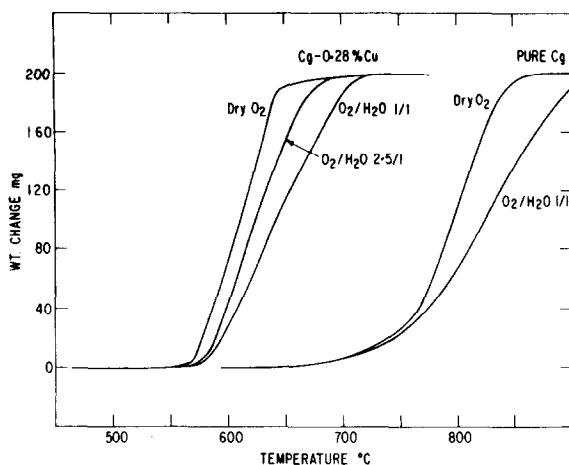


Fig. 5. Effect of water vapor on rate of oxidation of graphite. Thermograms for pure graphite and graphite-0.28 wt% Cu. Heating rate = 300°C/hr.  $O_2$  flow rate = 250 ml/min.

pits were either circular or hexagonal in shape, the latter being of 'parallel' orientation, with two of the pit sides parallel to the twin bands. Typical arrays of etch pits are shown in Fig. 6. Similar results have been obtained by Thomas[3], who has studied the uncatalyzed oxidation of natural graphite in considerable detail. In the absence of catalyst, oxidative attack thus occurs preferentially at the cores of nonbasal dislocations rather than at the edges of the flakes.

Oxidation in the presence of a copper catalyst produced quite different topological changes. Crystallites from an evaporated droplet of copper acetate or formate solution decomposed on raising the temperature to 250°–300°C in flowing oxygen to give an amorphous residue dispersed over the basal plane of the graphite crystal. On increasing the sample temperature to 700°–750°C motion of the smaller catalyst particles began after an induction period of about 10 min at 750°C. Mobility was confined to particles in the size range below  $5\mu$ , the rate of motion decreasing rapidly with increasing particle size. As noted previously for other catalytic materials[13], the motion of the particles resembled a Brownian movement,

the particles gyrating and migrating freely over flat areas of the graphite surface. The irregular shape of the particles was maintained during the motion and the frequent collisions between particles did not result in coalescence. Unlike palladium particles [14], the copper catalyst particles did not behave like liquid droplets.

Motion of the catalyst particles was generally accompanied by the formation of irregular channels, many of the particles being found at the actively growing tips of the channels, as shown in Fig. 7. As found previously by Hennig[15] the channel diameter generally increased with distance from the particle at the tip, as a result of uncatalyzed oxidation of the channel sides. The channeling effect was most noticeable at the edges of the graphite flakes (Fig. 8) and at the steps on the basal plane (Fig. 9) and, in general, the rate of oxidation of a graphite flake occurred much more rapidly at the flake edges in the presence of a copper catalyst than in the absence of the catalyst, in which case attack was mainly by etch pit formation. In many cases subsurface tunnels were observed to grow from edges and steps in the graphite basal plane, these appeared as shadowy depressions on the surface (Fig. 10). It is likely that these tunnels were formed by the intercalation and migration of catalyst particles between the graphite layers.

The migration of the catalyst particles showed a reversible temperature effect, motion ceasing below 700°C and beginning again at slightly higher temperature. Particles larger than about  $10\mu$  showed no mobility or catalytic activity and areas of graphite covered by a thick layer of catalyst were apparently not oxidized. In general etch pits were not observed in regions of active catalytic mobility and attack, although pits sometimes grew in areas on the graphite surface which were devoid of catalyst particles.

If the flowing oxygen was saturated with water vapor before entering the hot stage, the subsequent motion of the catalyst par-

ticles was much more sluggish and the initial induction period was lengthened. However, catalytic activity was not inhibited completely and a higher temperature ( $\sim 800^\circ\text{C}$ ) always brought about catalyst particle motion even in the presence of water vapor.

### 3.3 Chemical nature of the catalyst particles

In order to obtain some information on the nature of the catalytically active entities involved during oxidation of graphite in the presence of copper, the products of the decomposition of copper acetate and formate in contact with graphite and flowing oxygen were examined by thermogravimetric analysis.

Cupric acetate,  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$ , (sample weight = 200 mg), heated at  $150^\circ\text{C/hr}$  in flowing dry oxygen gave the thermogram shown in Fig. 11. Weight loss was first detected at  $110^\circ\text{C}$  and increased rapidly to a single step at  $160^\circ\text{C}$ . The weight change at this point (17 mg) corresponded to the loss of one  $\text{H}_2\text{O}$ . The anhydrous salt then remained at constant weight to  $250^\circ\text{C}$  when a very rapid weight loss occurred. The total weight change (121 mg) corresponded to the conversion,  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O} \rightarrow \text{CuO}$  (Calculated weight loss = 120 mg). Thus decomposition of cupric acetate was complete at  $295^\circ\text{C}$  to give only cupric oxide  $\text{CuO}$  in the presence of oxygen.

