



PII: S0008-6223(96)00174-1

# REDUCTION OF NICKEL OXIDE BY CARBON: III. KINETIC STUDIES OF THE INTERACTION BETWEEN NICKEL OXIDE AND NATURAL GRAPHITE

S. K. SHARMA, F. J. VASTOLA and P. L. WALKER, JR.

Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16801, U.S.A.

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

**Abstract**—The rate of interaction of equi-molar micron-sized particles of NiO with plate-like particles of natural graphite has been studied between 900 and 1000°C in both a closed system and *in vacuo*. Both CO and CO<sub>2</sub> are primary products of the reaction. In both a closed system and *in vacuo*, reaction proceeds essentially to complete reduction of NiO. Reduction *in vacuo* is more rapid than in a closed system. Reduction of NiO *in vacuo* is described by first order plots, with the increase in rate constant values with temperature having an activation energy of 75 kcal mol<sup>-1</sup>. © 1997 Elsevier Science Ltd

**Key Words**—A. Carbon, natural graphite, D. kinetics.

## 1. INTRODUCTION

Reduction of nickel oxide (NiO) by carbon has been studied by a number of workers, and several theories have been put forth to explain the mechanism and kinetics of the reaction. For example, Boukloh and Springerum [1] observed that plots of (metallic film thickness)<sup>2</sup> versus time gave a straight line and concluded that the reaction proceeds by the diffusion of carbon through the Ni layer formed during the reaction. According to Bogatskii [2], NiO dissociates into Ni<sub>2</sub>O and O during the reaction. Pavlyuchenko and Shelkanoviseva [3] and Kohl and Marineck [4] suggested that the NiO is reduced both by carbon and CO which is formed during reaction. Zhuravleva *et al.* [5] found that small amounts of potassium and sodium carbonates considerably accelerate the reaction.

It appears that the mechanism and kinetics of the NiO/carbon reaction are not completely understood. There are conflicting views, even regarding the reaction products. Some workers [3,4] suggest that CO is the only product of the solid state reaction between NiO and carbon, while another [6] suggests that CO<sub>2</sub> is the primary product. More work is, therefore, needed to have a better understanding of the reaction. In part I [7] and part II [8] of the present series, a visual description of how NiO and graphite react with each other was presented. The present work describes the kinetics and the gaseous products 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 that have an average thickness of about 0.5 μm and an average diameter of about 25 μm. The particles either approach single crystals closely or are made up of large crystallites highly aligned. The BET surface area was 1.8 m<sup>2</sup> g<sup>-1</sup>. The NiO used was 99.99% pure and had an average diameter of about 2 μm. It was obtained from the Organic/Inorganic Research Chemical Corporation, Sun Valley, California; it has a BET surface area of 0.65 m<sup>2</sup> g<sup>-1</sup>. Carbon dioxide and CO used were of research grade obtained from Air Products and Chemicals, Inc. and Matheson, Inc., respectively.

### 2.2 Apparatus

Details of the apparatus used have been described earlier [7,8]. Briefly, 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 annular volume between the two walls of the reaction tube was evacuated continuously so as to avoid diffusion of oxygen into the reaction tube at high temperatures. The reaction tube was connected to: (i) two expansion bulbs, (ii) a vacuum system capable of producing a low pressure of 10<sup>-8</sup> Torr, (iii) a liquid nitrogen trap, (iv) a MKS Baratron pressure gauge, and (v) a mass spectrometer.

### 2.3 Experimental

In most of the experiment equal molar mixtures of NiO and SP-1 graphite were used. 100 mg of the mixture were evacuated in the reaction tube for 6 hours at 300°C. The boat containing the mixture was then moved out of the furnace, and the temper-

ature of the furnace raised. When the desired reaction temperature had stabilized, the reaction was started by pushing the sample back into the furnace.

The reaction was carried out both in a closed system (where the gases evolved were allowed to accumulate) as well as *in vacuo* (where the gases evolved were continuously pumped out of the system). For reaction in the closed system, the liquid nitrogen trap was closed; and the gases were allowed to accumulate in the apparatus by isolating it from the vacuum pumps. A small amount of the gas was taken after different intervals of time and its composition determined using the mass spectrometer. Knowing the amount of gases (CO and CO<sub>2</sub>) evolved, the amount of NiO reduced could be calculated.

For reaction *in vacuo*, the gases evolved were continuously pumped through the liquid nitrogen trap, so as to condense any CO<sub>2</sub>, while allowing CO to escape. The details have been described previously [8].

