



REDUCTION OF NICKEL OXIDE BY CARBON: II. INTERACTION BETWEEN NICKEL OXIDE AND NATURAL GRAPHITE

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(Received 15 October 1996; accepted in revised form 6 November 1996)

Abstract—The interaction of micron-sized particles of NiO with plate-like particles of natural graphite has been studied at 950°C using scanning electron microscopy. The gases evolved (CO and CO₂) upon reduction of NiO to Ni were continuously pumped out of the system. The graphite particles consisted of highly aligned, large crystallites. Attack occurred predominantly at the edge of prismatic surface of the particles, which constituted only 4–5% of the total surface area. Nickel produced in the reduction reaction covered the NiO with a sintered layer. Removal of the Ni layer revealed unsintered particles of NiO of similar shape to the original particles. The particles showed considerable porosity, presumably a result of selective attack at cracks in the NiO produced as reaction proceeds. © 1997 Elsevier Science Ltd

Key Words—A. Carbon, natural graphite, C. scanning electron microscopy (SEM).

1. INTRODUCTION

Although a number of investigations [1–7] have been carried out on the reduction of nickel oxide (NiO) by carbons, very few attempts have been made to study the effect of the nature of the reactants as well as the reaction products on the course of the reduction. It has been well established that the reactivity of carbons is greatly influenced by the nature of their surfaces [8–11]. In part I of this series [12] it was shown that the reaction between NiO and pyrolytic graphite takes place mostly at the edges of the basal planes. It has also been shown that the nature of the NiO can play an important role in determining its reactivity. For example, Cech [13] suggested that the reduction of NiO with H₂ is enhanced by the presence of cracks in the crystal lattice which act as active sites for the reaction. Charcosset *et al.* [14], during their studies on the reduction of NiO by H₂, removed Ni formed during the reaction and demonstrated that the reduction takes place only at some preferred sites constituting defects and dislocations in the crystal lattice. Kohl and Marineck [7] found that during the reduction of NiO plates with graphites, a Ni layer is formed between NiO and graphite; and further reaction takes place by diffusion through this layer.

It was thought of interest to study the physical changes produced in NiO and graphite during the reaction of their powder mixtures, in order to get a deeper insight into the factors influencing the mechanism of the reaction.

2. EXPERIMENTAL

2.1 Materials

SP-1 graphite used in this investigation was obtained from the then Carbon Products Division,

Union Carbide Corporation. It is a high purity spectroscopic grade natural graphite having a maximum impurity content of <6 ppm. It consists of flakes which have an average diameter of about 25 μm and an average thickness of about 0.5 μm. The particles either approach single crystals closely or are made up of large crystallites highly aligned. The BET surface area was 1.8 m² g⁻¹. The NiO was 99.99% pure and had an average particle diameter of about 2 μm; the BET surface area was 0.65 m² g⁻¹. It was obtained from the Organic/Inorganic Research Chemical Corporation, Sun Valley, California.

2.2 Apparatus

The reaction apparatus used was the same as described earlier [12]. The double-walled quartz reaction tube was placed horizontally in a furnace, the temperature of which was controlled by a Gardsman West temperature controller. The reaction tube was connected to: (i) two expansion bulbs, (ii) a vacuum system capable of producing a low pressure of 10⁻⁸ Torr, (iii) a liquid nitrogen trap, (iv) a MKS Baratron pressure gauge, and (v) a mass spectrometer (CEC 21-614 residual gas analyzer). The details are given elsewhere [12].

2.3 Experimental

SP-1 graphite and NiO powders were mixed in a 1:1 ratio of their molecular weights, and the mixture was carefully homogenized. 100 mg of this mixture were weighed into a small quartz boat which was placed inside the reaction tube and evacuated at 300°C for 6 hours. The boat was then removed from the furnace and the temperature of the furnace raised to 950°C. When the reaction temperature had stabi-

lized, the boat was again pushed into the furnace to start the reaction. The gases evolved were pumped out through the liquid nitrogen trap in order to trap CO_2 while allowing CO to escape. After the reaction had proceeded for a definite interval of time, t , the liquid nitrogen trap was closed, the pumps cut off, and the reaction allowed to proceed to equilibrium. After equilibrium was reached (which was less than 1% on the side of NiO at 950°C), the gases accumulated in the system (consisting of CO_2 and CO) were measured using the mass spectrometer. The system was again evacuated, and CO_2 in the liquid nitrogen trap allowed to expand into the system and measured.