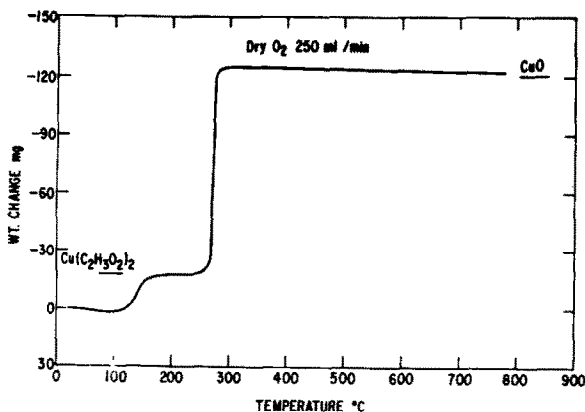


Fig. 11. Decomposition of cupric acetate,  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$  in dry oxygen. Heating rate =  $150^\circ\text{C/hr}$ .

In an inert atmosphere a mixture of copper metal and cuprous oxide  $\text{Cu}_2\text{O}$  was obtained.

The analogous decomposition of cupric formate,  $\text{Cu}(\text{COOH})_2 \cdot 4\text{H}_2\text{O}$ , is shown by the thermogram of Fig. 12. In this case, loss of water occurred between  $50^\circ$  and  $120^\circ\text{C}$ , with an arrest corresponding to  $\text{Cu}(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$  at  $90^\circ\text{C}$  (Calculated weight loss = 31 mg).

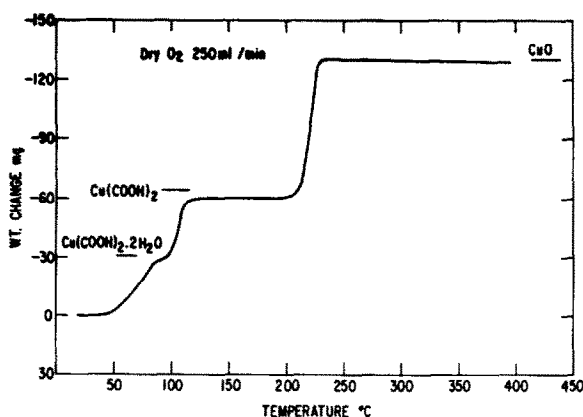


Fig. 12. Decomposition of cupric formate,  $\text{Cu}(\text{COOH})_2 \cdot 4\text{H}_2\text{O}$  in dry oxygen. Heating rate =  $150^\circ\text{C/hr}$ .

Beginning at  $200^\circ\text{C}$ , the anhydrous formate decomposed rapidly, the constant weight plateau at  $230^\circ\text{C}$  being cupric oxide, formed by the conversion,  $\text{Cu}(\text{COOH})_2 \rightarrow \text{CuO}$  (weight change observed = 61 mg, calculated = 65 mg).

Thermograms obtained for 1/1 mixtures of graphite and cupric acetate and formate (anhydrous) are shown in Figs. 13 and 14 respectively. In the former case, the exothermic decomposition of the salt at  $250^\circ\text{C}$  triggered the ignition of the graphite and loss in weight occurred in a single step to the level for  $\text{CuO}$  at  $280^\circ\text{C}$ . With cupric formate a distinct level for  $\text{CuO}$  was found at  $260^\circ\text{C}$  and ignition of the graphite did not occur until  $520^\circ\text{C}$ .

As these results suggested that the active catalytic phase in the oxidation of graphite was cupric oxide, a thermogram was obtained for a 1/1 mixture of graphite and cupric oxide in flowing nitrogen. As shown by the