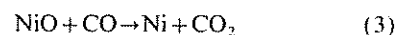
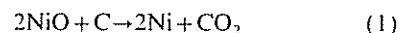
The reaction was studied in the temperature range 900 to 1000°C.

### 3. RESULTS AND DISCUSSION

Results from the reduction of NiO with SP-1 graphite in a closed system, at various temperatures, are given in Fig. 1. The reaction is very slow at 900°C but increases with increase in the reaction temper-

ature. At 1000°C, the reaction proceeds to equilibrium within 100 minutes.

During the reaction, both CO<sub>2</sub> and CO were evolved, with CO<sub>2</sub> predominating throughout the reaction. Figure 2 shows the amounts of CO<sub>2</sub> and CO evolved during reaction at 950°C. It is seen that the ratio CO<sub>2</sub>/CO increases sharply at first and after reaching a maxima decreases slowly in the final stages of reaction. It seems that the solid state reaction starts initially resulting in the production of both CO<sub>2</sub> and CO. The subsequent sharp increase in the CO<sub>2</sub>/CO ratio is thought to be due to a fast reaction between CO and NiO. The decrease in the CO<sub>2</sub>/CO ratio during the last stages of reaction may be due to a catalyzed (by Ni formed during the reaction) reaction between CO<sub>2</sub> and graphite [9]. It appears, therefore, that the reaction between NiO and carbon in a closed system is a complex process; and at least the following four reactions may be taking place simultaneously.



Reactions (1) and (2) are solid state reactions, while (3) and (4) involve the gas phase. In the initial stages, reaction (3) is faster than reaction (4) and, hence,

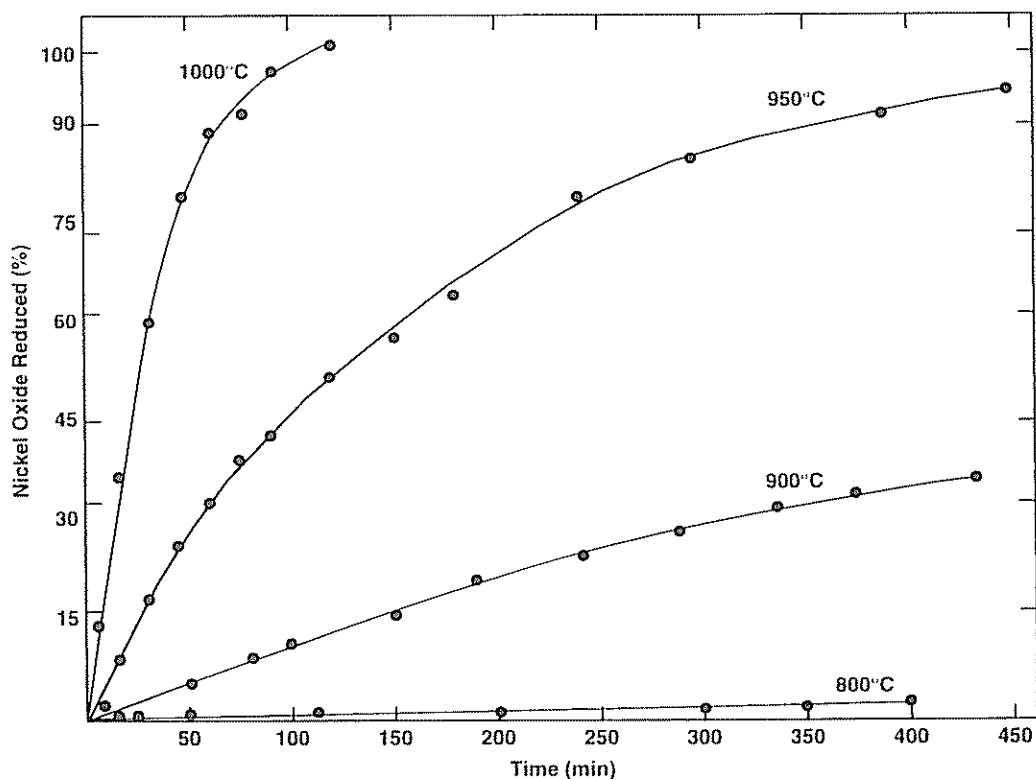


Fig. 1. Reaction between NiO and graphite at various temperatures in a closed system.

