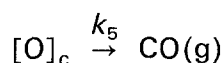
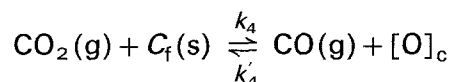
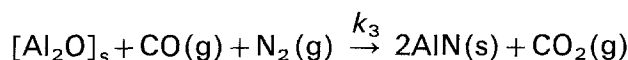
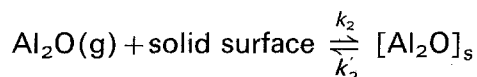
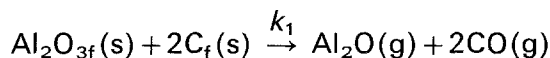


# Mechanism of the reduction of carbon/alumina powder mixture in a flowing nitrogen stream

H. K. CHEN, C. I. LIN\*

Department of Chemical Engineering, National Taiwan Institute of Technology, Taipei, Taiwan 106

The mechanism of the reduction of carbon/alumina powder mixture in a flowing nitrogen stream was studied. Five steps were found to be involved in the overall reaction.



The consumption rates of  $\text{Al}_2\text{O}_3$  and carbon, and the production rate of AlN, were determined to be

$$\begin{aligned} \frac{d[\text{Al}_2\text{O}_3]}{dt} &= -143.88(1+m)\exp(-290580/RT) [\text{Al}_2\text{O}_3] [\text{C}]^2 / \\ &\quad \left\{ 1 + 5.83 \times 10^{14} \exp(-427497/RT) \frac{[\text{CO}_2]}{[\text{CO}]} \right\}^2 \text{ kg mol s}^{-1} \text{ m}^{-3} \\ \frac{d[\text{C}]}{dt} &= -409.504 \exp(-254500/RT) [\text{Al}_2\text{O}_3] [\text{C}]^2 / \\ &\quad \left\{ 1 + 5.83 \times 10^{14} \exp(-427497/RT) \frac{[\text{CO}_2]}{[\text{CO}]} \right\}^2 \text{ kg mol s}^{-1} \text{ m}^{-3} \\ \frac{d[\text{AlN}]}{dt} &= 53.24(1+m) \exp(-290580/RT) [\text{Al}_2\text{O}_3] [\text{C}]^2 / \\ &\quad \left\{ 1 + 5.83 \times 10^{14} \exp(-427497/RT) \frac{[\text{CO}_2]}{[\text{CO}]} \right\}^2 \text{ kg mol s}^{-1} \text{ m}^{-3} \end{aligned}$$

in the temperature range 1648–1825 K.

## 1. Introduction

The carbothermic nitridation of aluminium oxide has been investigated in several previous reports [1–8]. The effects of operating variables on the final yield of AlN is the primary focus of most of them, but the mechanism of the carbothermic nitridation of aluminium oxide was discussed in two papers [2, 8].

One part of a comprehensive study by this laborat-

ory involving the carbothermic nitridation of aluminium oxide is covered in this investigation. The effects of several variables upon the rates of reaction have been previously presented [5]. A general interpretation of the kinetic relationships is discussed. In continuation of the previous work, the mechanism of the reaction in which solid alumina is converted into aluminium nitride, was also studied.

\* Author to whom all correspondence should be addressed.

## 2. Experimental procedure

Nitrogen (Lien-Hwa) with a minimum purity of 99.99% was employed. Reagent grade alumina and carbon black were supplied by Cerac Incorporated and Johnson Matthey Electronics, respectively.

Powders of  $\text{Al}_2\text{O}_3$  and carbon black were separately dried and screened. The powders with known sizes and predetermined proportions were mixed in a V-blender for 43 200 s with ethanol employed as a dispersing medium. The mixed samples were then dried in a nitrogen stream at 323 K and transferred to an alumina crucible with  $2.4 \times 10^{-2}$  m diameter and  $2.0 \times 10^{-3}$  m height. The weights of solid samples were  $2.6 \times 10^{-4}$  kg.

Reactions were carried out in a reaction tube heated by a tubular furnace. The solid sample was placed on the left-hand side of the tube once the temperature of the tube was closer to the desired value. Both ends of the tube were closed by silicon plugs and a nitrogen gas flow was initiated. Once the temperature had reached the predetermined value and remained stable for approximately 300 s, the solid sample was pushed by an alumina rod into the reaction zone to react. The pressure in the reaction tube was maintained at 0.03 m  $\text{H}_2\text{O}$  higher than atmospheric. The solid sample was removed and quenched by an argon stream once the reaction time had been reached. During the reaction, the gas leaving the tube was occasionally fed into a gas chromatograph (Hitachi model 263-30) to analyse the composition of CO and  $\text{CO}_2$ .

