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A Review of In-Situ Electron Microscopy Studies of Metal/Metal Oxide–Graphite Interactions*

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Controlled atmosphere electron microscopy has been used to gain a unique insight into the manner by which various additives interact with carbonaceous solids, particularly graphite. With this technique it is possible to observe directly, at the nano-scale level, changes taking place in the appearance of a solid while it is undergoing reaction with a gaseous environment at elevated temperature. Based on the studies of many metal/graphite-oxygen systems, a rationale has been presented to account for both the catalytic action of some additives and the inhibiting effect of others in the reaction. This experimental approach has also been applied to the investigation of the behavior of metal/graphite systems in both hydrogen and steam. These fundamental investigations have a direct impact on a number of industrially important areas, including indirect conversion of coal into liquid fuels, removal of carbon deposits from deactivated catalysts, corrosion of graphite electrodes and moderators in gas-cooled nuclear reactors and the oxidation protection of carbon composite structures used in aerospace applications. A review of the information gained from these studies is given along with a discussion of the interfacial phenomena associated with the different modes of catalytic action encountered in these reactions.

INTRODUCTION

The gasification of carbonaceous solids is an area of tremendous industrial importance, having impact in several diverse processes. It has been known for many years that a small amount of an inorganic impurity can have a profound effect on the rate of gasification of carbon.^{1–4} This feature is taken advantage of in both coal conversion processes and removal of carbon from coked catalyst particles. Catalytic gasification is a unique example of a heterogeneous catalyst system because the carbonaceous support is also a reactant and is consumed during the reaction. It is a fascinating reaction since one can directly observe, with the aid of an electron microscope, the catalyst in action. The most important gasification reactions of carbon are those with oxygen, carbon dioxide, hydrogen and steam, and catalysts are used extensively to increase the rates of these process.

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Much of the early fundamental investigations in this area had their genesis in the nuclear industry where graphite is used both as a moderator of fast neutrons and a structural material. Under these circumstances the material not only has to withstand temperatures of between 600 and 1000°C in the presence of either CO₂ or trace amounts of steam, but is also exposed to fast neutrons and gamma radiation. These high-energy sources are responsible for damaging the graphite structure and producing an appreciable increase in the gasification rates.^{5,6} The problem is further exacerbated by the presence of metallic impurities, which can accelerate the rate of oxidation in both of these gas environments.⁷

A further area where the results of investigations of metal-graphite interactions can have a significant impact relates to the interfacial problems encountered with carbon fiber reinforced metal composites. In this regard, a knowledge of the key factors controlling the adherence of the metallic phase to the carbon substrate would be of great importance in establishing the optimum conditions for maximizing the interaction between the two components.

In recent years, the requirement to protect carbon solids, particularly when in the form of a composite, has become an issue of major concern. These materials are being employed in a variety of aerospace applications which demand that they maintain their chemical and mechanical integrity under extremely hostile conditions. This aspect has generated a considerable amount of research effort that is devoted to the development of various treatments designed to improve the oxidation-resistance of these materials.⁸ Two major approaches have been used in an attempt to solve this shortcoming. The first involves the addition of oxidation inhibitors to the substrate surface and the second, the coating of the composite with protective layers that function as oxygen diffusion barriers. McKee⁴ reviewed the different types of oxidation-inhibitors for carbon and concluded that besides halogens the most effective compounds were phosphorus and boron oxides.⁹⁻¹⁴

Graphite undergoes uncatalyzed oxidation by loss of carbon atoms from imperfect regions of the basal plane, steps and crystal edges. The loss of carbon from the perfect regions of the basal plane itself is extremely slow. Some of the salient features of the graphite structure are shown in the schematic illustration, Figure 1. If we consider the basal plane, Figure 1a, it can be seen that there are two arrangements of carbon atoms, the "arm-chair" configuration which is aligned along the $\langle 10\bar{1}0 \rangle$ crystallographic directions, and the "zig-zag" configuration which is parallel to the $\langle 11\bar{2}0 \rangle$ crystallographic directions. These two latter configurations will be referred to in the present text as edge sites or prismatic faces.

When graphite specimens are examined in the electron microscope the orientation of the various features can usually be determined by reference to the position of twin bands which are always present in the crystal. Twinning is a result of a rotation about an axis in the basal plane and along the carbon-carbon bonds, as shown in Figure 1b. When viewed in the microscope the twin band appears as a black line and is always aligned along the $\langle 10\bar{1}0 \rangle$ directions.

Important advances in the understanding of the manner by which various metals and metal oxides interact with graphite, in the presence of both oxidizing and reducing environments, have been made by the use of controlled atmosphere electron microscopy (CAEM).¹⁵ This technique allows one to observe directly the changes taking

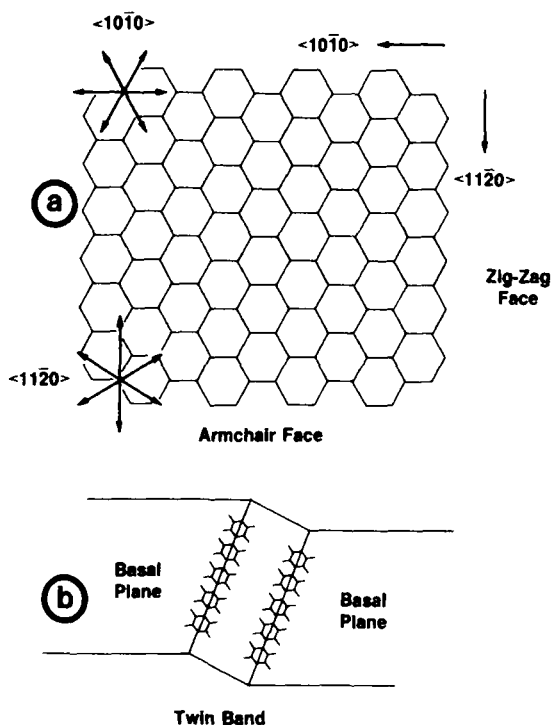


FIGURE 1 Schematic illustration of (a) the graphite basal plane with the crystallographic directions of the prismatic faces, and (b) the formation of a twin band.

place in the transmission image of a solid as it is heated to temperatures of up to 1000°C in a reactant gas. Since the dynamics of the reaction are recorded on video-tape, it is possible to obtain not only qualitative information on the behavior of a surface, but also quantitative estimates of kinetic parameters from the rates of motion of various features and chemical analysis of the specimen at reaction conditions using *in-situ* electron diffraction.

The current paper is a review of the information obtained on the interaction of metal and metal oxide particles with graphite from studies using CAEM. The aim is to focus on some of the factors that control the behavior of the particles in various gas atmospheres. Attention is also given to the manner by which selected additives modify the wetting characteristics and, as a consequence, alter the rate of the catalytic attack exhibited by a particular metal during graphite gasification reactions.

EXPERIMENTAL

The experiments reported in this paper were performed in a modified JEOL 200 CX TEM electron microscope. This instrument is equipped with a custom-designed environmental cell, which accommodates a heating stage. Using this arrangement it is possible to heat specimens at a controlled rate up to a temperature of 1000°C while, at

the same time, being exposed to a gas environment at pressures up to 5.0 Torr. The resolution of this instrument when used in conjunction with a high-sensitivity, closed-circuit television camera is better than 0.4 nm.¹⁶

Transmission specimens of graphite were prepared from natural single crystals obtained from Ticonderoga, New York State. After purification in HCl and HF the crystals were pre-cleaved between glass slides coated with a polystyrene cement, and then released and washed in acetone. Selected crystals were then mounted on glass slides with aqueous polyvinylpyrrolidone (PVP), a water-soluble adhesive. The PVP was allowed to harden under a heat lamp and the flakes further cleaved with Scotch® tape until optically-transparent sections remained affixed to the slide. Such crystals having thicknesses ranging from 15 to 100 nm were found to be excellent electron transmission specimens. The cleaved crystals were released from the slide onto a clean water surface and picked up on a 3 mm electron microscope grid.

Two procedures were used to introduce metals onto transmission specimens of single-crystal graphite. In the first method, the metal, in the form of a spectrographically pure wire, was deposited onto the graphite substrates by evaporation from a heated tungsten filament at a residual pressure of 10^{-6} Torr. By careful control of the weight of the wire and the distance between the filament and the specimen it was possible to produce a metal coating of approximately one monolayer in average thickness. In the second approach, the metal was introduced as an atomized spray from a dilute aqueous solution of a soluble salt, generally a metal nitrate. The only drawback with this latter method is the difficulty of controlling the metal loading. Subsequent heating of these specimens within the electron microscope reaction facility resulted in nucleation and growth of discrete particles ranging in size from 1.0 to 2.5 nm in diameter.

The reactant gases used in this work, oxygen, hydrogen and argon were 99.999% minimum purity (Scientific Gas Products Inc. and Alphagaz Co.) and were used directly. Steam was introduced into the system by allowing argon to flow through a bubbler containing deionized water maintained at 0°C prior to entering the environmental cell, conditions which produced an argon/water ratio of about 40:1.