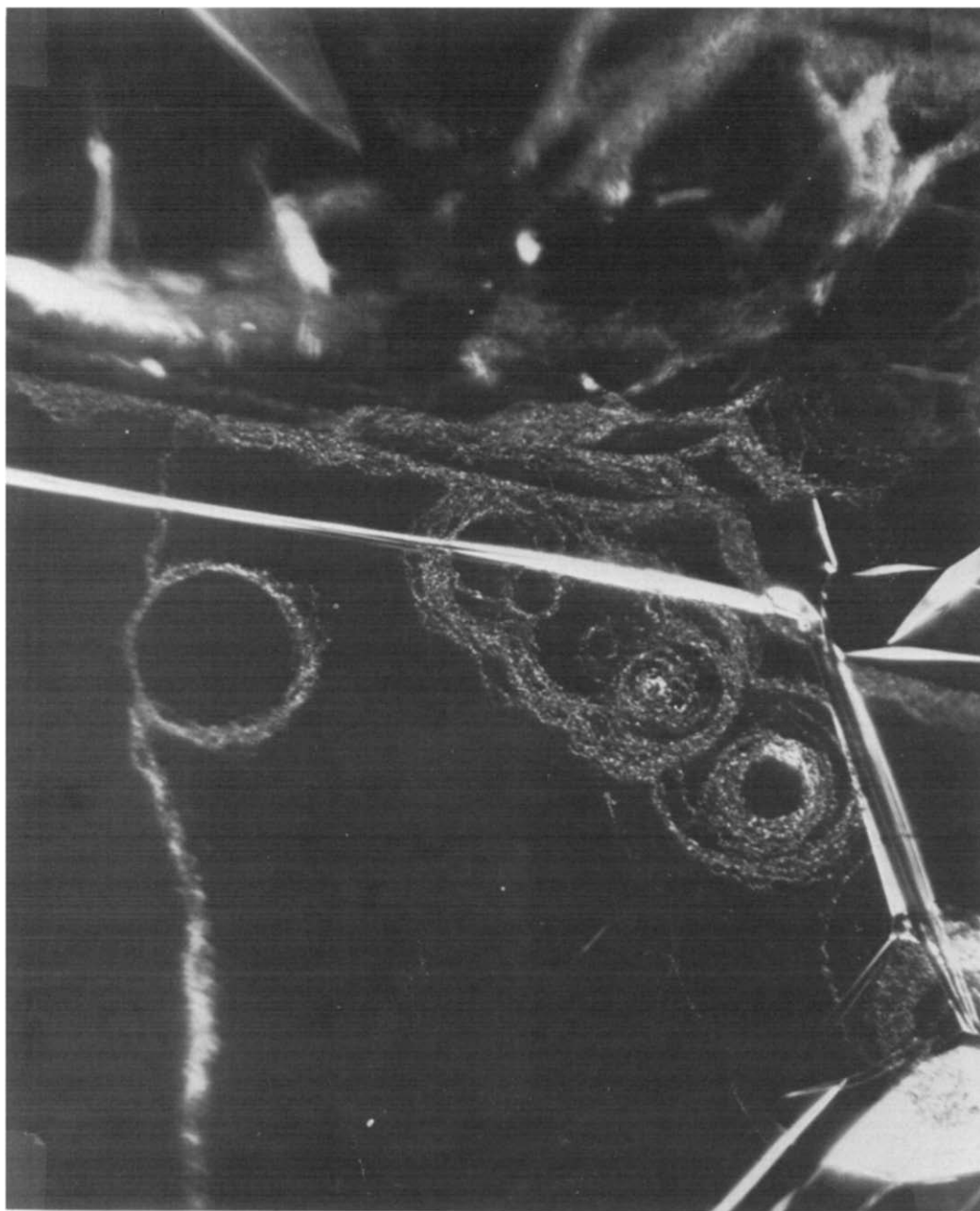


Fig. 6(a). Etch pits on natural graphite flake after oxidation at 800°C in flowing dry oxygen. (x224). Dark field illumination.