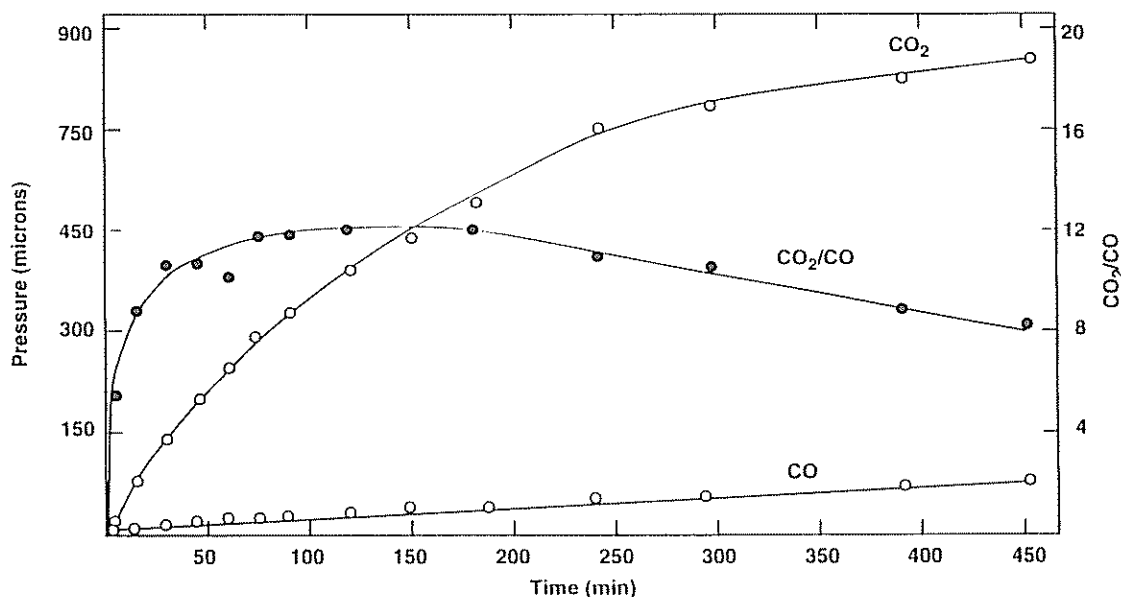


Fig. 2. Evolution of CO<sub>2</sub> and CO during reaction between NiO and graphite at 950°C in a closed system.

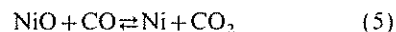
the increase in the CO<sub>2</sub>/CO ratio. However, in the final stages when the amount of NiO has been reduced, reaction (4) which is catalyzed by the Ni formed is faster; and, hence, a slight decrease in the CO<sub>2</sub>/CO ratio occurs. It is also evident that in a closed system, the NiO is being reduced not only by the solid state reaction but also by a reaction involving CO which is a product of the solid state reaction. In order to determine the effect of the presence of CO on the reduction of NiO, the reaction was carried out after introducing some CO at the beginning of the reactions. As can be seen by comparing Fig. 1 with Fig. 3, the reaction is faster in the presence of added CO than in its absence. The fast depletion of CO in the initial stages (Fig. 3) indicates a rapid reaction between CO and NiO. This shows that in a closed system, the gas phase reduction of NiO affects the overall reaction kinetics.

It has been suggested [3,4] that the reaction between metal oxides and carbon, which starts at the oxide/carbon interface, proceeds later on only through the gas phase reaction involving CO. In order to determine the influence of the gas phase reaction on the overall reaction and to determine whether the reaction in the later stages primarily proceeds through the gas phase, the reaction was carried out *in vacuo*, i.e. the gases evolved were continuously pumped out in order to minimize the possibility of any gas phase reaction. Figure 4 shows the amounts of CO<sub>2</sub> and CO evolved when the reaction is carried out *in vacuo* at 950°C. The fact that the reaction proceeds to equilibrium even *in vacuo* (as will be seen shortly) suggests that the reaction does not necessarily proceed through the gas phase as suggested by some workers [3,4]. Also, since the evolution of CO<sub>2</sub> predominates even when

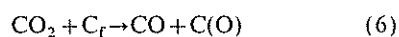
the chances of reaction between CO and NiO are very small, as the gases are being continuously pumped out, it is evident that both CO<sub>2</sub> and CO are primary products of the solid state reaction between NiO and carbon. Thus, the suggestion of some workers [3,4] that CO<sub>2</sub> is formed only by the reaction between CO and NiO is not justified.

