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REDUCTION OF NICKEL OXIDE BY CARBON: I. INTERACTION BETWEEN NICKEL OXIDE AND PYROLYTIC GRAPHITE

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Abstract—The interaction of micron-sized particles of nickel oxide with pieces of stress-recrystallized pyrolytic graphite has been studied between 950 and 1000°C using optical and scanning electron microscopy. The gases evolved (CO and CO₂) upon reduction of NiO to nickel were continuously pumped out of the system in most of the runs. Examination of the cleavage (basal) surface and prismatic (edge) surface of the pyrolytic graphite after reaction reveals considerable mobility of selected oxide particles, creating shallow channels and pits on the graphite surface. Attack at the prismatic surface is more general and rapid than at the cleavage surface. Periodic examination of the cleavage surface during reaction revealed that many particles do not show any mobility or reaction, suggesting that reaction takes place only at active sites. Copyright © 1996 Elsevier Science Ltd

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1. INTRODUCTION

The reduction of metal oxides by carbons has been the subject of numerous investigations with a number of theories being proposed to explain experimental results. For example, Hopkins *et al.* [1] suggested that the metal oxide first dissociates into metal and oxygen, and subsequently the oxygen reacts with carbon. According to Baukloh and Shringerum [2], the reduction which occurs at the interface is controlled by the diffusion of carbon through the reaction product layer. Yun [3], however, from his studies on the reduction of iron oxide by graphite, suggested that the diffusion of metal through metal oxide, and not the diffusion of carbon through the metal layer, was the rate-determining step. Susukida and Sano [4] and Tatievskoya *et al.* [5] proposed the formation of an intermediate gaseous product, CO, which reacts with the metal oxide, forming CO₂. Kohl and Marineck [6] also suggested the formation of CO as an intermediate step during the reduction of oxides of iron, cobalt and nickel by graphite.

The mechanism of the reduction of metal oxides by carbon is still not well understood. There are many conflicting views and many aspects of the problem that have not been studied comprehensively. For example, although considerable work has been done on the kinetics of the process, little attention has been paid to the physical changes which occur in the metal oxide and the carbon during the reduction process. One important aspect which needs to be investigated is the effect of the nature of the carbon surface on the solid-state reaction between carbon and metal oxides. It is well known that the nature of the carbon surface has a marked effect on its reactivity

with gases [7-9] and solutions [10-12]. It was of interest to us to investigate this particular aspect in the reduction of NiO by carbon. The present work, which describes the reduction of NiO at the cleavage as well as at the edge surface of pyrolytic graphite, was therefore undertaken.

2. EXPERIMENTAL

2.1 Materials

Stress-recrystallized pyrolytic graphite was used in this investigation. This material has been hot-pressed at a temperature in excess of 3000°C. This highly oriented graphite was easily cleaved, having a Bacon anisotropy factor of around 6. The cleavage surfaces were optically flat to the eye and mirror-like. Samples used were usually about 1 × 1 cm in the basal plane dimension by from 0.8 to 1.5 mm in thickness. In some of the experiments, where edge-surface reaction was examined, the sample thickness varied from 3 to 8 mm.

The nickel oxide (NiO) used was 99.995% pure and had an average particle diameter of about 2 μm. It was obtained from the Organic/Inorganic Research Chemicals Corp., Sun Valley, California.

2.2 Apparatus

The reaction apparatus was mainly constructed of Pyrex glass, except for the reaction tube, which consisted of a double-walled fused quartz tube placed horizontally in an electric furnace, the temperature of which was controlled by a Gardsman West temperature controller. The annular volume enclosed by the double walls was evacuated to minimize diffusion of air into the reaction tube from the atmosphere at the

high temperatures used in this investigation. The graphite sample was placed in a quartz boat, which was attached to a long handle having a quartz-enclosed iron piece at one end. Using a magnet, the handle could be moved; and, hence, the boat containing the reaction sample could be pushed in and out of the furnace.

The reaction tube was connected to (i) two expansion bulbs (11.2 and 1.1 l), (ii) two oil diffusion pumps 15 l s^{-1} each backed by rotary oil pumps, and (iii) a 8 l s^{-1} Vacion ionization pump. After initial evacuation by the diffusion pumps, the system could be evacuated by the ionization pump to an ultimate vacuum of 10^{-8} Torr. The system was also connected to a Baratron differential manometer and a mass spectrometer (CEC 21-614 residual gas analyzer) through a molecular leak. These were used to analyze the gases evolved in some of the experiments.

A liquid N_2 trap was also included in the apparatus so that the gases evolved during the reaction could be pumped out through it in order to trap the CO_2 evolved. Results for CO and CO_2 production will be discussed in a later paper.