RESULTS AND DISCUSSION

The Metal-Graphite-Gas Interface

The factors that control the mode of action of a catalyst in graphite-gasification reactions can be divided into chemical and physical aspects. Since electron microscopy has only recently contributed to the understanding of the chemical features, this area will be mentioned only superficially. Some general requirements for the additive to perform as a catalyst in these systems include: (a) the ability to adsorb and, in some cases, dissociate a reactant gas molecule, (b) a capacity to dissolve carbon atoms from the graphite and allow these species to diffuse through or over the surface of the catalyst particle.

In this paper the emphasis is placed on information obtained from electron microscopy examinations related to the physical factors which determine whether a particular additive will act as a catalyst for these reactions and the mode by which it will

function. Studies performed in the CAEM have demonstrated that for an additive to become catalytically active for graphite gasification, the particles must be located at either an edge or step site and that prior to attack they undergo a distinct change in morphology, resulting in a transformation from a non-wetting to a wetting condition.¹⁷ Provided that the chemical requirements are satisfied, the subsequent mode of catalytic attack is governed by the strength of the interaction with the graphite.

A more fundamental understanding of the mechanisms of adherence and the factors governing the nature of interaction of the particles with the graphite can be obtained from a consideration of the surface forces acting at the metal-graphite-gas interface. For a metal particle located on the edge site of a graphite crystal, as illustrated in Figure 2, the contact angle, Θ , at equilibrium, is determined by the surface energy of the support, γ_{GS} , the surface energy of the metal, γ_{MG} , and the metal-support interfacial energy, γ_{MS} , and is described mathematically by Young's equation:

$$\gamma_{GS} = \gamma_{MS} + \gamma_{MG} \cos \Theta \quad (1)$$

The ability of particles to undergo a transformation from a non-wetting ($\Theta > 90^\circ$) to a wetting state ($\Theta < 90^\circ$) indicates that a significant degree of atomic mobility exists, particularly in the surface layers. It follows, therefore, that there will be a minimum temperature, related to the melting point of the metal or metal oxide, where such a phenomenon can occur. Spreading of the additive along the graphite surface takes place when the work of adhesion is greater than the work of cohesion within the particle and can be expressed as:

$$\cos \Theta = \frac{\gamma_{GS} - \gamma_{MS}}{\gamma_{MG}} \quad (2)$$

The subsequent modes of catalytic attack generated by these two diverse morphological states is shown schematically in Figure 3. Under conditions where the additive remains as a discrete particle and exhibits a wetting action with the graphite, then attack proceeds by a channeling action. Throughout the reaction the active particles maintain contact with the graphite interface and, as a consequence, always remain at the leading face of the channel. Once this form of attack has been initiated, the particles will undergo frequent changes in shape, but the leading faces will always have hexagonal facets; characteristics which are dictated by the graphite structure. Figure 4

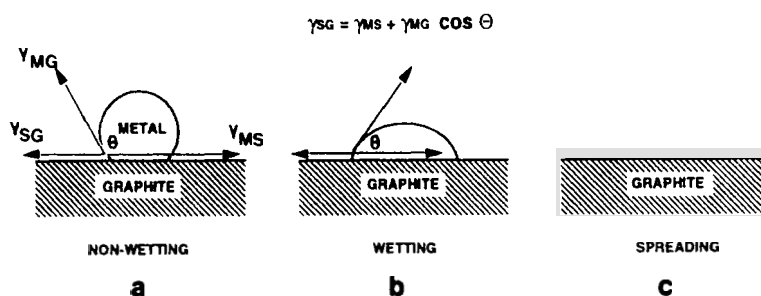


FIGURE 2 Changes in particle shape as a function of the strength of the interaction between the additive and the graphite support.

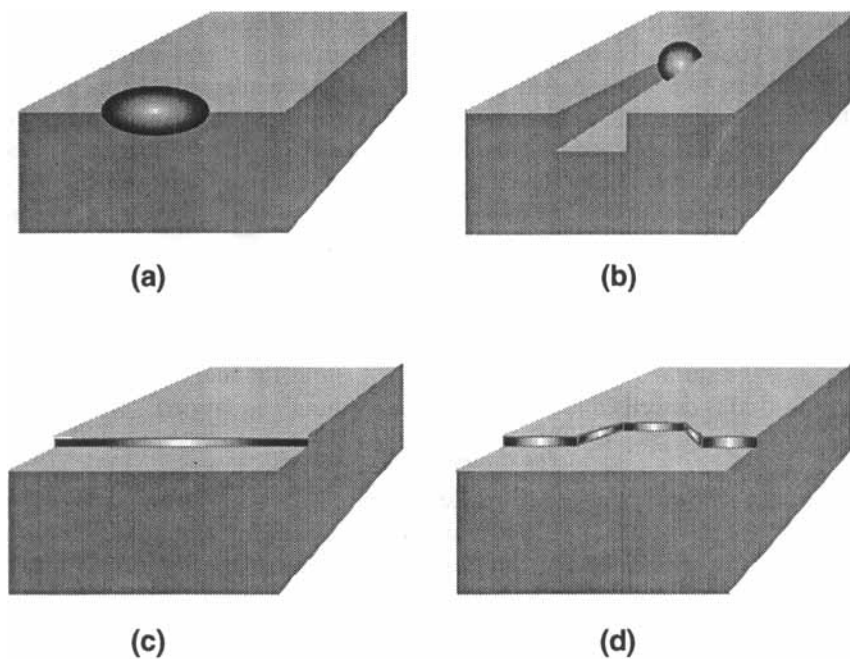
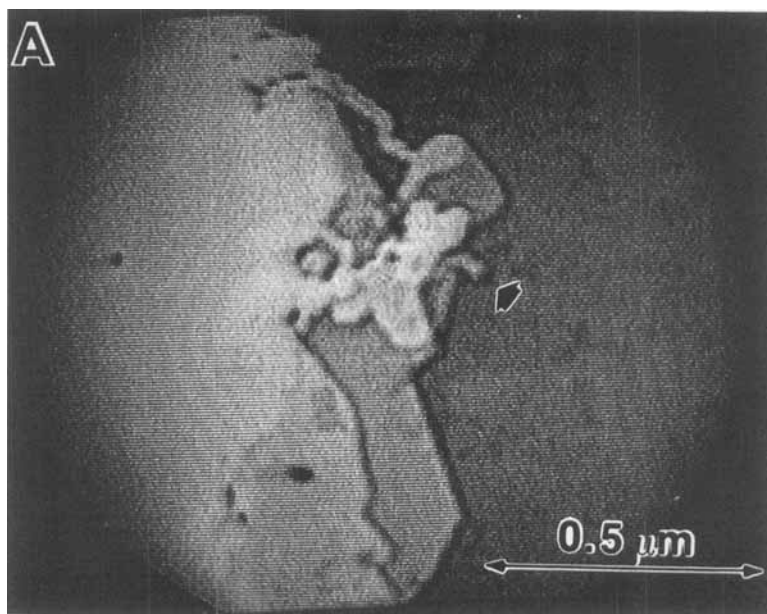


FIGURE 3 Schematic representation of (a) non-wetting unreactive particle, (b) catalyst particle in a wetting condition creating a channel, (c) catalyst material in a spread condition along graphite edge region, and (d) subsequent form of edge recession attack.



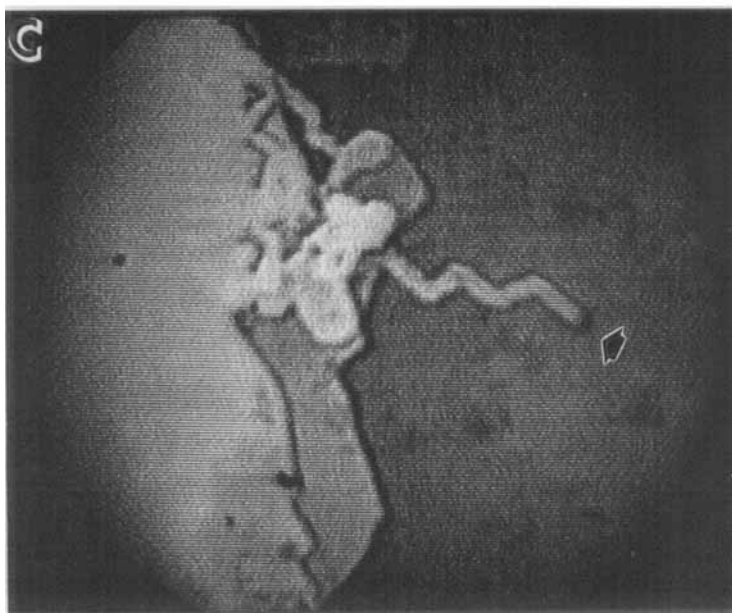
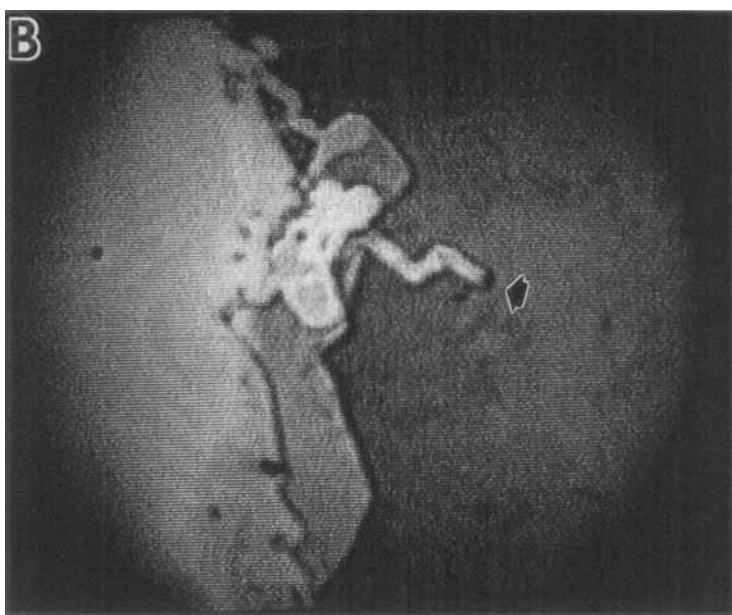