On comparing the reaction in a closed system with that *in vacuo* (Fig. 5), it is seen that the reaction is faster *in vacuo* than in a closed system. Since in the closed system, NiO is reduced both by the solid state reaction as well as by the gas phase, the reduction of Ni should be faster than *in vacuo*, instead of being slower. This can only mean that the gas phase consisting of CO<sub>2</sub> and CO in some way adversely affects the solid state reaction. Since the presence of CO in the system is expected to favor the reduction of NiO as shown earlier, it appears that it is the CO<sub>2</sub> which retards the solid state reaction.

The adverse effect of CO<sub>2</sub> on the solid state reaction between NiO and graphite cannot be due to equilibrium limitations because at the temperatures studied the equilibrium in the reaction



is essentially completely on the side of CO<sub>2</sub> as shown earlier [9]. Rather it is thought that CO<sub>2</sub> interacts with carbon free active sites (C<sub>f</sub>) according to reaction (6)



covering some of them with oxygen complex, that is C(O). Such coverage decreases the number of carbon free active sites available to reduce the NiO.

Figure 6 presents first order plots for the reduction

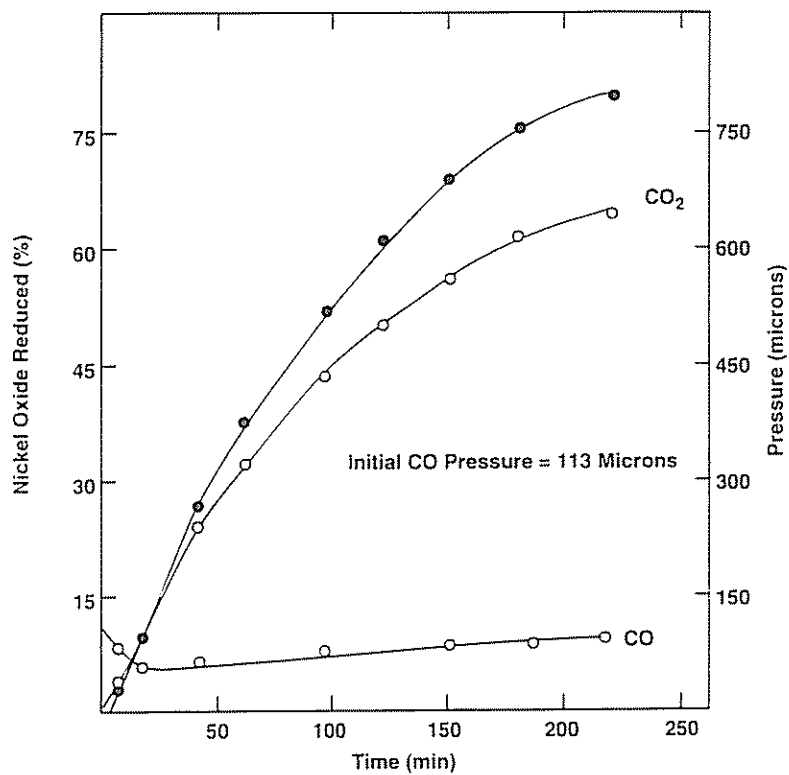


Fig. 3. Reaction of NiO with graphite and added CO at 950°C in a closed system.