2.3 Experimental procedure

Pyrolytic graphite was cut to the desired size with a jeweller's saw. The edge surface was then polished using various grades of polishing paper, and finally an ashless filter paper. This resulted in a surface having a shiny, smooth visual appearance. Nickel oxide powder was sprayed onto the surface with an atomizer. The graphite sample was then placed in the quartz boat and evacuated at 300°C for 6 hours. The boat was then moved out of the furnace and the temperature of the furnace raised. When the desired reaction temperature had stabilized, the boat was again pushed into the furnace. The gases evolved were continuously pumped out through the liquid N_2 trap. After the reaction had proceeded for a specific period of time, the liquid N_2 trap was closed and the sample allowed to cool in vacuum. The amount of CO_2 trapped was estimated by allowing it to expand into the system and analyzing it with the mass spectrometer and the Baratron.

After reactions, surfaces of the graphite and the nickel oxide were examined by optical and scanning electron microscopy. In some cases, the sample was treated with bromine solution in methanol so as to selectively remove the nickel formed during reaction.

3. RESULTS AND DISCUSSION

Preliminary experiments indicated that the reaction between nickel oxide and graphite takes place very slowly below 900°C . The reaction was, therefore, studied at temperatures above 900°C , mostly at 950°C and 1000°C .

3.1 Reduction of nickel oxide at the cleavage surface

The microscopic examination of the cleavage surface after reaction with NiO revealed that the oxide particles show considerable mobility during the reaction, rotating and migrating over the surface and creating shallow channels and pits (Figs 1–3). In order to have a clearer understanding of the mobility of the particles, the graphite sample was removed from the reactor after a few minutes of reaction and examined microscopically. It was again placed into the reaction tube, and reaction was allowed to proceed for a few more minutes before examining the sample again. This procedure was repeated a number of times. By examining some particular area of the surface each time, it was possible to follow particle movement. Particle motion was random and

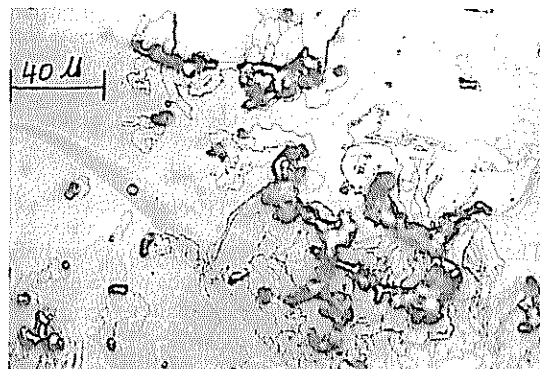


Fig. 1. The cleavage surface of pyrolytic graphite after its reaction with NiO at 1000°C for 2 hours. The nickel oxide particles have moved randomly, creating shallow channels, and have come to rest after agglomerating.

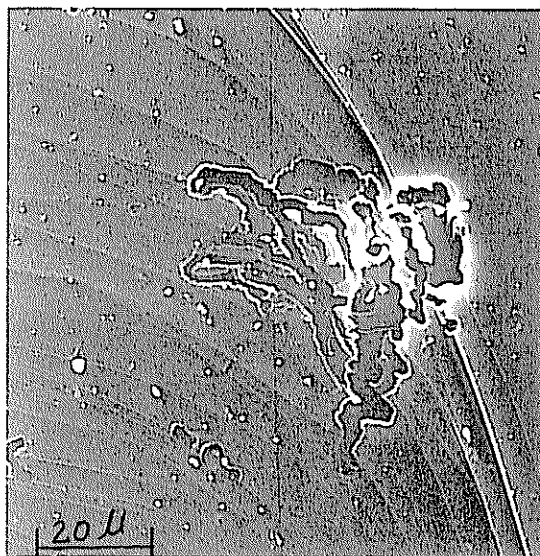


Fig. 2. The cleavage surface after its reaction with NiO at 950°C for 2 hours and after treatment with bromine solution in methanol. The channels created by movement of NiO particles can be seen. The channels appear to have formed by the movement of NiO particles across the surface steps.