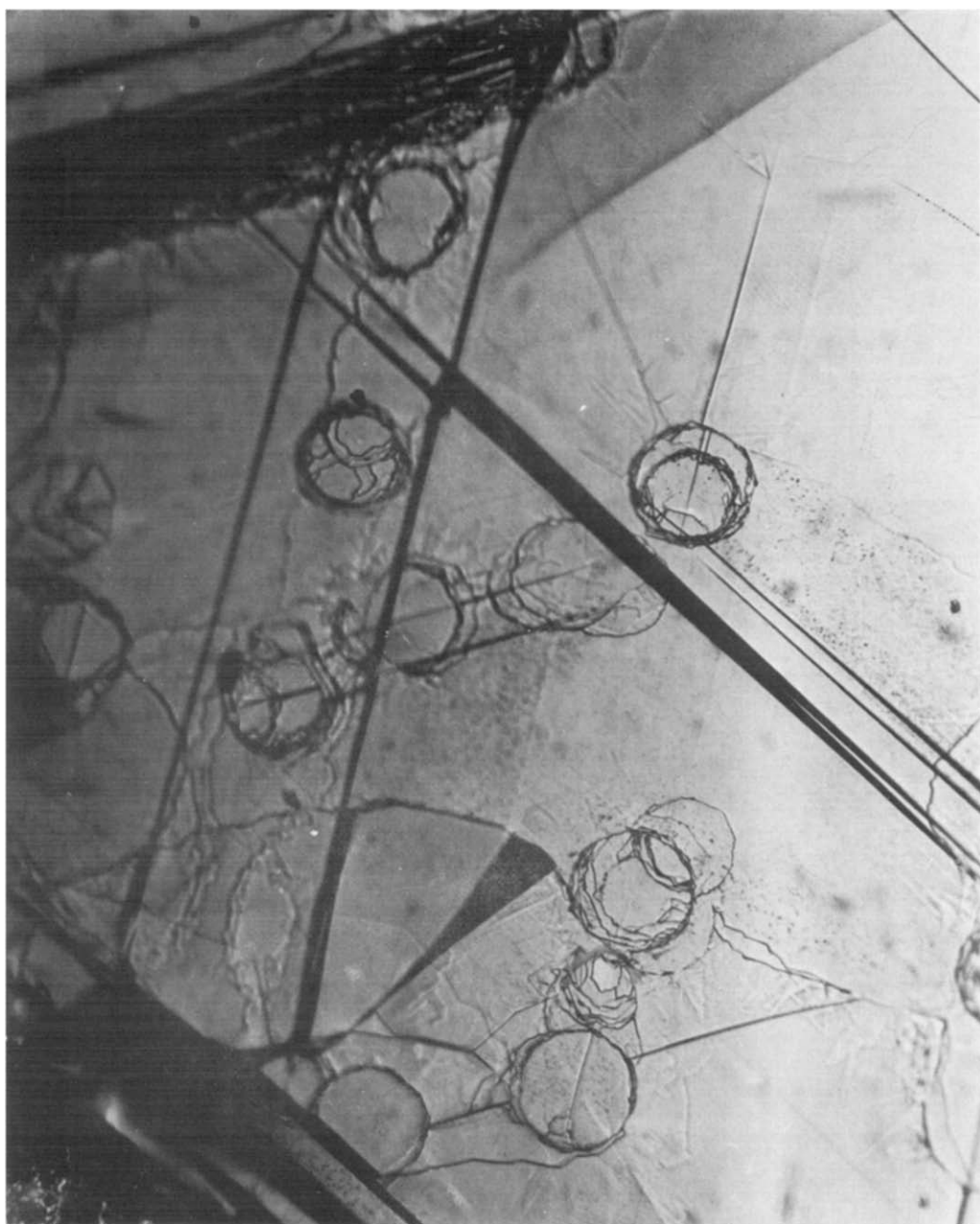


Fig. 6(b). Etch pits on natural graphite flake after oxidation at 800°C in flowing dry oxygen. (x224). Bright field illumination.





Fig. 7. Channeling by copper catalyst particles on natural graphite flake after oxidation at 750°C in dry O<sub>2</sub>. ( $\times 1218$ ).