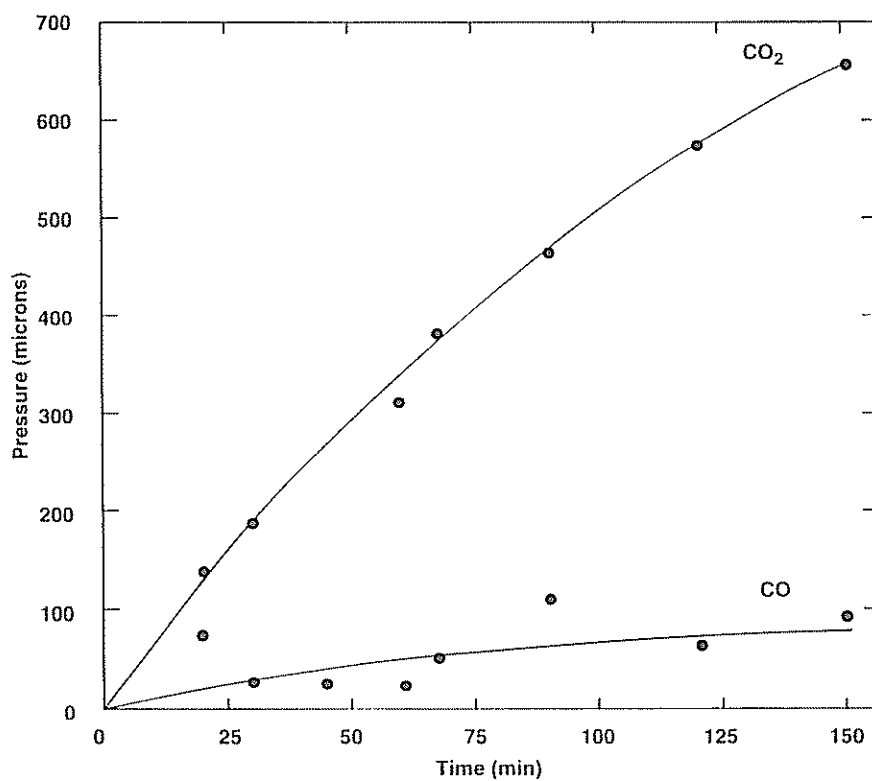


Fig. 4. Evolution of CO<sub>2</sub> and CO during reaction between NiO and graphite at 950°C *in vacuo*.

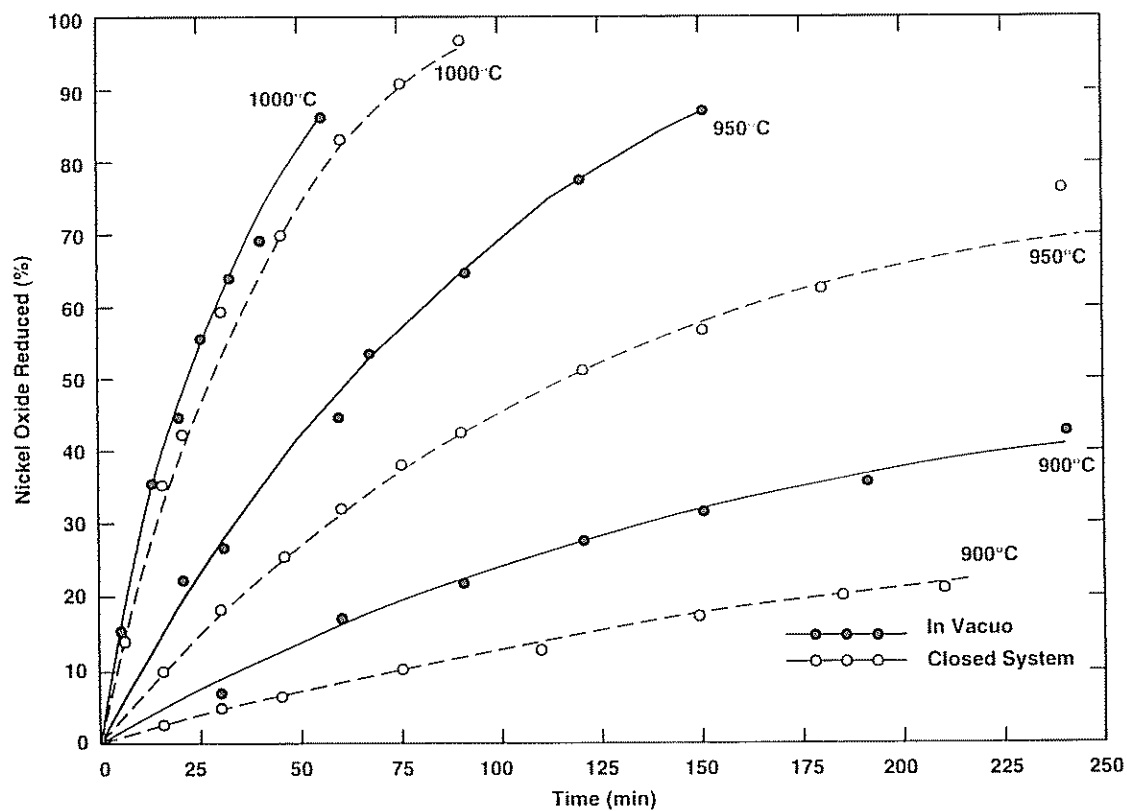


Fig. 5. Reaction between NiO and graphite at various temperatures *in vacuo* and in a closed system.