FIGURE 4A - D Sequence showing the propagation of channels across the basal plane surface of graphite by platinum-iridium particles at 1030°C in 5.0 Torr oxygen. Time interval between each frame is 10 sec. (reprinted with permission from Academic Press, Ref. 34).

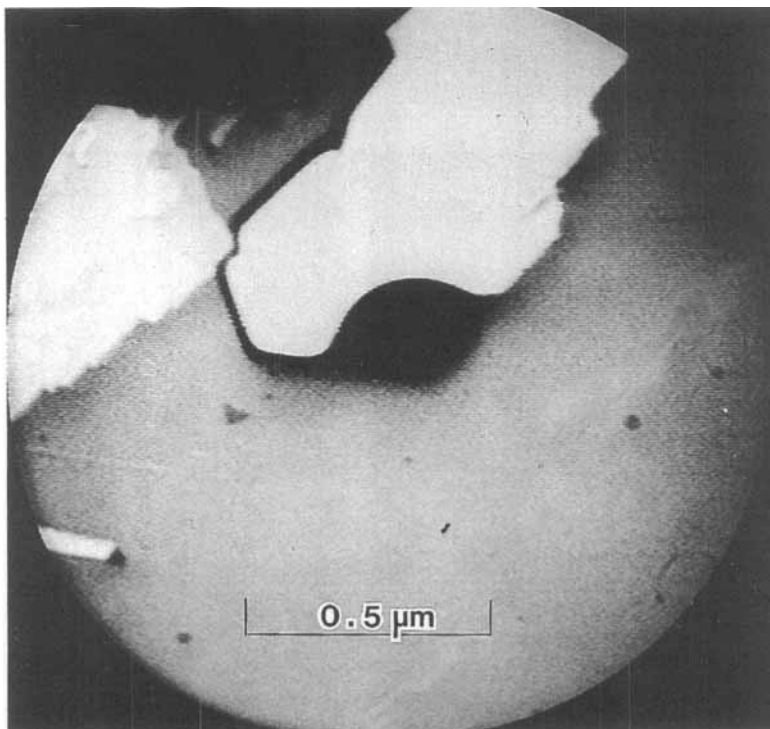


FIGURE 5 Catalytic channels produced from the reaction of molybdenum/graphite with 5.0 Torr oxygen at 635°C. (reprinted with permission from Pergamon Press, *Carbon* 12, 179 (1974)).

is a sequence of stills taken from the TV monitor showing the propagation of channels across the graphite surface by platinum-iridium at 1030°C in 5.0 Torr oxygen; the electron-dense metal particle at the leading face of the channel is indicated by an arrow. The detailed appearance of as catalyst particle in the act of cutting a channel can be seen in the micrograph, Figure 5. In this system, molybdenum/graphite-oxygen at 635°C, the active particles leave material on the sides of the channel. If the catalyst material preferentially wets one of the graphite faces, then the channels tend to be straight with occasional 60° and 120° bends. An example of this form of channeling action is presented in Figure 6, taken of a nickel/graphite specimen after reaction in hydrogen at 950°C. If no preferential wetting occurs, then channels will follow random pathways, behavior generally observed when metal/graphite systems are heated in oxygen.

For the situation where the additive undergoes a strong interaction with the graphite then spreading along the edges in the form of a thin film will occur and the ensuing catalytic attack will proceed by the edge recession mode. This form of gasification, like channel propagation, may exhibit a very ordered motion if the catalytic material undergoes preferential wetting of a particular graphite face. The spreading action results in the most effective use of the additive since each atom in the catalyst is in contact with a surface carbon atom in the graphite. Figure 7a–7d is a sequence showing the progressive depletion in size of a metal particle as it undergoes wetting and spreading to form a thin film at the edges of the substrate. This reorganization in particle geometry precedes the edge recession form of catalytic attack presented in the series of micrographs, Figure 8a–8d, which is taken of a calcium/graphite specimen during reaction in steam at 715°C. The direction of the receding edges, which are coated with a thin layer of CaO, is indicated.

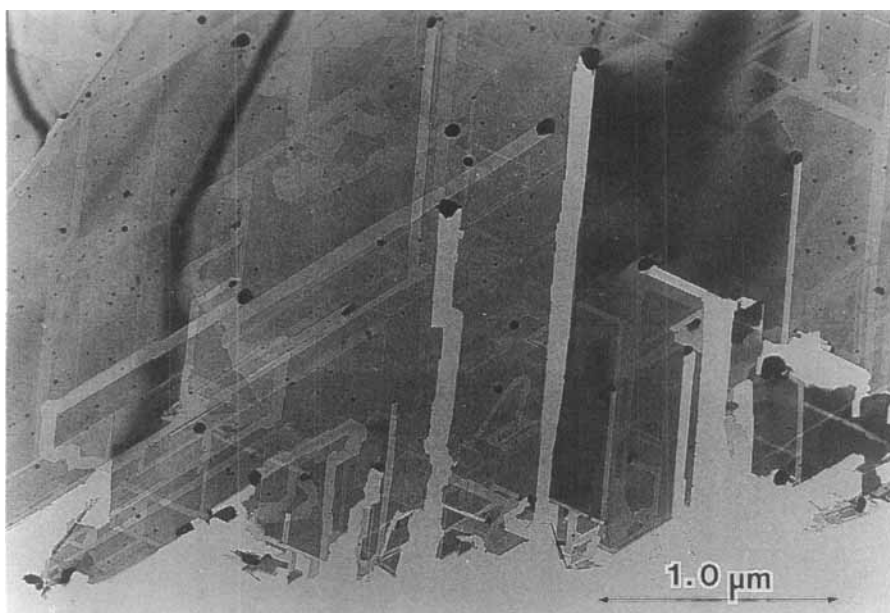
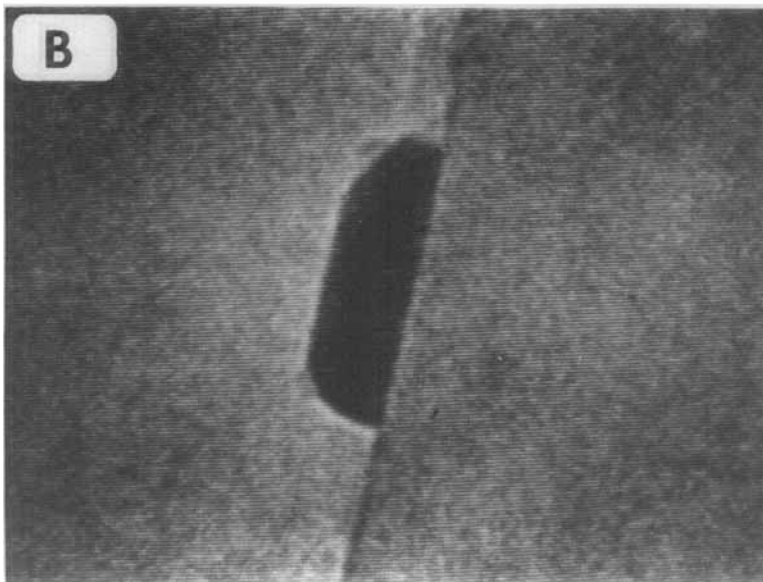
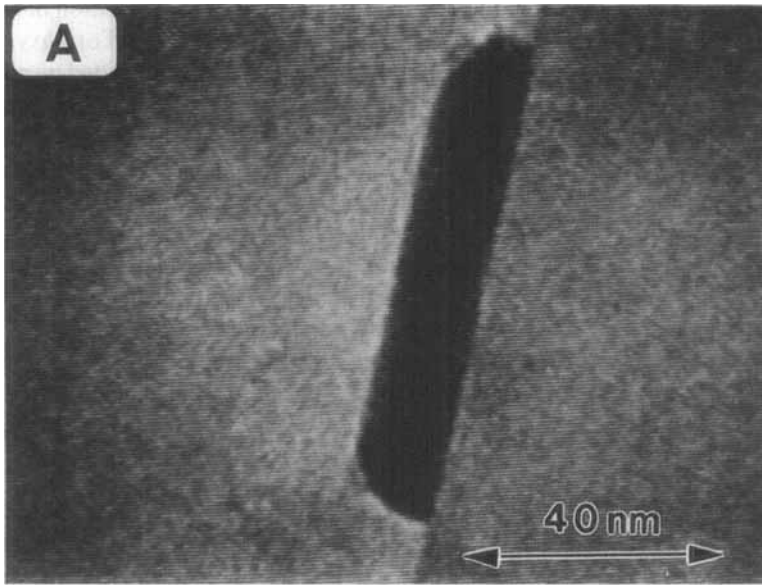


FIGURE 6 Catalytic channeling by nickel particles across the graphite basal plane in 1.0 Torr hydrogen at 950°C.