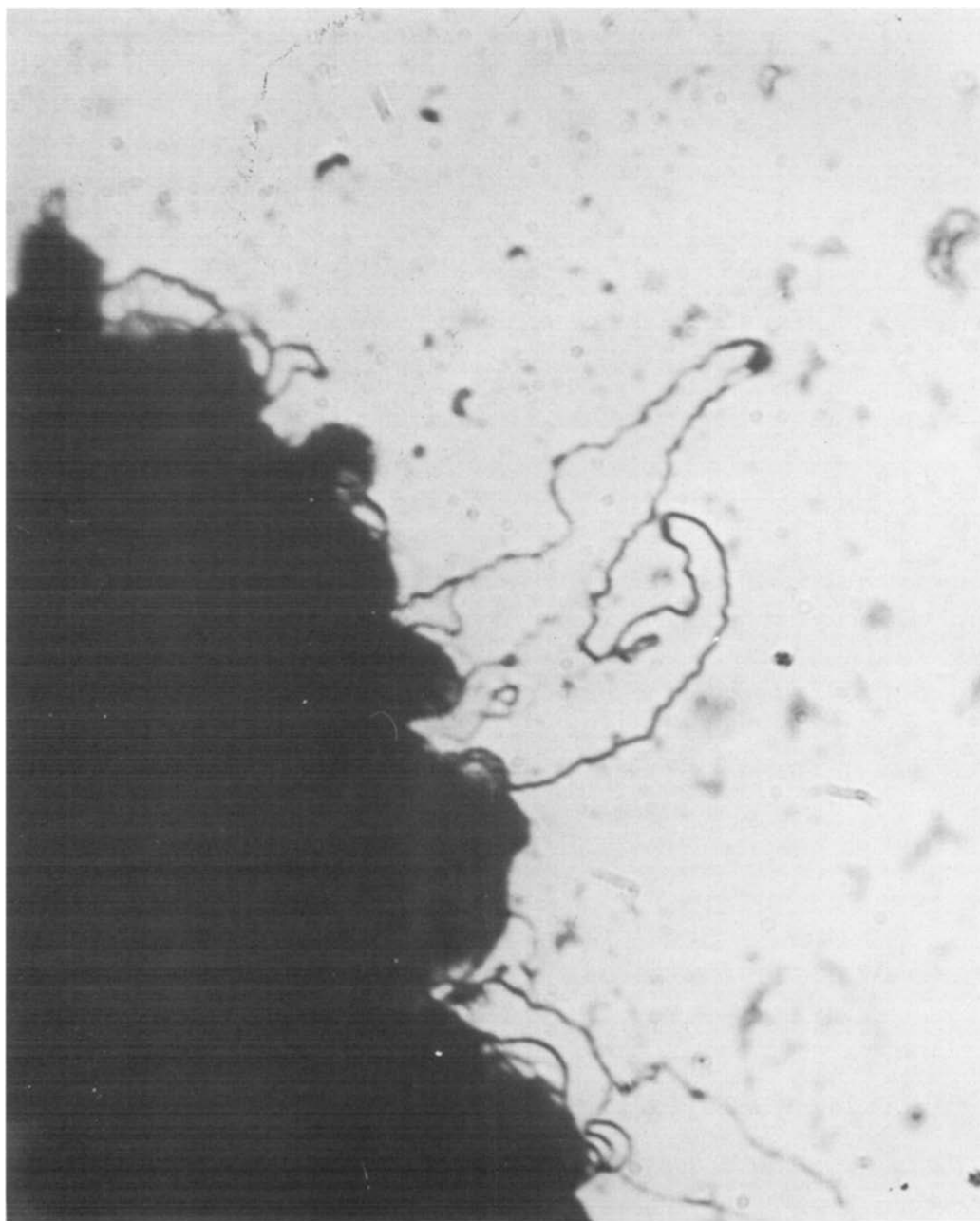


Fig. 8. Catalytic channeling by copper near edge of graphite flake ( $\times 1218$ ).