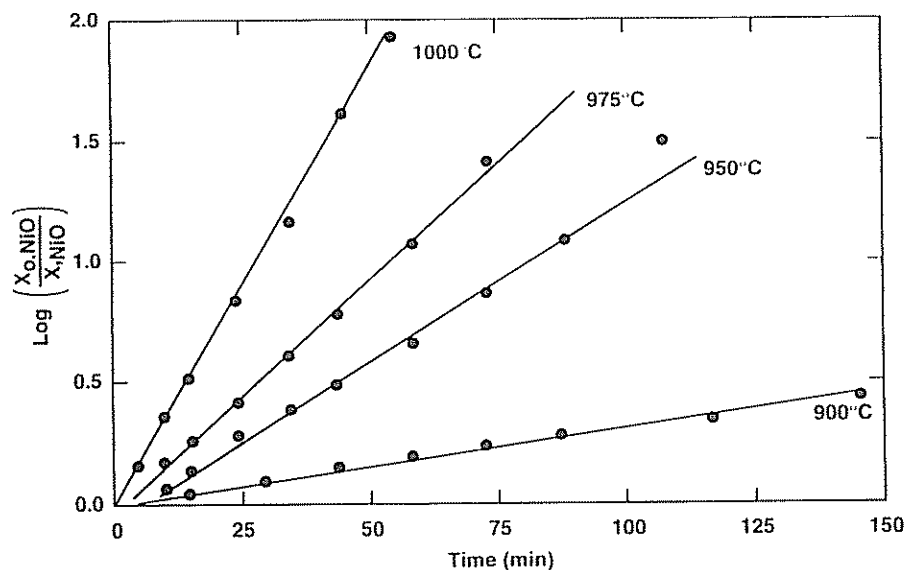


Fig. 6. First order plots for reaction between NiO and graphite *in vacuo*.

of NiO *in vacuo* over the temperature range 900–1000°C. Or

$$\frac{-d(\text{NiO})}{dt} = k(X_{0,\text{NiO}} - X_{\text{NiO}}) \quad (7)$$

From the slopes of the first-order plots, values for the rate constant,  $k$ , can be calculated. Figure 7 then presents an Arrhenius plot for the rate constants, yielding an activation energy of 75 kcal mol<sup>-1</sup>.

It is interesting that the rate of reduction of NiO

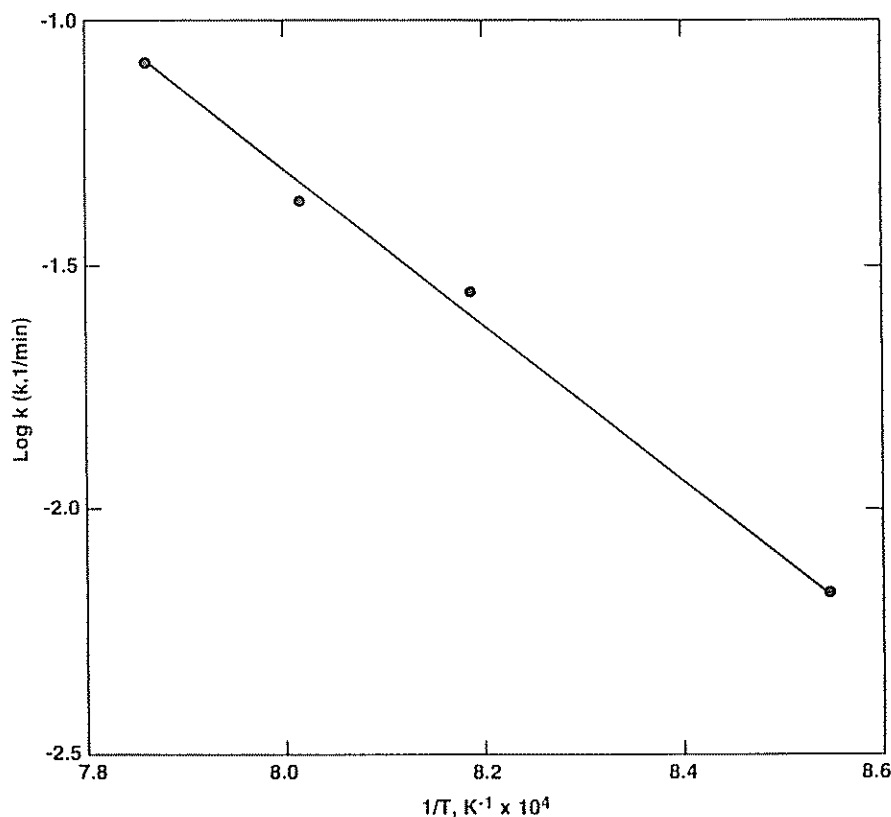


Fig. 7. Arrhenius plot of the rate constants for the reaction between NiO and carbon *in vacuo*.