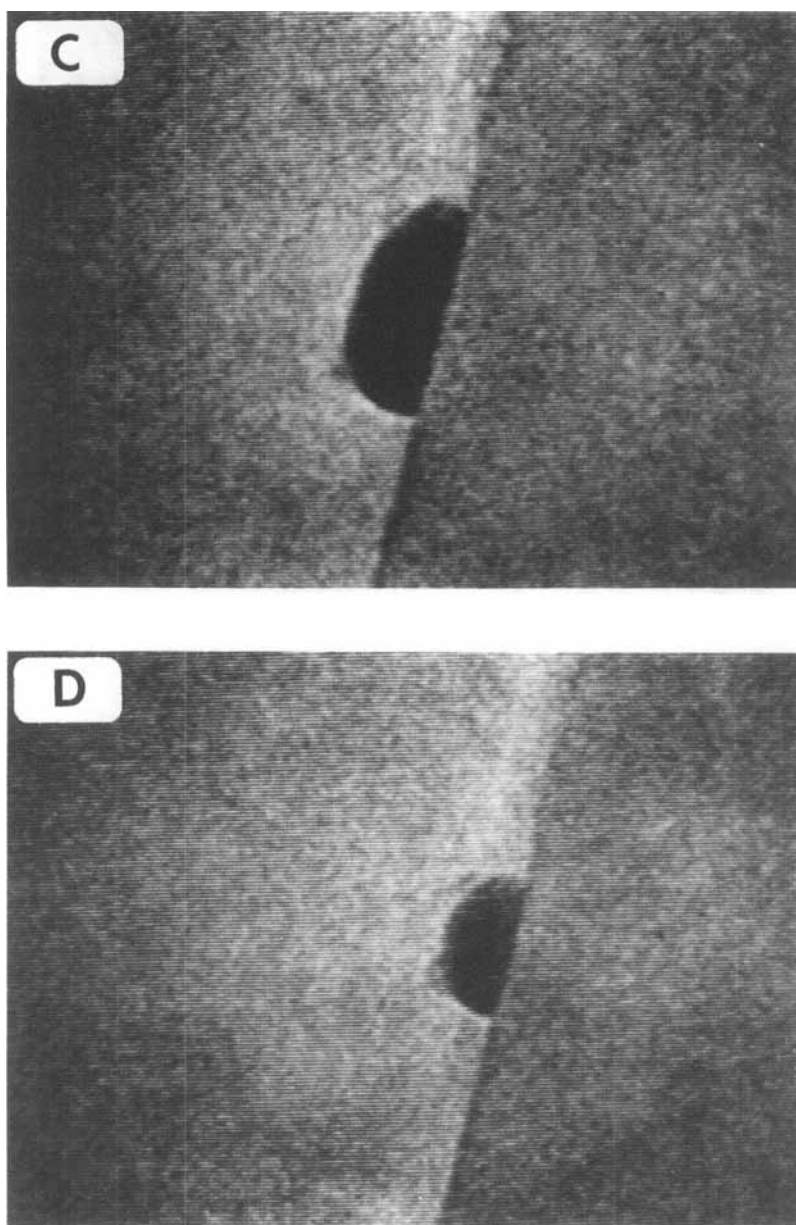
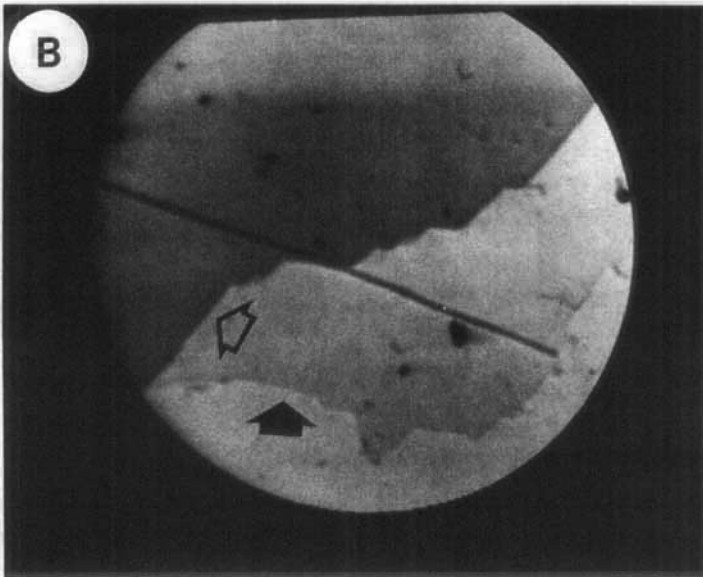
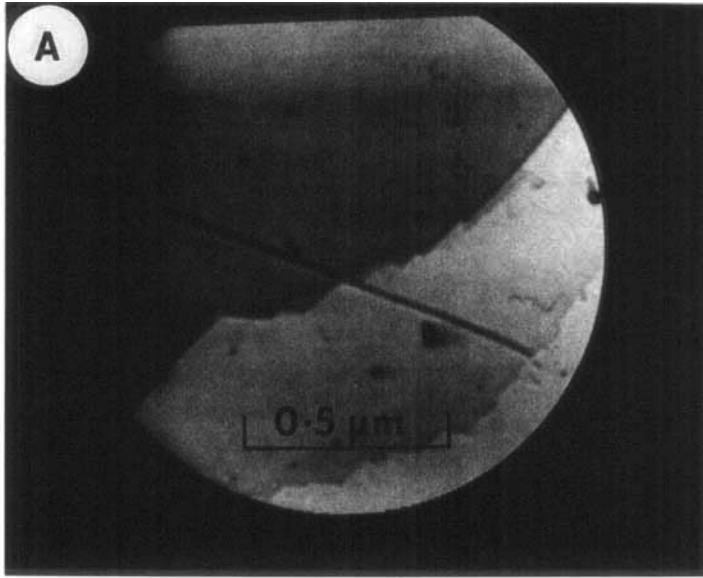


FIGURE 7A-D Sequence showing the spreading action of a metal particle along the edge of a support.

Particle Mobility and Transformation in Morphology

Early studies with the CAEM technique showed that when iron particles supported on graphite were heated in various gas environments, the particles became mobile on the surface at a definite temperature, 700°C .¹⁸ Subsequent studies with other



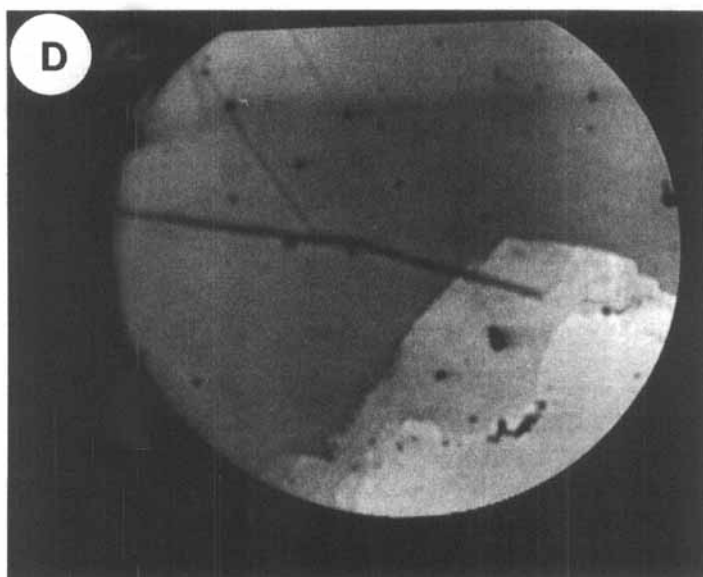
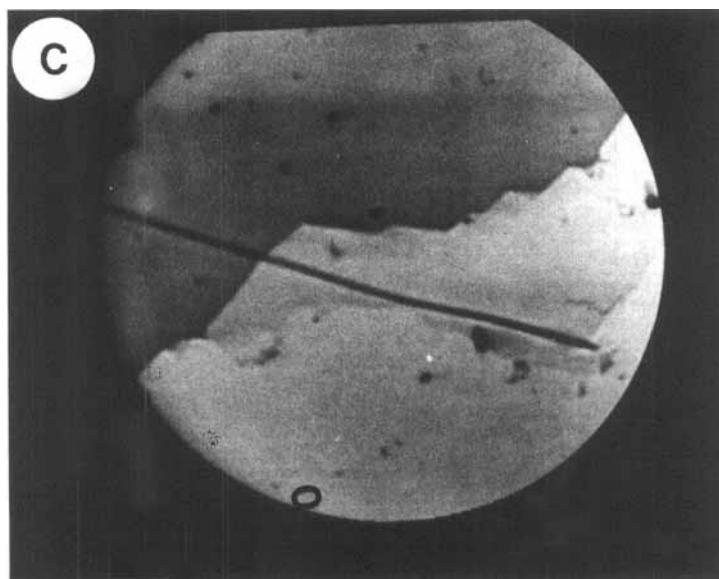


FIGURE 8A-D Sequence showing catalyzed edge recession attack by calcium in steam at 715°C (receding edges are indicated by the arrows. (reprinted with permission from Pergamon Press, Ref. 70).