In a separate experiment, the amount of oxygen evolved as CO_2 and CO when 100 mg of the mixture was allowed to react in a closed system to equilibrium at 950°C was estimated. Knowing this total amount and the amounts of oxygen measured as oxides of carbon, as stated above, the amount of CO which escaped during reaction *in vacuo* in time t could be estimated. Then knowing the amount of CO_2 (trapped in liquid nitrogen) and CO (by calculation) evolved during time t , the amount of NiO reduced in time t could be calculated. The results obtained were fairly reproducible.

For the purpose of preparing samples for microscopic studies, 100 mg portions were allowed to react *in vacuo* for different intervals of time. In each case, after the reaction had proceeded for a definite interval of time, the mixture was pushed out of the furnace and allowed to cool *in vacuo*. In order to determine the amount of NiO reduced in each case, separate runs were made with the reaction allowed to proceed to equilibrium as described above. The amount of NiO reduced was calculated in each case.

The prepared samples were examined under a scanning electron microscope. The graphite particles were separated using a heavy fluid and examined. The rest of the mixture containing Ni and NiO was examined as such, as well as after selective removal of Ni by treatment with bromine solution in methanol.

3. RESULTS AND DISCUSSION

3.1 Examination of the graphite particles

Examination of the mixture before and after various stages of the reaction throws considerable light on the way graphite and NiO react with each other. For instance, examination of graphite particles showed that most of the reaction had taken place along the edges of the particles. SP-1 graphite consists of thin flakes of various sizes and shapes but having well defined edge surfaces (Fig. 1). However, after reaction with NiO, the edge surface does not remain well defined or smooth as is evident from Figs 2–6, showing graphite particles after various degrees of reaction. From Figs 3 and 4 (showing graphite particles after 17 and 32% reaction respectively), it can be clearly seen that the edges of the particles have

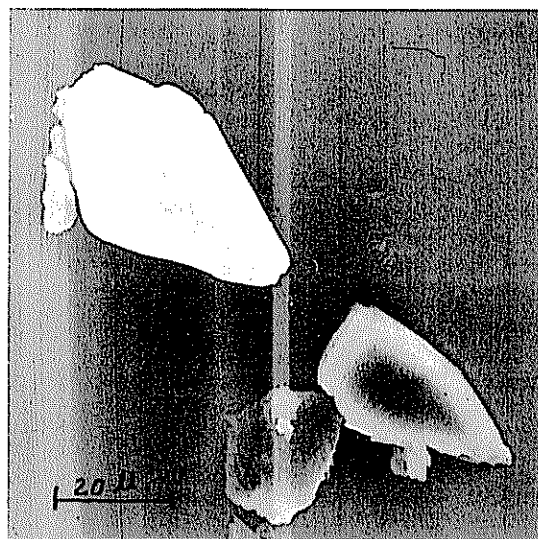


Fig. 1. SP-1 natural graphite particles before reaction.

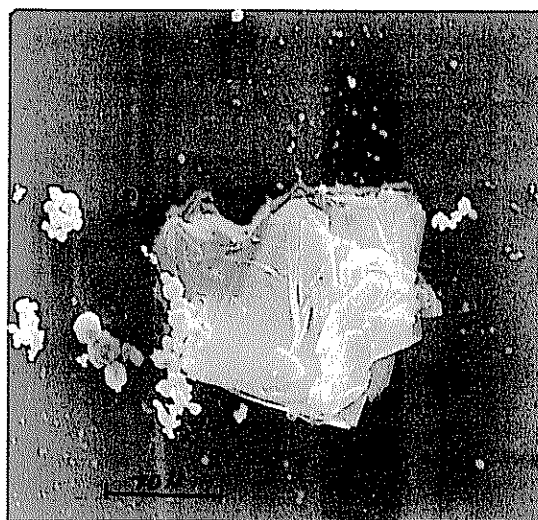


Fig. 2. SP-1 particle after 17% reduction of NiO at 950°C . Erosion of the edge surface as a result of reaction can be seen.