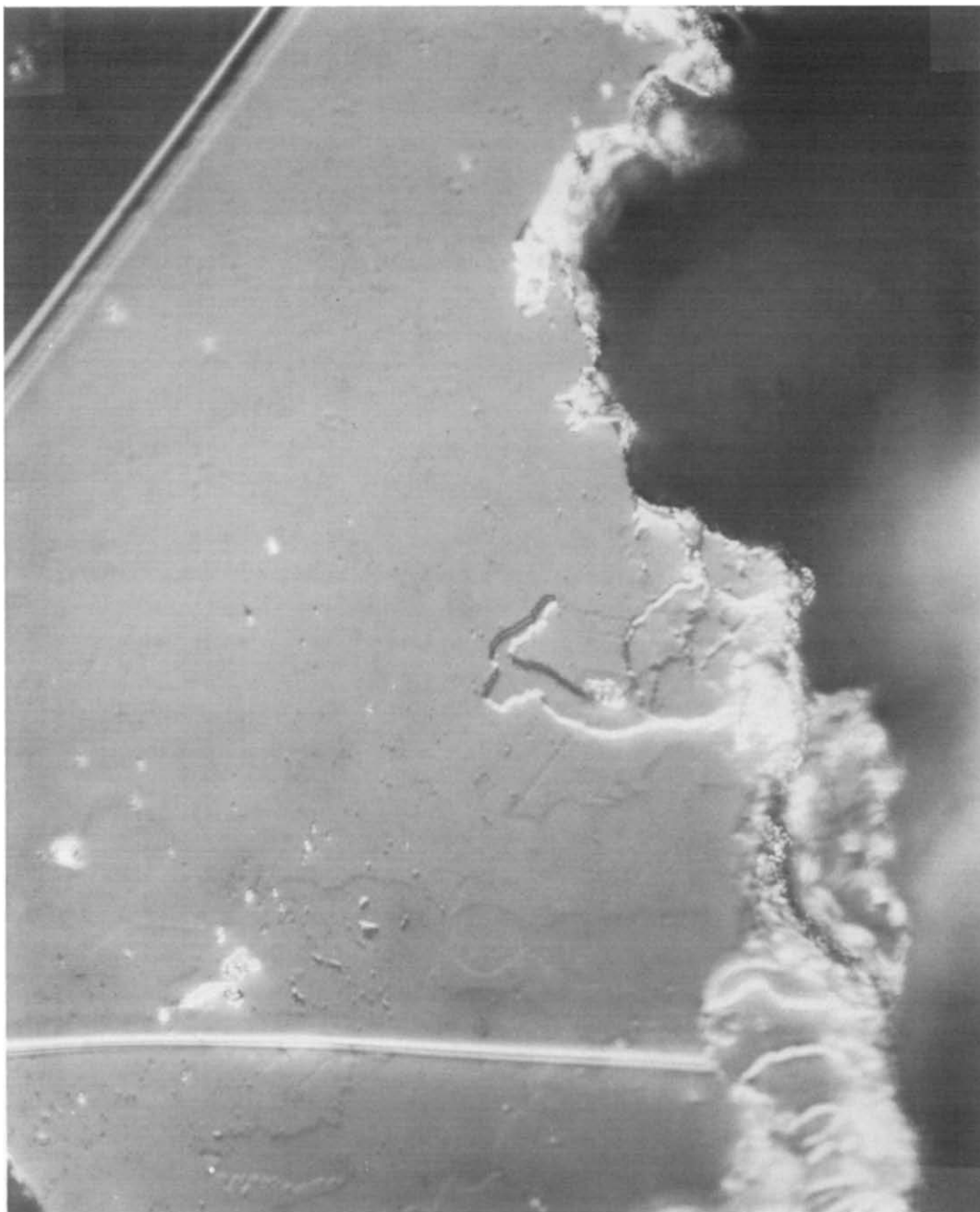


Fig. 9. Catalytic channeling by copper. Interference contrast ( $\times 700$ ).

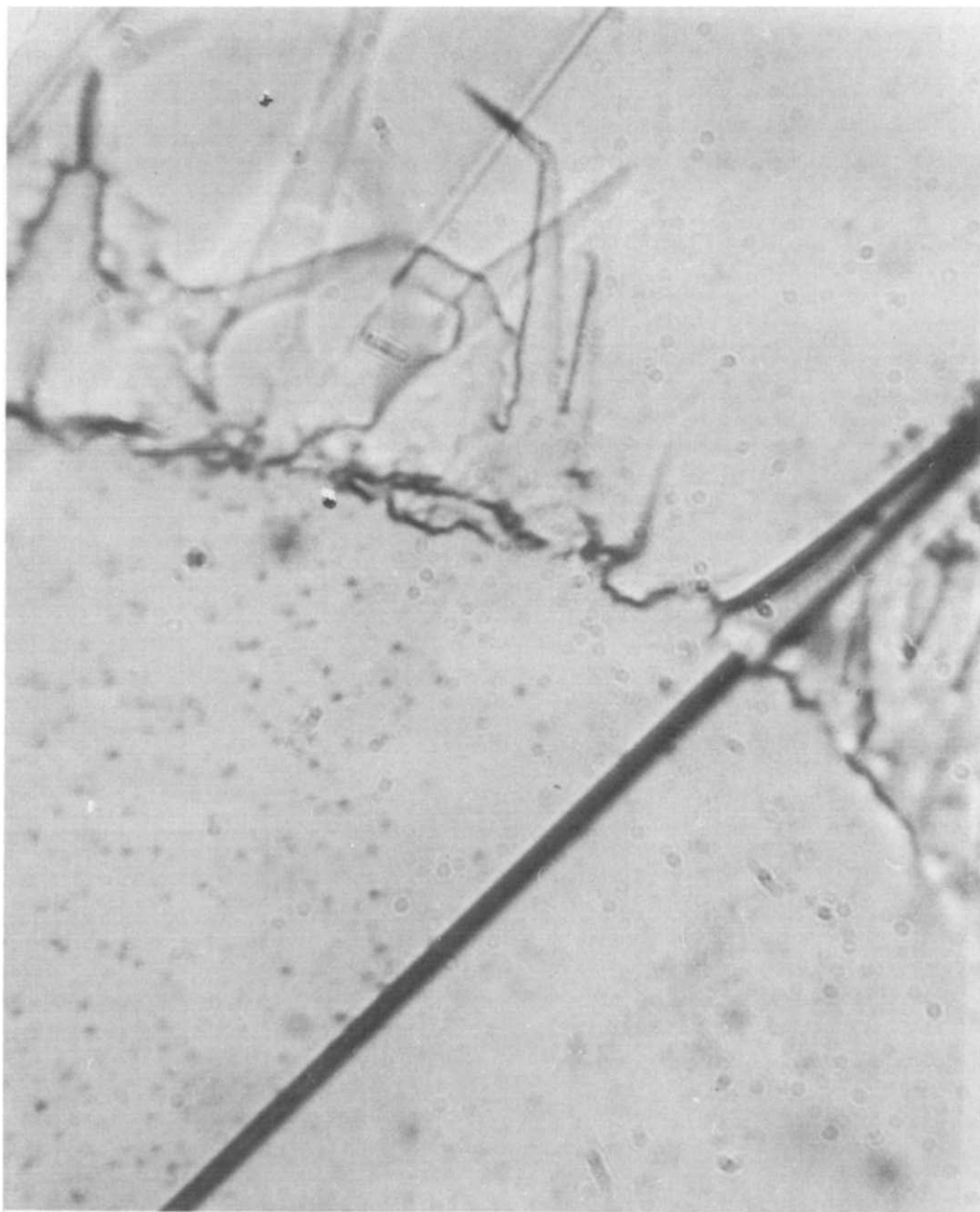


Fig. 10. Sub-surface tunneling at step on basal surface of graphite crystal ( $\times 1218$ ).