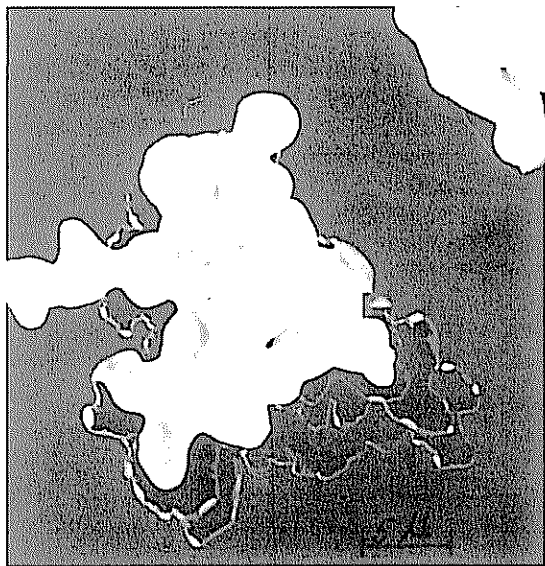


Fig. 3. The cleavage surface after its reaction with NiO at 950°C for 4 hours. The pit with steps or ledges around the agglomerated NiO particles indicates that mobility along the surface has decreased as the reaction proceeds.

decreased considerably only a short period after the start of the reaction. The loss of mobility was accompanied by a decrease in the rate of NiO reduction, as indicated by the rapid decrease in the rate of CO₂ evolution. After initial movement, the particles appear to merge and come to rest in shallow pits. The shallow pits under the particles were revealed by examination of the surface after treating it with bromine solution in methanol, which resulted in the selective removal of nickel.

Periodic examination of the cleavage surface during reaction also revealed that many particles did not show any mobility. In such cases, no channels or pits were produced around the particles; and it appeared that the reaction at such sites was taking place very slowly. This shows that the reaction takes place only at some active sites and not over the entire cleavage surface. It therefore suggests that only those particles which come into contact with some point or line surface defects undergo reaction. Once reaction starts, it proceeds through the movement of the particles which again creates more active sites for the reaction. The conclusions are similar to those drawn by Hennig [13] in his studies on metal-catalysed oxidation of graphite. He observed that only those particles which came into contact with surface steps showed catalytic activity and mobility.

It was also seen that the particles did not move along the surface steps, but cut across the steps, producing channels (Fig. 2). In some cases pits were produced at the site of oxide particles and extended in a direction parallel to the cleavage surface, possibly due to the rotation of the particles. In some cases, where the reaction was carried out for long intervals of time, shallow pits with ledges were produced

(Fig. 3). Oxide particles were not usually found at the tips of the channels. The particles usually showed a tendency to agglomerate and come to rest at one location, where slow pitting occurred. Examination of such agglomerates showed that sintering had occurred; this was probably one of the causes of loss in mobility.

The movement of the particles may be the result of the interaction between NiO and the substrate at the contact surface, the energy evolved being sufficient for the movement of the particle. The reaction probably starts at some active sites constituting surface steps or dislocations. The motion of the particles resulting in creation of channels suggest the formation of bonds between reactive carbon atoms and the oxide, probably metal-oxygen-carbon bridges which may be an intermediate step in the reduction of NiO. The cessation of mobility could result from the loss of direct contact between the oxide and the substrate, due to the formation of a nickel layer between them. Further reaction in that case can only take place by diffusion of carbon or oxygen through the nickel layer. In either case, the reaction will be much slower and the energy evolved may not be sufficient to move the particle. This can result in the cessation of mobility and the slow formation of pits rather than channels.

Many workers [13-17] have observed similar mobility of metal particles over the graphite surface, and theories have been put forward to explain this phenomenon. For example, Sears and Hudson [18], while interpreting the mobility of silver over graphite and molybdenite as observed by Bassett [14], suggested that the motion represents Brownian movement of the particles. It takes place over a chemisorbed gas layer, due to a weak interaction between the metal particle and the chemisorbed layer. According to them, the cessation of the mobility was due to the formation of a true metal substrate contact when the critical shear stress, which is small in the presence of a gas layer between them, increases abruptly. Thomas and Walker [19] applied the above interpretation to their own observations on mobility of metal particles [15,16] made during their studies on the effect of metal impurities on the gaseous oxidation of graphite monocrystals. They suggested that other factors, especially the mode of removal or displacement of the chemisorbed layer leading to the cessation of mobility, have to be explained satisfactorily before the above view can be fully accepted.