Following weight measurement, the sample was calcined in air at 973 K for 21 600 s and the weight of the calcined sample was again determined. The amount of residual carbon in the sample following reaction could be calculated from the weight loss of the sample. The calcined sample was subjected to X-ray diffractometry to determine the aluminium nitride content.

## 3. Results and discussion

The reactants in this reaction system were  $\text{Al}_2\text{O}_3(\text{s})$ ,  $\text{C}(\text{s})$ , and  $\text{N}_2(\text{g})$ ; the main solid product was  $\text{AlN}(\text{s})$ . The amounts of aluminium oxynitride and aluminium oxycarbide were so small that the X-ray diffractometer was unable to detect them. From gas chromatograph analysis, the product gas was known, from the results shown in Fig. 1, to contain mostly CO and very little  $\text{CO}_2$ . Because gas containing aluminium has been pointed out to be possibly produced during the reaction [9], a comparison was made between the measured and calculated weight of  $\text{AlN}$  produced in order to determine if any other gas was produced in the reaction. It was assumed that no aluminium-containing gas was produced, in the calculation of the weight of  $\text{AlN}$  produced. The measured and the calculated results at 36 000 s are shown in Table I. The measured values in this table are observed always to be smaller than the calculated ones. Gas containing aluminium is indicated to be produced in the reaction system.  $\text{Al}_2\text{O}$  and  $\text{AlO}$  have been previously mentioned as the possible gases, and that the probability of production of  $\text{Al}_2\text{O}$  is substantially higher than that of  $\text{AlO}$  [9]. This proposition was adopted in this study. Most of the

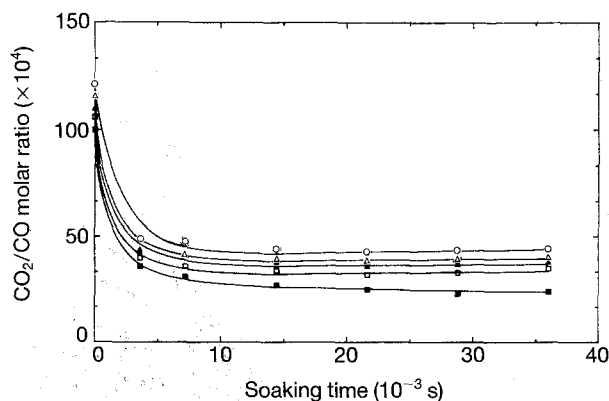


Figure 1 Plot of the  $\text{CO}_2/\text{CO}$  molar ratio against soaking time; the effect of reaction temperature: (○) 1648 K, (△) 1698 K, (▲) 1748 K, (□) 1800 K, (■) 1825 K.

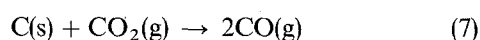
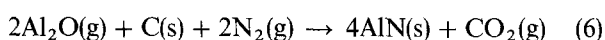
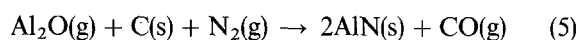
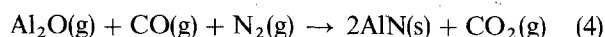
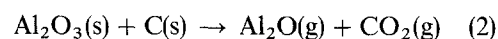
TABLE I Measured and calculated weights of  $\text{AlN}$  produced at 36 000 s

Temperature (K)	Production of $\text{AlN}$	
	Measured (mol)	Calculated (mol)
1648	0.0008	0.0011
1698	0.0019	0.0022
1748	0.0038	0.0040
1800	0.0054	0.0058
1825	0.0063	0.0065

$\text{Al}_2\text{O}$  gas was converted to  $\text{AlN}(\text{s})$ , but some of it was carried out in the nitrogen stream. Minimal  $\text{Al}_2\text{O}$  gas was converted to aluminium oxynitride and aluminium oxycarbide, and was retained in the solid sample. Based on the above discussion, the reactants of this system are  $\text{Al}_2\text{O}_3(\text{s})$ ,  $\text{C}(\text{s})$  and  $\text{N}_2(\text{g})$  as well as the products  $\text{AlN}(\text{s})$ ,  $\text{CO}(\text{g})$ ,  $\text{CO}_2(\text{g})$ ,  $\text{Al}_2\text{O}(\text{g})$ , aluminium oxynitride and aluminium oxycarbide.