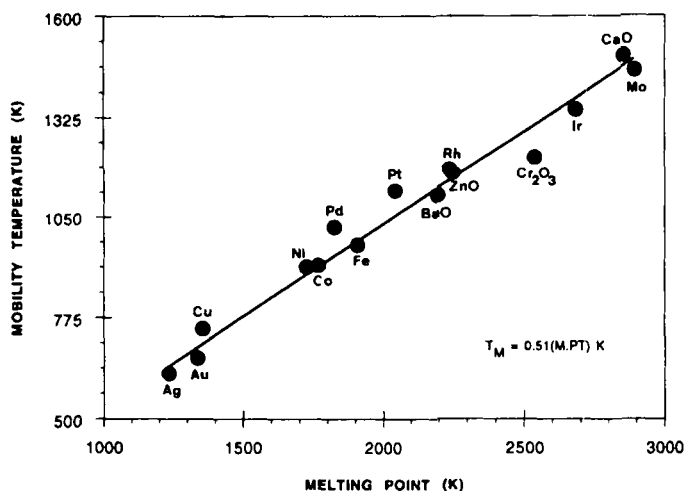


FIGURE 9 Relationship between observed mobility temperature of 10 nm sized particles on graphite in the presence of either oxygen or argon and their respective bulk melting points.

metals dispersed on graphite also revealed that there was a characteristic mobility temperature which was related to the bulk melting point. From the plot presented in Figure 9 it can be seen that the mobility temperature for 10 nm particles of various metals and metal oxides is approximately half their respective bulk melting points, when the temperature is expressed in absolute units. For the most part these mobility temperatures were found to coincide with the Tammann temperature of these materials, which is calculated from 0.52 Bulk Melting Point (K).¹⁹ This is an empirical relationship based on the finding of the existence of a minimum temperature at which a solid is capable of undergoing a solid-solid interaction. Since the initial discovery, there have been a number of studies where marked increases in the rates of various processes involving small particles are found to occur at a temperature corresponding to about half the value of the absolute melting point of the material.²⁰⁻²²

One of the most outstanding studies was that by Derouane and co-workers²³ who used the CAEM technique to observe directly the wetting and spreading action of iridium particles on graphite in hydrogen at 965°C. This type of behavior, which is displayed in Figure 7, has since been observed in a number of systems. These workers performed quantitative measurements of the rate of particle disappearance and the changes in contact angle between the particles and the support as a function of a number of variables. The results were discussed in terms of a model in which particles have a cherry-like structure, consisting of a "hard-core" surrounded by a "viscous layer". The presence of a "hard-core" was believed to exert an influence on not only the spreading rate, but also the wetting characteristics of the metal particles. It was found that the depletion of the small iridium particles was kinetically controlled by their size. Since this transformation was observed at more than 100°C below the Tammann temperature of iridium, it was suggested that enhanced atomic mobility may be present in the surface layers possibly caused by exothermic surface processes which increase the local temperature. Such observations illustrate the power of the technique to reveal

transformations in particle dimensions and shape resulting from interactions with a support in the presence of a gas.

Addition of hydrogen sulfide to the gas phase has been found to induce major perturbations in both the morphology and growth characteristics of supported metal particles.²⁴ In a series of very elegant CAEM experiments Hayden and co-workers²⁵ compared the behavior of molybdenum on alumina and graphite when heated in oxygen and hydrogen sulfide/hydrogen mixtures. In an oxidizing environment at 550°C molybdenum oxide particles were observed to wet and spread on the alumina support due to the formation of a strong oxide-oxide interaction. The interaction between molybdenum oxide and graphite was significantly weaker and at 655°C the particles were observed to exhibit mobility. On mixed support specimens containing both alumina and graphite regions, the mobile oxide particles on graphite were observed to disappear when they contacted alumina edges due to a rapid spreading action. The molybdenum oxide-alumina interaction was broken by treatment in the hydrogen sulfide/hydrogen mixture at 475°C, with the formation of molybdenum sulfide crystallites. When the temperature was raised, the size of these particles increased appreciably. On the graphite support a molybdenum sulfide rag-phase was formed from the metal oxide crystallites and a strong sulfide-support interaction was created, which was not broken by a high temperature oxidation treatment.

Catalyzed Graphite-Oxygen Reactions

Early work by Hennig²⁶ demonstrated the power of transmission electron microscopy to reveal some of the intimate details surrounding the manner by which metallic particles influenced the oxidation of graphite. He found that on graphite crystals that were relatively free of defects, the active metal particles attacked in a direction parallel to the basal plane to create channels. It was proposed that the motion of the particle along its catalytic track was due to the attractive forces between the metal and the carbon atoms at the channel tip. He argued that since the carbon atoms at these locations were continuously being removed by the oxidation reaction, only the leading faces of the catalyst particle could maintain contact with edge atoms. A further aspect was the claim that catalytic attack was restricted to the particle/graphite interface and that any modification in the Fermi level of conduction electrons in the substrate was not a contributing factor to the reaction.

The pioneering studies of Hennig inspired other workers to continue and expand his efforts in this area. A variety of *in-situ* microscopy techniques were used to observe directly the action of metal particles during the graphite-oxygen reaction.^{1,27-30} One of the most important findings to emerge from these investigations was the realization of the dangers in attempting to determine the chemical identity of a catalytic species using bulk thermodynamic data for a system where the concern centers around the stability of phases at interfaces.^{1,27} For the most part, these studies tended to focus on the characteristics and kinetics of particles which operated by the channeling mode.

Evidence that catalytic attack could also take place by edge recession was first reported by Harris and co-workers.³¹ They used the CAEM technique to follow the manner by which lead enhanced the oxidation of graphite and observed that at temperatures below 545°C the rate of edge recession was approximately 10^5 times




faster than that found with a pure graphite specimen. This result led them to suggest that under these conditions the catalytic species was present as an extremely thin film spread along the edge and step regions of the substrate.

This same experimental approach was used by Baker and various co-workers³²⁻³⁸ to examine the effect of a number of metals and metal oxides on the graphite-oxygen reaction. These studies highlighted both the qualitative and quantitative kinetic features associated with individual particles in a given system; however, the factors which governed the mode of operation of the catalyst, such as channeling or edge recession, remained obscure for many years. This enigma was eventually solved by taking into consideration both the predicted chemical state of the catalyst at various stages of the reaction and the wetting characteristics such species might be expected to exhibit with a graphite surface containing oxygenated groups.

The activity patterns exhibited by a number of elements is summarized with respect to their position in the Periodic Table in Figure 10. Elements marked in the shaded boxes were observed to undergo readily a spreading action on the graphite edge and step regions and this action preceded oxidation of the substrate by the edge recession mode. It is known that over the temperature ranges where these reactions occur all this group of metals adsorb oxygen dissociatively and are present on the graphite as metal oxides.³⁹ It is probable that under such circumstances strong interfacial bonding will occur between the additive and the oxygenated carbon edge atoms. The strength of this interaction will be sufficient to induce a spreading of the catalyst material, culminating in attack by the edge recession mode.

In contrast, once the metals indicated in the open boxes nucleated into small particles they remained in this form throughout the reaction period and those which came into contact with edge and step sites were observed to create channels across the graphite surface. The onset of this action varied from one system to another and appeared to be related to the Tammann temperature of the metal under examination. At the reaction conditions where the channeling attack occurred it is found that oxygen is adsorbed in a non-dissociative manner and, as a consequence, the particles are likely to be present in the fully-reduced state. It is, therefore, reasonable to expect that this set

IVB	VB	VIB	VII B	VIII B	VIII B	IB	IIB	
Ti	V	Cr		Fe	Co	Ni	Cu	Zn
		Mo		Ru	Rh	Pd	Ag	
		W	Re		Ir	Pt	Au	

FIGURE 10 Catalytic behavior of various metals on the graphite-oxygen reaction as a function of their respective position in the Periodic Table.  represents attack by the edge recession mode;  indicates attack by the channeling mode; and metals which do not exhibit sustained catalytic activity are marked by .

of metals will exhibit a somewhat weaker interaction with the oxygenated carbon edge atoms than those which are converted into oxides and, as a consequence, in this case, spreading of the catalytic material will not be favored.