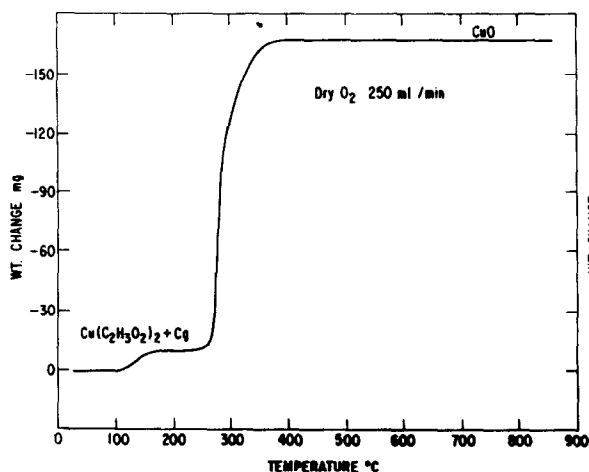


Fig. 13. Thermogram of graphite-cupric acetate (1/1) mixture in dry flowing oxygen. Heating rate = 300°C/hr.

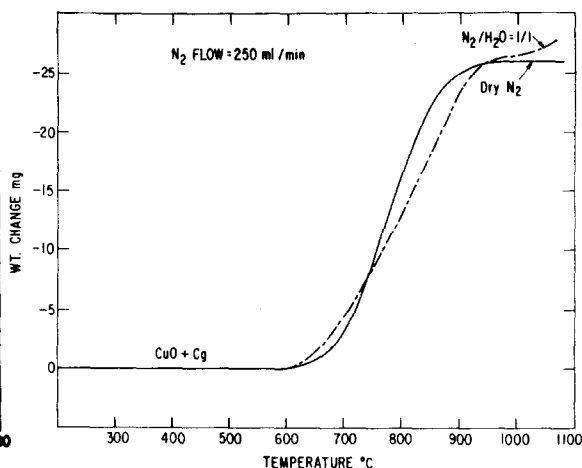


Fig. 15. Thermogram of graphite-cupric oxide (1/1) mixture in dry flowing nitrogen. Heating rate = 300°C/hr.

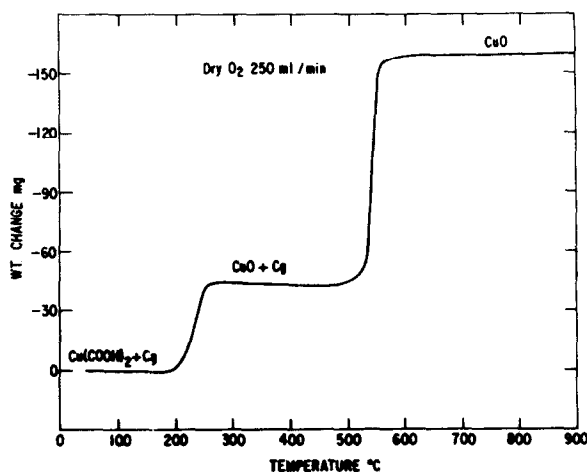
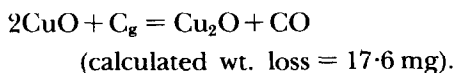
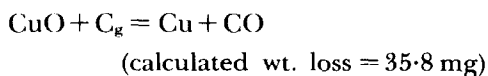


Fig. 14. Thermogram of graphite-cupric formate (1/1) mixture in dry flowing oxygen. Heating rate = 300°C/hr.

solid curve of Fig. 15, interaction between the two solid phases occurred smoothly in the temperature range 650°–900°C. The observed weight change at 1000°C, (26 mg) suggested that copper metal was the main product of the decomposition. Thus:



Although the rate of this reaction will obviously depend on the particle sizes of the solid reactants, it is significant that the reaction occurred at an appreciable rate in the same temperature range as the copper-catalyzed oxidation of graphite (Fig. 1).

The dotted curve in Fig. 15 shows the thermogram for the CuO/graphite mixture in wet nitrogen. The presence of water vapor retarded this reaction to some extent, probably by forming an adsorbed layer on the graphite surface. The additional loss in weight above 1000°C is due to the onset of the  $\text{C}_g\text{-H}_2\text{O}$  reaction. A separate experiment on the oxidation of copper metal (325 mesh powder), indicated that water vapor had no appreciable effect on this reaction, which occurred readily in the 400°–700°C temperature range.

### 3.4 Inhibition of copper catalysis

As the catalytic effect of copper in the oxidation of graphite depends on the formation of a cupric oxide layer on the metal surface, it should be possible to inhibit the catalytic action of copper by coating the metal with an inert layer of a second metal or oxide.