It may, however, be pointed out that the mobility of silver particles, as observed by Bassett [14] and interpreted by Sears and Hudson [18], may be different from the mobility of metal particles observed during catalytic oxidation by other workers [13,15-17] as well as in the present studies. While there is no indication that the graphite substrate was involved in a chemical reaction in the former cases, it was definitely so in the latter case where the formation of channels and pits took place due to the

motion of the particles. It follows that the view of Sears and Hudson [18] may not be valid in the case of the mobility of metal particles observed during the metal-catalysed oxidation of graphite as well as during the present studies. The work described in this paper clearly strongly suggests that the motion of the particles is due to interaction between NiO and the graphite substrate. A similar explanation can be given for the mobility of metal particles during catalytic oxidation, where a reaction between an oxide layer on metal particles (formed due to the presence of an oxidising gas) and the substrate can be envisaged. It is possible that the formation of carbon-oxygen-metal bridges may be an intermediate step during the catalytic oxidation of graphite. The cessation of mobility will occur when the possibility of such bond formation becomes less. In the case of NiO reduction in vacuum, it probably occurs when a metal layer is formed on the oxide particle. In the case of catalytic oxidation, it can happen when both the graphite as well as the metal particles are covered with oxygen.

The above view was further supported by the fact that the presence of CO₂ in the reaction system greatly reduced the mobility of the oxide particles. Even a small pressure of CO₂ (about 0.5 Torr) was sufficient to cause almost complete cessation of mobility and an appreciable decrease in rate of reaction. This suggests that the presence of CO₂ in some way inhibits the contact between graphite and the nickel oxide. This does not seem to be due to the presence of a gas layer between the oxide and the substrate since the gas pressure is too low to effectively separate the particles from graphite. Moreover, if this were the case, all gases should have the same effect. However, the presence of inert gases like He and Ar were seen to have no such effect. The reason for this reduction in mobility may be the reaction of CO₂ with graphite, resulting in the chemisorption of oxygen. Since the nickel oxide-carbon reaction is also expected to take place on the same active sites where the CO₂-carbon reaction takes place, there is a competition between nickel oxide and CO₂ for such active sites. This results in the decrease in the number of active sites available for the reaction with NiO, and hence the solid-state reaction between nickel oxide and graphite decreases considerably. These observations show that the motion of the particles does not take place over a chemisorbed gas layer in the present case, as was suggested by Sears and Hudson [18] for the mobility of silver over graphite.

3.2 Reaction at the edge surface

A few samples of pyrolytic graphite having considerable edge surface were used in order to study the reaction at the edge surface. A microscopic examination of the surface after heating with NiO particles at 950°C in vacuum revealed that unlike the reaction at the cleavage surface, the particles showed negligible movement. Insignificant mobility along the surface

was noted even when the reaction was carried out for 8 hours. On the other hand, it was noted that the particles became embedded in the graphite as the reaction proceeded. To obtain a clearer picture of the graphite surface after reaction, nickel formed during the reaction was removed by treatment with bromine solution in methanol. Microscopic examination after such treatment revealed deep pits at the sites where nickel oxide was located prior to reaction (Figs 4-6). The pits appeared to be several μm deep, even when the reaction was carried out for only 30 min (Fig. 4). When large agglomerates of nickel oxide were

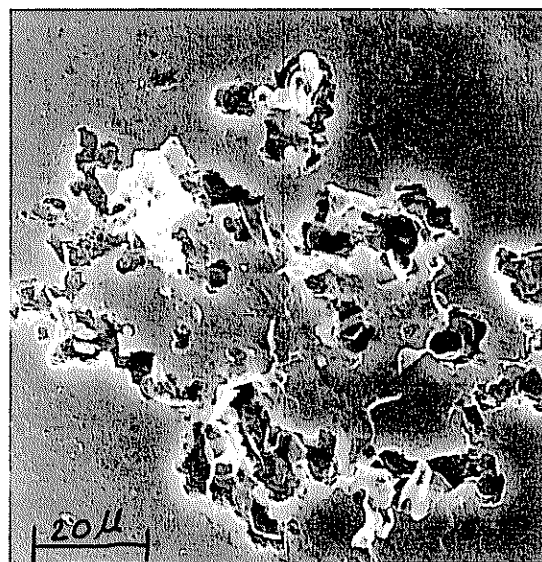


Fig. 4. The edge surface after its reaction with NiO at 950°C for 30 min and after removal of nickel. Deep pits formed during the reaction can be seen.

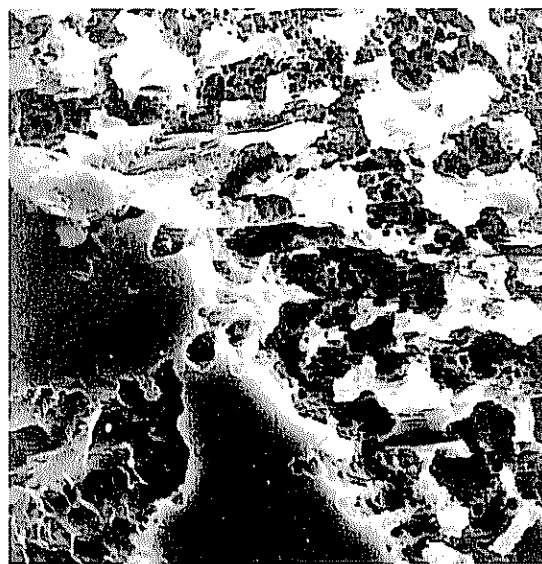


Fig. 5. The edge surface after reaction with large NiO agglomerates at 950°C for 2 hours and after removal of nickel.