In addition to these two extreme catalytic states there are examples of additives which are present in the initial stages of the graphite gasification reaction as oxides and as the temperature is gradually raised they undergo disproportionation so that the metal becomes the stable solid phase.^{40,41} Consistent with the arguments presented above is the finding that over the lower temperature range the catalyst operates *via* the edge recession mode and as the temperature is increased to a critical level this action ceases with the simultaneous reformation of particles along the graphite edges. Immediately following this transformation in particle morphology there is a corresponding change in catalytic attack from edge recession to channeling. Furthermore, this behavior is reflected in a major modification in the rate of the catalyzed graphite oxidation reaction. The additives that have been studied which fit into this category include cobalt, ruthenium, rhenium and iridium.

Finally, there are some elements which do not exhibit sustained catalytic activity for the graphite-oxygen reaction. These include the elements iron and nickel, labelled by the cross-hatching on Figure 10. Although the wetting and spreading behavior of these particles along the graphite edges is a facile process, there is no evidence that the rate of edge recession is promoted by the presence of the additive film. Previous workers have established that for an additive to be capable of attacking graphite it must have the ability to undergo a redox cycle at the carbon interface, a necessary requirement of the oxygen-transfer mechanism which is believed to be operative in the reaction.⁴² Based on this understanding, it was suggested that the inactivity of these metals was related to the fact that under these conditions they all form very stable oxides, which do not readily undergo reduction to a lower oxidation state by interaction with graphite.

We have recently extended the scope of these studies by correlating the changes in the activity pattern of a given additive with that of its chemical state at various stages of the gasification reaction. CAEM studies have shown that cobalt particles supported on graphite exhibit a very unexpected reactivity pattern during reaction in oxygen. In this system, the cobalt particles were observed initially to wet and spread along graphite edges and accelerate the removal of carbon atoms from these locations *via* the edge recession mode. This type of action persisted up to 880°C, at which point particles reformed and the mode of action changed to that of channeling. Quantitative kinetics analysis of these events showed the existence of three distinct activity regions, which corresponded to the formation of three oxidation states of cobalt, CoO (475–640°C), Co₃O₄ (665–880°C) and Co (> 880°C) as determined from *in-situ* electron diffraction analysis.⁴³ It was significant that post-reaction electron diffraction examination failed to show the presence of the metallic phase in specimens that had been cooled from 900°C to room temperature.

Inhibition of the Graphite-Oxygen Reaction

Based on the fundamental studies of the manner by which particles operate during the catalytic graphite-oxygen reaction, one is now in a strong position to establish certain criteria which are essential for an additive to perform as an inhibitor for this reaction.

These include the following aspects:

- (i) the additive should react with oxygen to form a thermally-stable metal oxide, which does not undergo a redox reaction with the carbon substrate,
- (ii) the additive should undergo a strong interaction with the carbon substrate and exhibit a wetting and spreading action to form a strongly adherent film along the reactive carbon edges,
- (iii) the additive must remain in the form of a film during temperature cycling, *i.e.*, it should not nucleate into particles on cooling or heating,
- (iv) the additive should be stable and maintain the above morphological characteristics in wet environments.
- (v) All the above requirements could be accomplished if the additive formed a stable chemical bond with the carbon edges or became incorporated within the structure.

It was these factors which provided the framework for the studies by Rodriguez and co-workers^{14,44} who used the CAEM technique coupled with *in-situ* electron diffraction to examine the influence of phosphorus and boron on the graphite-oxygen reaction. Continuous observation of the boron/graphite-oxygen reaction showed that at 450°C the additive, in the form an oxide, underwent a strong interaction with both the prismatic and basal plane regions of the substrate. This action resulted in spreading of the boron oxide to form a uniform, thin, adherent coating over the entire graphite specimen, and provided a very effective protection for the structure towards attack by oxygen at temperatures up to 815°C. Unfortunately, at higher temperatures the oxide exhibited a change in its wetting characteristics, which resulted in a weakening of the interaction with the “armchair” $\langle 10\bar{1}0 \rangle$ faces and these regions then became susceptible to oxidation.

In a further series of experiments the influence of phosphorus on the graphite-oxygen reaction was investigated. In this case, the additive completely suppressed the gasification of all faces at temperatures below 830°C. At higher temperatures it became apparent that the “arm-chair” $\langle 10\bar{1}0 \rangle$ faces were undergoing attack at a significantly slower rate than the “zig-zag” $\langle 11\bar{2}0 \rangle$ faces, indicating that phosphorus species were undergoing preferential interaction with the former sites. Detailed kinetic analysis of the video recordings of many experiments showed that the inhibiting effect of phosphorus on the reaction was maintained up to temperatures in excess of 1000°C. Under these conditions the rate of oxidation of a phosphorus-coated edge was about 15 times slower than that of an uncoated specimen. From the *in-situ* electron diffraction data it was suggested that at elevated temperatures a complex is formed in which the phosphorus species are incorporated into the graphite structure. This is a unique type of chemical bonding where both phosphorus and oxygen electrons are integrated into the delocalized π -system of the graphite. It was argued that this arrangement was responsible for conferring thermal stability on the phosphorus species.

In summary, the CAEM studies have shown that boron and phosphorus exhibit quite different wetting and subsequent bonding characteristics on the graphite edge sites, which is related to atomic size and geometrical arrangement of the two elements when incorporated into the graphite crystal structure. Boron easily substitutes the carbon atoms in the “zig-zag” faces without disturbing the inter-planar distance, whereas this process is restricted for phosphorus. On the other hand, a single

phosphorus atom is readily accommodated at the "armchair" faces in what appears to be a much more stable structure than that achieved with boron at the same sites. One may conclude, therefore, that a mixture of these additives, when introduced under the correct conditions, would provide the most effective means of inhibiting the oxidation of graphite at temperatures up to 1000°C.

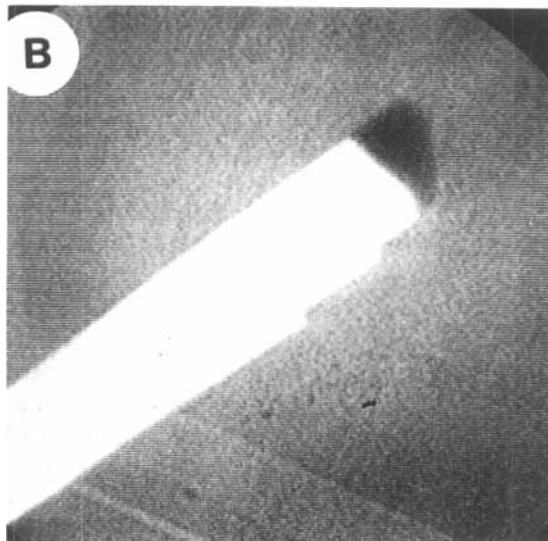
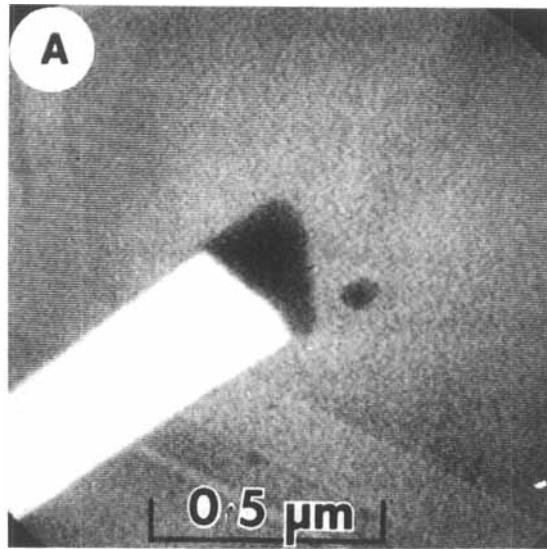
Catalyzed Graphite-Hydrogen Reactions

Considerably less attention has been given to the catalyzed hydro-gasification of graphite than that devoted to the comparable oxidation process. The first detailed report of the behavior of metal particles on the graphite-hydrogen reaction was published about twenty years ago by Tomita and Tamai.⁴⁵ These workers carried out intermittent observations in an optical microscope of graphite specimens containing selected transition metal particles, at various stages of reaction in hydrogen at ~850°C. In spite of the resolution limitation of this approach, they were able to establish that catalytic attack took place by the channeling mode and that the tracks propagated by active particles tended to be straight with occasional 60° and 120° bends, and aligned along the $\langle 11\bar{2}0 \rangle$ crystallographic orientations of the graphite. These findings indicated that in the presence of hydrogen the catalytic material exhibited a preferential wetting action with respect to "arm-chair" faces of the graphite and that the particles move in such a manner to maintain contact with the carbon atoms in this arrangement.