been eroded considerably while the rest of the surface, which consists of the basal planes, has been hardly affected. In some cases, there was evidence of some reaction having taken place on the basal surface also (Fig. 4). But it is evident that the reaction at the basal surface has taken place in a direction parallel to the basal surface, only resulting in the removal of a few basal plane layers at certain places. It seems that the reaction in such a case also starts at the edges of the basal planes.

In some cases the graphite particles are seen to have reacted uniformly all along the edges (Fig. 5), resulting in elliptical shaped particles, while in other cases the particles were almost divided into two parts due to erosion of the edges along certain areas (Fig. 6). But in no case was evidence of appreciable

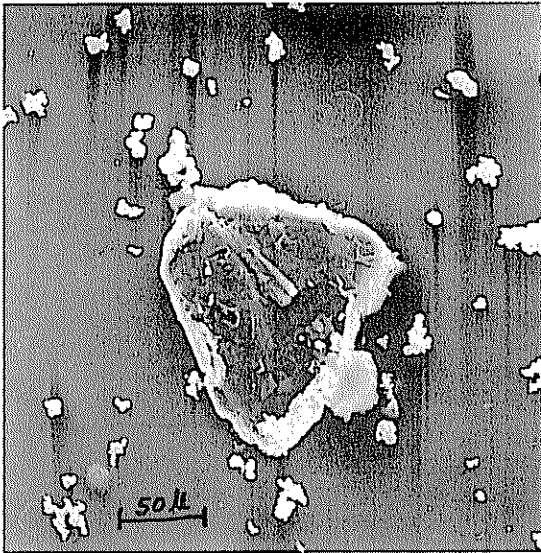


Fig. 3. SP-1 particle after 32% reduction of NiO at 950°C.

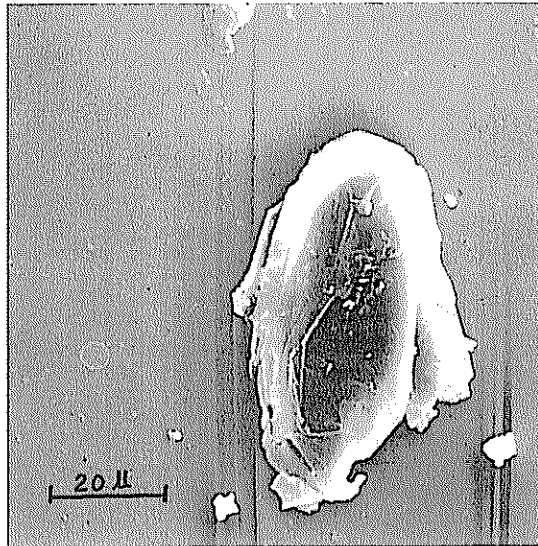


Fig. 5. SP-1 particle after 67% reduction of NiO at 950°C. It appears that the graphite has reacted all along the edges, resulting in the elliptical shaped particle. The middle portion of the particle has remained unaffected.

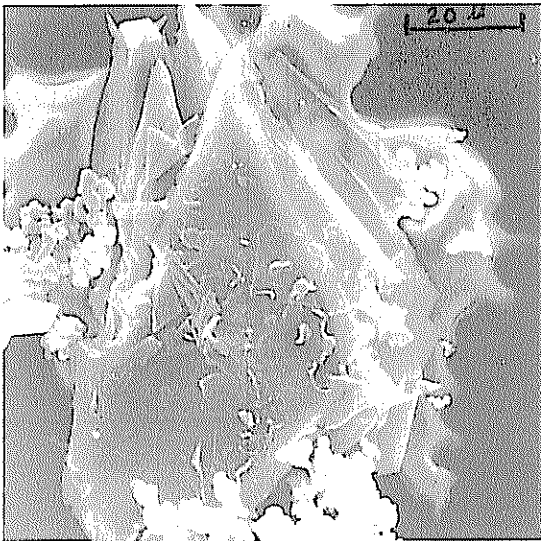


Fig. 4. SP-1 particle after 42% reduction of NiO at 950°C. Erosion along the edges can be seen. Some reaction appears to have taken place on basal plane surfaces, but it has started at the edges of the basal planes.