can be described by a simple first-order reaction. The reaction is thought to proceed as follows. Carbon atoms first interact with the NiO surface producing Ni. Carbon atoms then go into solution in the Ni layer surrounding the NiO particles, diffuse through this layer (which is building up in thickness as reaction proceeds) to the NiO/Ni interface where some reduction proceeds. Carbon atoms also diffuse across the surface of the porous NiO particles, where additional reduction occurs. Carbon monoxide and CO<sub>2</sub> are produced. *In vacuo*, the gaseous reaction products are rapidly removed, diffusing through cracks present in the Ni coating. The cracks are produced by strain developed due to reduction in volume as reaction proceeds.

The rate of reduction of NiO is expected to depend upon the rate at which carbon atoms reach the Ni/NiO interface as well as the extent of reduction of NiO. The rate at which carbon atoms reach the NiO/Ni interface should depend upon the concentration of active sites in the carbon surface and contact area between the active sites in the carbon surface and the Ni surface. The importance of the contact area was confirmed by two experiments. In one experiment, the amount of graphite mixed with a constant weight of NiO was increased. It resulted in an increase in reduction rate of NiO, described again by first order kinetics. In a second experiment, the NiO and carbon were first mixed as before but

then pelletized under pressure. The coherent pellet is expected to have a higher contact area between the NiO and carbon than does the loose mixture. The result was an increase in reduction rate of the NiO, again described by a first order reaction.

The fact that the rate of reduction of NiO can be described by a simple first order reaction suggests that the contact area between the Ni surface and the carbon active surface changes little during reduction. It is known that the active site concentration per unit total surface area of SP-1 graphite increases as the graphite is consumed by its gasification [10]. It is suggested that a similar increase in active surface area concentration is produced as carbon atoms are consumed as a result of NiO reduction. Thus the active surface could remain essentially constant as NiO reduction proceeds.

It is understandable that the rate of diffusion of carbon atoms through Ni is not the rate controlling step in the reduction of NiO. That is, the activation energy for the diffusion of carbon atoms through Ni is reported to be about 33 kcal mol<sup>-1</sup> [11] – much lower than the experimental activation energy found for the reduction reaction, that is 75 kcal mol<sup>-1</sup>.

#### REFERENCES

1. Baukloh, W. and Springerum, F., *Z. Anorg. Allg. Chem.*, 1937, 230, 315.

2. Bogatskii, D. P., *Bull. Akad. Sci. (URSS), Cl. Sci. Tech.*, 1967, 105.
3. Pavlyuchenko, M. M. and Shelkanoviseva, N. A., *Get-erog. Khim. Reakts., Inst. Obshch. i Neorgan. Khim. Akad. Nauk Belorussk (SSR)*, 1965, 150.
4. Kohl, H. K. and Marineck, B., *Arch. Eisenhuettenwes.*, 1967, 38, 493.
5. Zhuravleva, N. M., Bogoslovskii, V. N. and Chufarov, G. I., *Zh. Fiz. Khimii.*, 1960, 34, 3704.
6. Visnyovszky, L., *Kohasz. Lapok.*, 1965, 98(6), 250.
7. Sharma, S. K., Vastola, F. J. and Walker, Jr., P. L., *Carbon*, 1996, 34, 1407.
8. Sharma, S. K., Vastola, F. J. and Walker, Jr., P. L., *Carbon*, 1997, 35, 529.
9. Walker, Jr., P. L., Shelef, M. and Anderson, R. A., *Chemistry and Physics of Carbon*, Vol. 4, ed. P. L. Walker, Jr. Marcel Dekker, New York, 1968, pp. 287-383.
10. Ranish, J. M., Ph.D. thesis, The Pennsylvania State University, PA, 1984.
11. Baker, R. T. K. and Harris, P. S., *Chemistry and Physics of Carbon*, Vol. 14, eds P. L. Walker, Jr. and P. A. Thrower. Marcel Dekker, New York, 1978, pp. 83-165.