In more recent years, both CAEM^{38,46,47} and high resolution transmission electron microscopy⁴⁸ have been used to investigate the influence of a variety of metals on the hydro-gasification of graphite. In addition to confirming many of the earlier optical microscopic observations, these more detailed studies have revealed a number of other facets of the catalytic pattern of behavior. Continuous observation of metal/graphite systems by CAEM shows that particles which come into contact with edges tend to undergo a spreading action at certain temperatures; however, unlike the corresponding oxidation reactions, this event is rarely accompanied by catalytic edge recession. It was proposed that this phenomenon occurred at the stage where elimination of adsorbed oxygen groups from the graphite surface had been achieved by reaction with active hydrogen species, presumably generated *via* dissociation of molecular hydrogen on the metal particles. Such a "clean up" operation would create conditions which favored the formation of a strong interaction between the metallic component and the oxygen-free graphite edge regions.

The temperature range over which the spreading action persisted was found to be limited and on continued heating particles were observed to re-appear at the edge sites. It was suggested that this change in the wetting characteristics of the additive was caused by an increase of dissolved carbon content in the metals at elevated temperatures, which results in a weakening of the metal/graphite interaction.⁴⁹ Immediately following this transformation the nucleated particles proceeded to generate channels, all of which originated from step or edge sites. The channels showed many similar characteristics to those formed under oxidation conditions, but it was clear that even at 1000°C or higher, they remained parallel-sided throughout their propagation period, indicating that the rate of uncatalyzed attack, which would be expected to result in a progressive widening of the tracks, was insignificant.

A fascinating variation of the general pattern of channeling behavior was observed when nickel particles dispersed on graphite were heated in hydrogen, Figure 11a–11d. As the temperature was increased to 975°C, it was possible to observe directly the gradual depletion in size of nickel particles which were in the act of creating channels across the graphite basal plane.^{50,51} In subsequent experiments, this apparent particle loss was shown to be caused by wetting and spreading of nickel on graphite resulting in the formation of a thin film of metal along the channel walls, as shown schematically in Figure 12. Restoration of particles along the sides of the original channels was achieved by replacing hydrogen with either oxygen or steam and heating the systems to



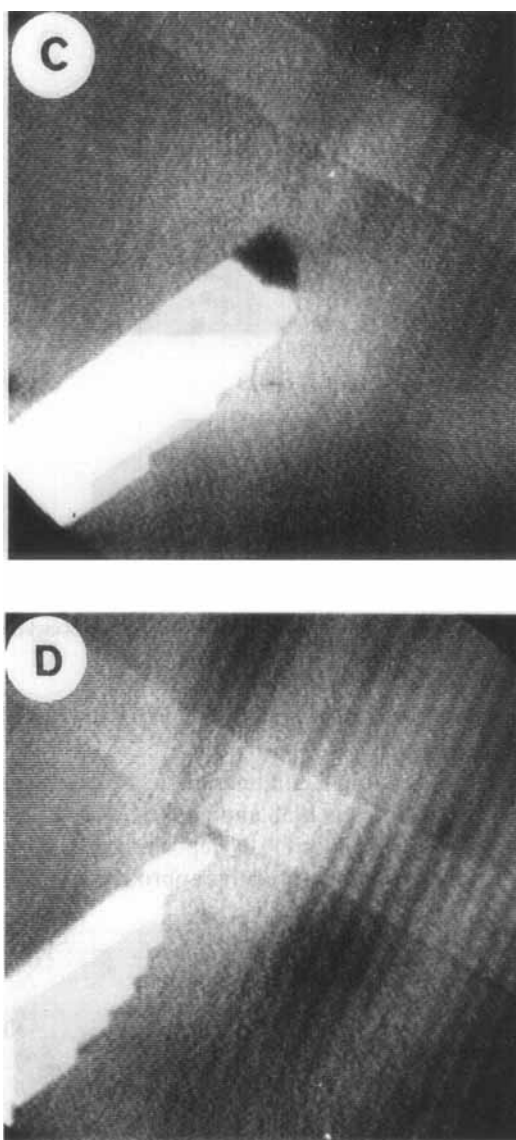


FIGURE 11A-D Sequence showing the gradual loss of activity of a nickel catalyst particle during the graphite/hydrogen reaction at 1000°C due to deposition of metal along the walls of the channel. (reprinted with permission from Academic Press, Ref. 52).

temperatures in excess of 900°C. If the specimens were heated to higher levels then these particles proceeded to create very fine channels emanating from the edges of larger ones. Figure 13a and 13b are schematic representations of the reactivation of nickel in steam and oxygen, respectively. Although the precise cause and nature of the interaction between nickel and carbon that gave rise to catalyst deactivation in hydrogen was

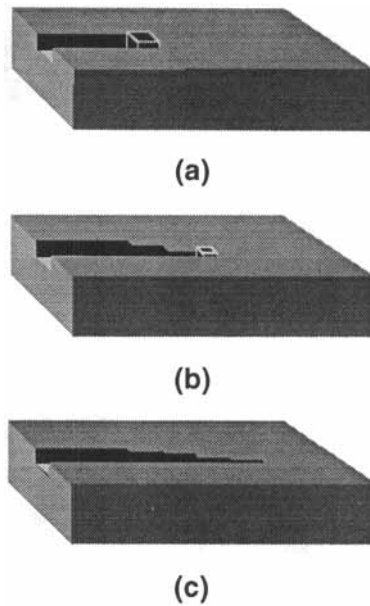


FIGURE 12 Schematic representation of the progressive spreading action of nickel along the channel walls during hydro-gasification of graphite at 1000°C.

not fully understood, the sequence of treatments provided the basis for a novel method of redispersing nickel particles.⁵²

The technique of etch decoration in conjunction with transmission electron microscopy was developed by Bassett⁵³ in 1958 and enables one to detect the presence of monoatomic steps on the surface of graphite by depositing gold particles onto a reacted specimen. Goethel and Yang⁵⁴⁻⁵⁶ have used this approach to study the catalysis of the

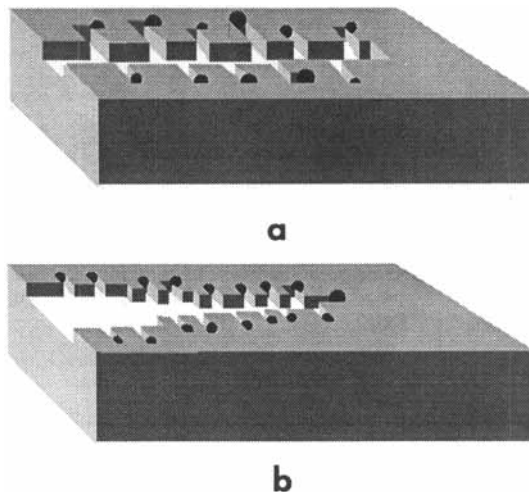


FIGURE 13 Schematic diagram showing the reactivation of the nickel film on graphite produced in hydrogen following subsequent reaction in (a) steam at 935°C, and (b) oxygen at 1065°C.

graphite-hydrogen reaction in the presence of several Group VIII metals. These workers were able to establish that catalyst particles not only attacked the graphite by a deep (multi-layer) channeling mode, but were also capable of generating monolayer channels across the surface. Furthermore, it was claimed that since the surface reaction on the catalyst was the rate-limiting step in both cases, these two forms of attack could make equal contributions to the overall rate of hydrogenation. Recent studies performed by scanning tunneling and atomic force microscopy⁵⁷⁻⁵⁹ have confirmed the existence of monolayer pits and channels, first revealed by the gold decoration technique.

Catalyzed Graphite-Steam Reactions

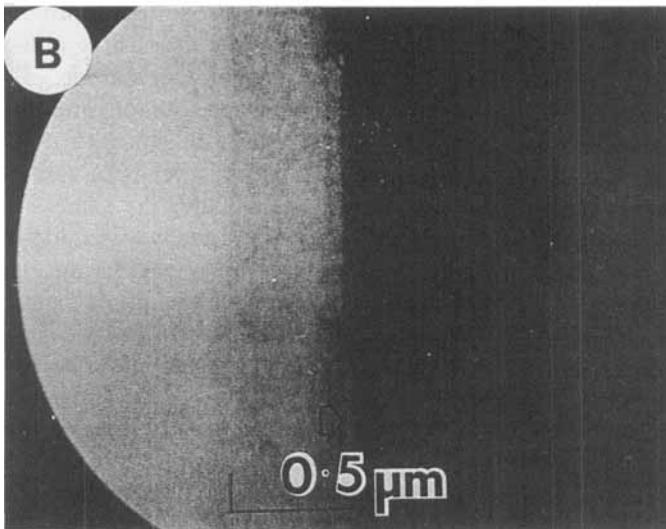
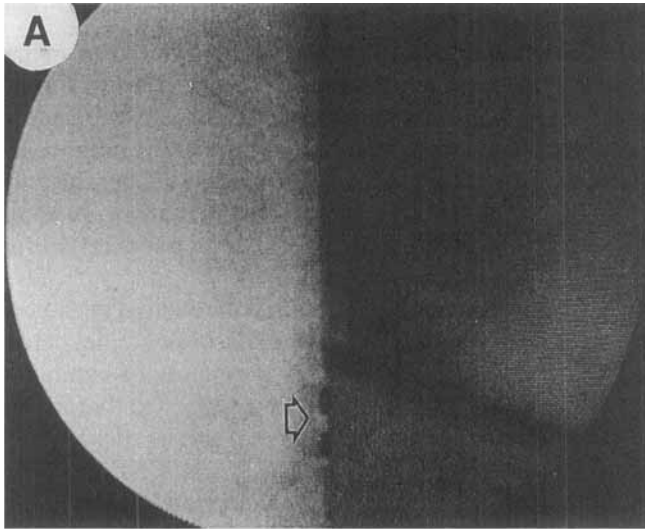
Steam gasification of carbonaceous solids is an area in which the intensity of research interest has oscillated for many years, because the reaction to form hydrogen and carbon monoxide is a key factor in many industrial processes, including coal gasification to produce substitute natural gas (SNG). The use of a catalyst in the system is essential if one is to be in a position to lower the process temperature and improve the selectivity to desired products.^{60,61} It is well known that alkali, alkaline earth and the iron sub-group transition metals are among the most active catalysts for the graphite-steam reaction.⁶²⁻⁶⁸