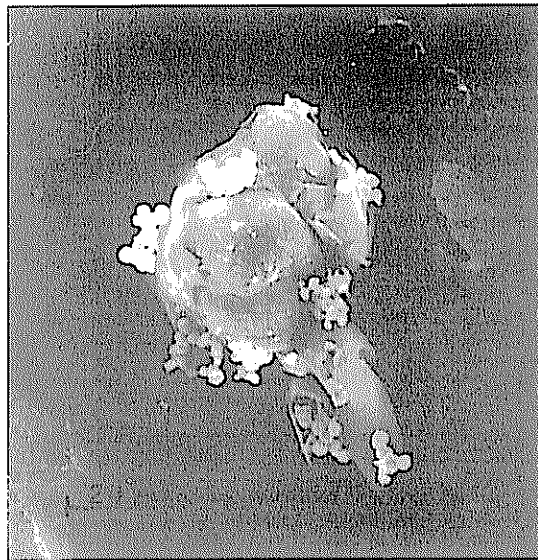


Fig. 6. SP-1 particle after 95% reduction of NiO at 950°C. Reaction has taken place along certain areas of the edge surface in such a way that the particle appears to have two parts.

pitting on the basal surface noted, which means that very little reaction is taking place in the perpendicular direction.

The observations recorded above clearly show that the reaction takes place mostly in a direction parallel to the basal surface of the graphite. The difference in the relative rates in parallel and perpendicular directions is apparent from the fact that the basal plane surface of the particles (which have an average thickness of $0.5 \mu\text{m}$ only) did not show any holes (or any pits) even when about 50% of the carbon had been consumed. Although it was not possible to determine accurately the difference between parallel and perpendicular reaction rates, it is apparent that

these must be differing by a few orders of magnitude at least.

These results are similar to those observed in the case of reaction of NiO with stress recrystallized pyrolytic graphite [12]. The graphite seems to react with NiO in a manner which is similar to its reaction with oxidizing gases. Freyer [15], during his electron microscopic studies of the oxidation of SP-1, observed similar changes in the graphite particles.

It is apparent that only the edge surface and not the total surface of graphite is involved in the reac-

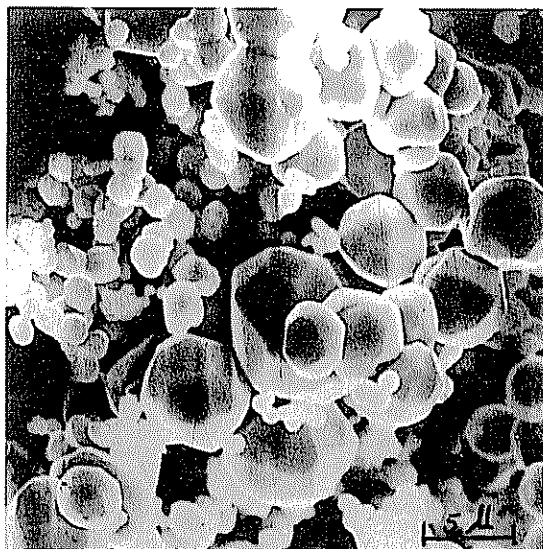


Fig. 7. NiO particles before reaction.