For these coating experiments the metals, zinc, aluminum and tin were chosen as these form stable oxides which are not reduced by

carbon below 1000°C. A 1/1 mixture of copper powder (325 mesh) and zinc dust was heated to 500°C for 1 hr. in a stream of hydrogen until the powder had attained a uniform brass-yellow color. Equal weights of this Cu-Zn powder and graphite were blended together and the oxidation of the mixture studied thermogravimetrically. Thermograms for this sample, a Cu-graphite and a Zn-graphite sample are compared in Fig. 16.

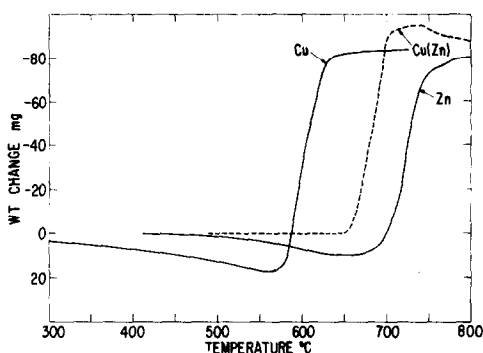


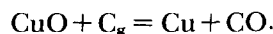
Fig. 16. Inhibition of copper-catalyzed oxidation of graphite by zinc. Graphite/catalyst = 1/1. Heating rates = 300°C/hr.

Zinc alone showed a very small catalytic effect on the rate of oxidation of graphite, and considering the large amount of zinc present, the effect was almost negligible. It is evident, however, that the strong catalytic effect of copper was considerably reduced when the copper was treated with zinc. In addition the increase in weight below 550°C due to formation of copper oxide was eliminated in the presence of zinc. Presumably if the whole of the copper surface can be covered with a zinc layer so that direct contact between copper oxide and graphite is completely prevented, then no catalytic effect would be shown. Similar inhibition of the catalytic effect of copper was found as a result of treatment with aluminum, and to a lesser extent, tin.

#### 4. DISCUSSION

The results of thermogravimetric analysis on the products of the decomposition of

cupric acetate and formate in the presence of oxygen suggest a simple chemical mechanism for the copper-catalyzed oxidation of graphite. Cupric oxide is formed on pyrolysis of these salts in oxygen at about 250°C and the resulting particles of CuO can then interact locally with the graphite substrate at temperatures in the range 500°–700°C, depending on the particle sizes of the two components. Similarly, oxidation of metallic copper under these conditions will give rise to an oxide layer of Cu<sub>2</sub>O with a surface coating of CuO[16]. As the lower and thermodynamically more stable oxide, Cu<sub>2</sub>O, is also readily reduced by carbon under these conditions, it is likely that CuO is reduced completely to metallic copper at the interface between catalyst particle and graphite,



The desorption of gaseous oxides of carbon at the particle-graphite interface, could readily account for the vigorous Brownian-like movement of the particles, the effect becoming more marked with decreasing particle size. The rotation and general mobility of the small particles would facilitate the diffusion of oxygen to the catalyst-graphite interface and hence promote the re-oxidation of the copper layer,



This re-oxidation process would be slow for immobile larger particles, which would therefore tend to be inefficient catalysts above a critical size, which appears visually to be in the neighborhood of 10 μ. The net result of this oxidation-reduction cycle will be a transfer of oxygen atoms from the gas phase to the graphite and a gasification of the carbon at the area of contact with the catalyst particle. This contact area would be greatest at edges and steps on the graphite surface and these would be the regions of preferred attack.

The presence of water vapor probably retards the rate of reaction (1) by forming

an adsorbed layer on the graphite surface. Earlier work by Montet[17], using tritiated water vapor, has shown that adsorbed water can remain on the graphite surface at temperatures up to 700°C although desorption can be completed at 900°C. By contrast, the presence of water vapor does not effect the rate of reaction (2) to any appreciable extent.

The reduction of CuO and Cu<sub>2</sub>O to copper metal by carbon at temperatures above 500°C is favored by the free energy of formation of these oxides[18], whereas the oxides of aluminum, tin and zinc are stable in the presence of carbon and are, therefore, inactive catalysts. When diffused into the surface layers of copper, these metals prevent the formation of cupric oxide and thereby hinder the catalytic effect of copper.

The cyclic oxidation and reduction of a metal oxide has often been suggested as a possible mechanism for the catalytic oxidation of graphite[5] and it is a fact that many catalytically active metals can, thermodynamically, undergo cycles of this type. However, in some cases such as iron[3], the oxides appear to be less active as catalysts than the elemental metal. The free energy decrease on reduction of Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> with carbon is less than that for the reduction of CuO to copper, and at least in the latter case, the 'oxygen-transfer' mechanism appears to offer a reasonable explanation of the main features of the catalyzed oxidation reaction.

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