In many steam gasification operations calcium is the catalyst of choice and this based to a large degree on the information derived from the basic studies carried out by Otto and co-workers.⁶⁵ From electron microscopy examinations combined with kinetic data obtained from bulk reactor experiments, they suggested that the enhancement in gasification rate was related to the ability of calcium species to maintain extensive and intimate contact with the graphite surface. The first CAEM studies of the calcium/graphite-steam system were performed by Coates and co-workers⁶⁹ who claimed that calcium was not an active catalyst for the reaction since it did not appear to generate channels across the substrate surface. This observation was confirmed by other workers using a similar experimental approach⁷⁰; however, consistent with the earlier work,⁶⁵ it was demonstrated that calcium, in an oxidized form, exhibited a very facile wetting and spreading action at the graphite edge sites and subsequently promoted the removal of carbon atoms by the edge recession mode.

The CAEM studies highlighted further aspects of the reaction, one of which was the tendency of the receding coated edges occasionally to come to a sudden halt, a phenomenon attributed to catalyst deactivation. This behavior was also observed when potassium/graphite specimens were reacted under the same conditions, and became more pronounced as the temperature was gradually raised to 900°C.⁷¹ It was suggested that deactivation was due to chemical changes in either the catalytic species and/or the nature of the graphite surface, factors which might be expected to induce major modifications in the bonding characteristics between the two components.

Barium was found to exhibit a somewhat different pattern of behavior to calcium in its catalytic action towards the steam gasification of graphite.⁷² The sequence of events which occurred before and during the initial stages of catalytic attack is presented in the series of stills taken from the video playback, Figures 14a-14c. When graphite specimens containing barium oxide was heated to 450°C in steam, the additive particles which had collected at the substrate edge sites were found to adopt a non-wetting

configuration (Figure 14a). As the temperature was progressively raised to 600°C these particles were observed to rearrange, initially to a wetting condition, and eventually to disappear as they spread along the edges in the form of a thin film (Figure 14b). On continued heating to 700°C, the coated edges and steps started to undergo recession in a very uniform manner in directions parallel to the $\langle 11\bar{2}0 \rangle$ crystallographic faces (Figure 14c). This observation was found to be consistent with earlier bulk studies by



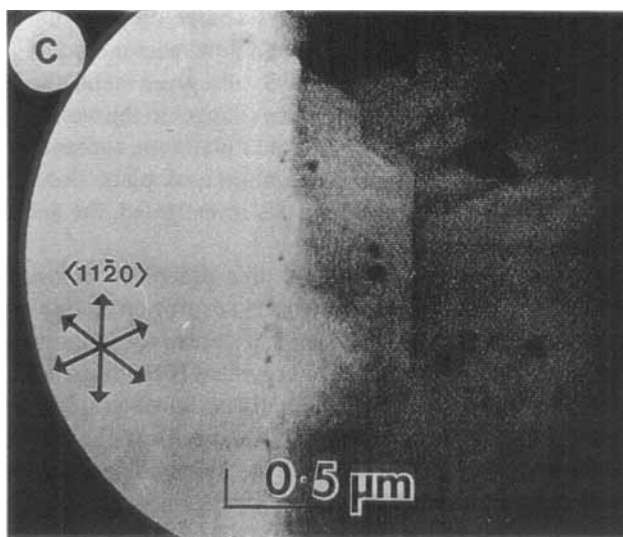


FIGURE 14A-C Sequence showing the disappearance of barium oxide particles as they spread along the graphite edges at 600°C in 2.0 Torr wet argon (the arrow marks the position of the particles before and after spreading), followed by catalyzed edge recession of the substrate at 700°C. (reprinted with permission from Academic Press, Ref. 72).

Magne and Duval,⁷³ who demonstrated that steam preferentially chemisorbed at $\langle 10\bar{1}0 \rangle$ sites and, as a consequence, during gasification carbon atoms at these positions would be selectively removed leaving behind those in a $\langle 11\bar{2}0 \rangle$ configuration.

A dramatic change in the mode of catalytic attack was detected at 900°C; edge recession came to an abrupt stop as particles once again were observed to nucleate at these locations. This transformation in catalyst morphology was accompanied by a switch in action to channeling, and this remained the exclusive mode of attack up to 1100°C. In some experiments the temperature was subsequently lowered from 1100 to 750°C, and under these circumstances the original edge recession activity was restored as active particles exhibited a spreading action at the graphite interface. The reversible nature of the modification in wetting characteristics and the consequent change in the mode of catalytic action was attributed to the participation of the hydrogen product in the reaction, the concentration of which became appreciable at high temperatures.

In an attempt to overcome the catalytic deactivation problem encountered with potassium in the steam gasification of graphite, Carrazza and co-workers⁷⁴ investigated the influence of adding nickel to the alkali metal. Using CAEM they were able to establish that while the mixed catalyst system operated in a similar manner to that found with potassium alone, the rate of edge recession increased in a smooth fashion over the temperature range 550 to 1000°C, and showed no signs of deactivation. The superior catalytic properties of the nickel/potassium mixture over that found when each additive was used separately was believed to arise from a co-operative effect between the components.

Finally, the concept of using bimetallic catalysts based on pairs of transition metals was explored using a combination of CAEM and flow reactor studies.⁷⁵ It was found that in addition to modifying the catalytic activity of a given metal, the introduction of a second metal into the system could also induce changes in the wetting characteristics of the particles on the graphite. In the presence of platinum, ruthenium and mixtures containing these metals, catalytic steam gasification took place along the "armchair" faces of graphite. In contrast, with other metals investigated, the action occurred in directions parallel to the "zig-zag" faces.

A rationale was presented to account for this difference in reactivity patterns which was attributed to an interplay between the adsorption characteristics of water molecules at the catalyst surface and the chemical state of the graphite prismatic faces when exposed to a steam environment. The argument is predicated on the report by Yang and Duan⁷⁶ that when water molecules dissociate on graphite they do so in a manner which favors chemisorption of hydrogen species at the "zig-zag" faces and hydroxyl groups at the "armchair" faces. Based on these findings, it would be expected that metals which dissociate steam and are left with an oxide or a hydroxide surface layer will preferentially react with the hydroxylated "armchair" edges of graphite. Metals that fall into this category include iron, nickel, the alkali and alkaline earths. In these systems catalytic attack will leave edges orientated parallel to the less reactive $\langle 11\bar{2}0 \rangle$ directions, *i.e.*, the "zig-zag" configuration. On the other hand, metals that do not readily dissociate steam and remain in the fully reduced state under such conditions would preferentially interact with the hydrogenated carbon surfaces. It follows, therefore, that in the presence of platinum and ruthenium, and in bimetallic systems where these metals would tend to segregate to the carbon interface, the residual edges will be aligned along the $\langle 10\bar{1}0 \rangle$ directions or in an "armchair" configuration.

SUMMARY

While transmission electron microscopy has proven to be an invaluable tool for the study of many aspects concerned with metal/support interactions, the major limitation is that materials can only be viewed in a vacuum. As a consequence, it is difficult to assess the impact of various treatments on a given specimen and such a task is generally attempted by comparison of the appearance of a specimen before and after reaction. While this procedure can yield useful information, some caution must be exercised since the specimen has been removed from the reaction environment and has undergone cooling. The use of controlled atmosphere electron microscopy (CAEM) overcomes many of these difficulties, since this type of investigation allows one to capture the transitory features occurring in the specimen as it undergoes reaction in the presence of a gas. It is this facility which has brought new insights into the understanding of many aspects related to the behavior of metal and metal oxide particles on the catalyzed graphite gasification reactions. We are now in a position not only to predict the interfacial behavior of a given additive with graphite, but also to manipulate its

interaction in such a system by the introduction of a second component into the particles or by careful control of the chemical nature of the reactive environment and temperature.

Acknowledgements

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