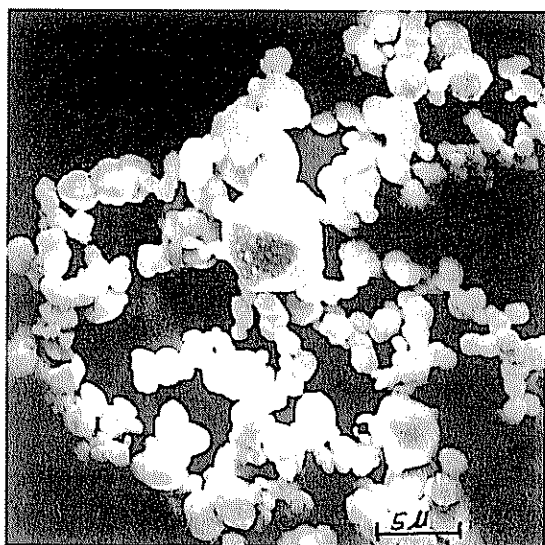


Fig. 8. NiO particles after 17% reduction with SP-1 graphite at 950°C. The particles have the general shape of the original particles, but some sintering appears to have taken place.

tion. Thus, the kinetics of the reaction are not likely to be influenced either by the amount of carbon or by the total surface but only by the edge or active surface, which in this case constitutes only about 4–5% of the total surface. However, it does not mean that an increase in the amount of the graphite will not increase the reaction rate because the active surface will also increase in such a case. It means that a carbon with larger active surface will be more reactive.

3.2 Examination of the nickel oxide particles

Examination of the NiO particles after varying degrees of reduction showed that considerable sintering had taken place during the reactions, as is

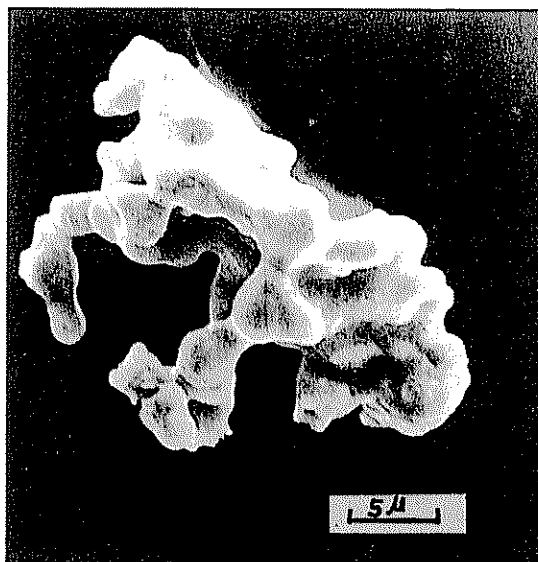


Fig. 9. NiO particles after 67% reduction with SP-1 graphite at 950°C. No individual particles can be seen. Only large agglomerates formed as a result of sintering of Ni on the surface.

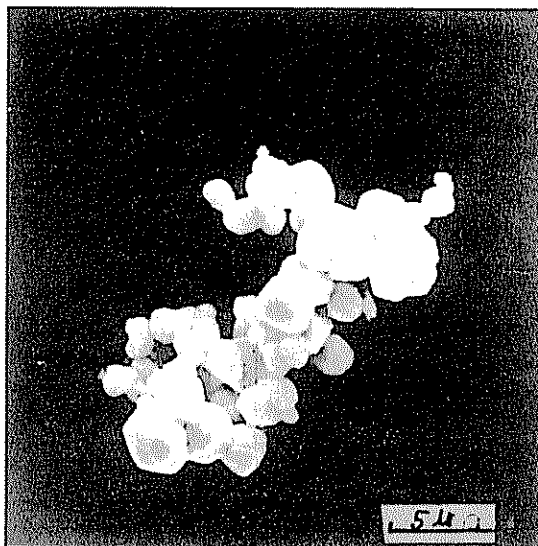


Fig. 10. NiO particles at 17% reduction with SP-1 graphite at 950°C and subsequent selective removal of Ni. The particles have the same general shape as that of the original particles.

evident from Figs 7–9 showing the NiO particles before and after reaction. When the particles were treated with bromine solution in methanol, the sintering disappeared; and the NiO particles, with shape and size similar to the original particles, were uncovered (Figs 10–12). It appears, therefore, that the apparent sintering was due to the deposition of Ni onto the surface of the NiO particles. These particles looked very similar in shape to the original particles when only a small fraction of the oxide had reacted (Fig. 10) but showed considerable porosity when