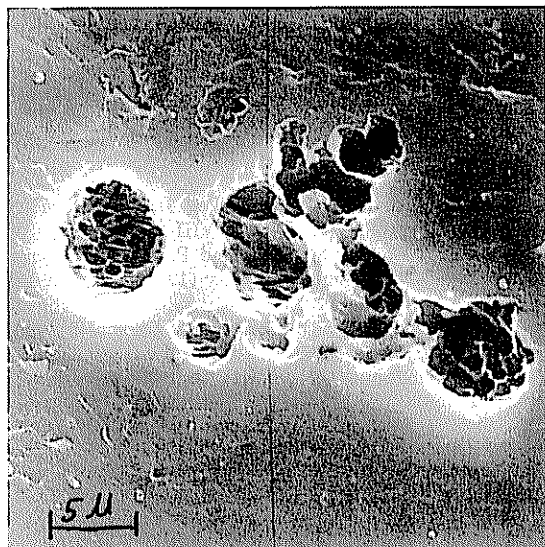


Fig. 6. The edge surface after reaction with NiO for 1 hour at 950°C and after removal of nickel. Deep pits having the size and shape of NiO particles can be seen.

involved in the reaction, several pits, separated from each other by thin boundary walls rather than one single large pit, were produced (Fig. 5). This again shows that there is very little movement along the edge surface. On the other hand, it appears that the particles move in a direction perpendicular to the c -axis (i.e. parallel to the cleavage surface), eroding the basal planes with which they come into contact. The shape of the pits is similar to the shape of the oxide particles or agglomerates in contact with the graphite surface.

Although the reaction at the cleavage surfaces, resulting in the formation of channels, appears to be different from the reaction at the edge surfaces, resulting in the formation of pits, basically, the mode of the reaction is the same. In both cases, the reaction takes place in a direction parallel to the cleavage surface. When an NiO particle reacts on the cleavage surface, it moves along the surface creating shallow channels, because at the cleavage surface, it can come into contact with only a small number of basal plane edges that it can erode. On the other hand, when a nickel oxide particle reacts at the edge surface, which in effect is made up of the edges of the basal planes, it erodes large numbers of basal planes, creating deep channels which appear to be pits when viewed from the edge surface. The reaction at the edge surface is much faster than at the cleavage surface since the number of active carbon sites which can come in contact with nickel oxide is much larger at the edge surface than at the cleavage surface.

It was found that when the reaction at the edge surface was carried out in a closed system in the presence of CO₂, the reaction rate was much slower than in vacuum. This becomes evident from the comparison of the pits produced in both cases under



Fig. 7. The edge surface after its reaction with NiO in the presence of CO₂ (616 μm pressure) at 950°C for 1 hour. The pits formed in this case are shallower than those formed under similar conditions when the reaction was carried out in vacuum (cf. Fig. 6) and even when it was carried out for only 30 min (cf. Fig. 4).

similar conditions of time and temperatures (Figs 6 and 7). The reason for this inhibiting effect is thought to be the chemisorption of oxygen at active sites on the graphite, as has been explained earlier in the case of reaction at the cleavage surface.

It is interesting to note that there are many similarities between the reaction of graphite with oxidizing gases and with NiO. It is well established that the reaction with oxidizing gases starts at some active sites and proceeds mostly in a direction parallel to the cleavage surface. These remarks can apply to the reaction with NiO as well. Hennig [7] has shown that the oxidation reaction rate in the parallel direction is higher than the rate in the perpendicular direction by a factor of 10¹⁰ or 10¹¹. In the present case, it also can be seen from the pit formation at basal and edge surfaces (Figs 3, 4 and 6) that the reaction in the parallel direction is much faster than the reaction in the perpendicular direction. It is difficult to get an accurate estimate of reaction rates in parallel and perpendicular directions in the present studies, because more channeling than pitting occurs during the reaction (Figs 1–3); and the absence of regular shape pits does not allow accurate measurements to be made as was done by Hennig. Even so, looking at the channels formed on the cleavage surface (Figs 1–3) and the pits on the edge surface (Figs 4–6), it can be estimated that the reaction in the parallel direction is faster by at least a few orders of magnitude.

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