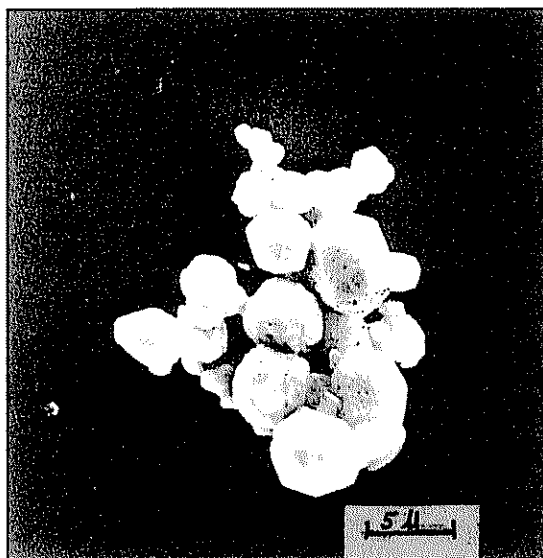


Fig. 11. NiO particles after 32% reduction with SP-1 graphite at 950°C and subsequent selective removal of Ni. The particles have the general shape as that of the original particles, but the surface contains pores distributed throughout the surface.

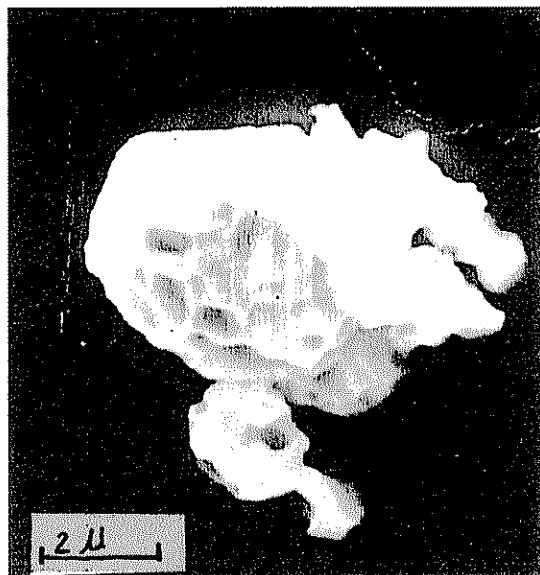


Fig. 13. NiO particles after 67% reduction with SP-1 graphite at 950°C and subsequent selective removal of Ni. The particles are highly porous and appear to be losing their shape.

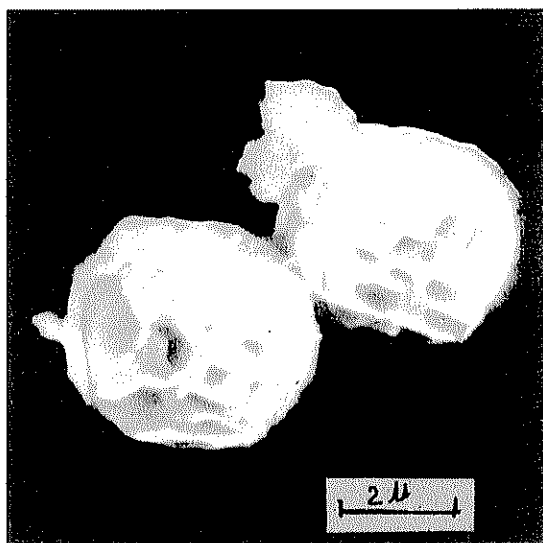


Fig. 12. NiO particles after 52% reduction with SP-1 graphite at 950°C and subsequent selective removal of Ni. The particles are highly porous and appear to be hollow.

more reaction had taken place (Figs 11 and 12). These pores were not confined to any particular areas but were distributed uniformly across the surface. The reason for the formation of pits (pores) may be the production of cracks in NiO all along the surface, when during reduction it comes under a strain owing to a decrease in volume. The conversion of NiO to Ni will result in a volume reduction of about 38%.

A discussion of the mechanism of the reduction of NiO by carbon will follow the presentation of

experimental results on the rates of reaction to be presented in the next paper in this series [16].

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