### 3.1. Reactions involved

The amounts of aluminium oxynitride and aluminium oxycarbide produced are rather small. Their formation reactions are, therefore, ignored here. Seven reactions can be involved in this complex reaction system

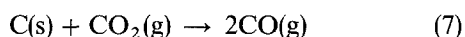
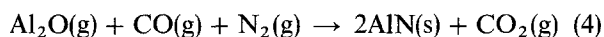
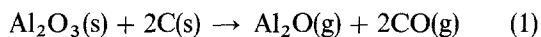


Alumina reacts with carbon to produce  $\text{Al}_2\text{O}$  and  $\text{CO}_2$  gases in Reaction 2.  $\text{CO}_2$  is, however, thermodynamically unstable with respect to CO under the temperature range 1648–1825 K. Reaction 2 can therefore be discounted.

Reaction 3 could be ruled out from the reaction system because of the results from the following experiment.  $\text{Al}_2\text{O}_3$  was employed in reacting with CO without carbon being present. The weight of the solid sample was indicated by the results to have not changed, and no  $\text{CO}_2$  was found in the exit gas.

Performing an experiment to find out whether  $\text{Al}_2\text{O}$  gas reacts with carbon or carbon monoxide is impossible because  $\text{Al}_2\text{O}$  gas is an intermediate which cannot be produced in our experimental system. Nevertheless, Reactions 5 and 6 can be ruled out here, for the following reason. Wang [2] pointed out that the AlN grains formed are isomorphous with the reactant alumina. This suggests that  $\text{Al}_2\text{O}(\text{g})$  is adsorbed on the surface of  $\text{Al}_2\text{O}_3$  and then reacts with  $\text{CO}(\text{g})$  and  $\text{N}_2(\text{g})$ . The reaction between  $\text{Al}_2\text{O}(\text{g})$ ,  $\text{C}(\text{s})$  and  $\text{N}_2(\text{g})$  seems impossible, thus Reactions 5 and 6 are ruled out.

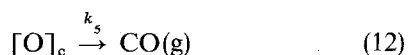
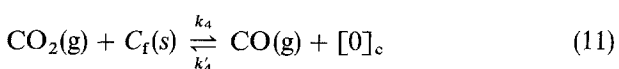
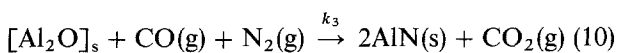
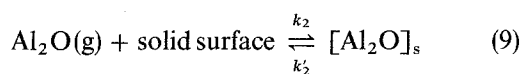
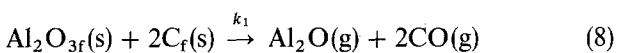
Now, only Reactions 1, 4 and 7 are retained in this complex reaction system



A reaction scheme is drawn in Fig. 2 to the reaction. A solid-solid reaction, observed from this figure to occur between  $\text{Al}_2\text{O}_3(\text{s})$  and  $\text{C}(\text{s})$ , produces gaseous  $\text{Al}_2\text{O}$  and CO.  $\text{Al}_2\text{O}$  is adsorbed during the nucleation stage on to the surface of  $\text{Al}_2\text{O}_3$  and reacts with CO and  $\text{N}_2$  to produce AlN and  $\text{CO}_2$ , as shown in Reaction 4. The growth stage begins once AlN has been produced. Reaction 4 takes place on the surfaces of both  $\text{Al}_2\text{O}_3$  and AlN.  $\text{CO}_2$  gas produced from Reaction 4 simultaneously adsorbs on to and reacts with carbon and releases CO gas through Reaction 7.

### 3.2. Reaction steps

Several elementary steps are involved in Reactions 1, 4 and 7. The following steps are proposed for this reaction system



Reaction 1 is an elementary reaction. Reaction 8, is, therefore, the same as Reaction 1. Reaction 4 contains Reactions 9 and 10. A "solid" appears in Reaction 9 which includes the solid surfaces of  $\text{Al}_2\text{O}_3$  and AlN.  $\text{Al}_2\text{O}$  adsorbs on to  $\text{Al}_2\text{O}_3$  during the nucleation stage, while  $\text{Al}_2\text{O}$  adsorbs both on to  $\text{Al}_2\text{O}_3$  and AlN during the growth stage. Reaction 10 represents the reaction

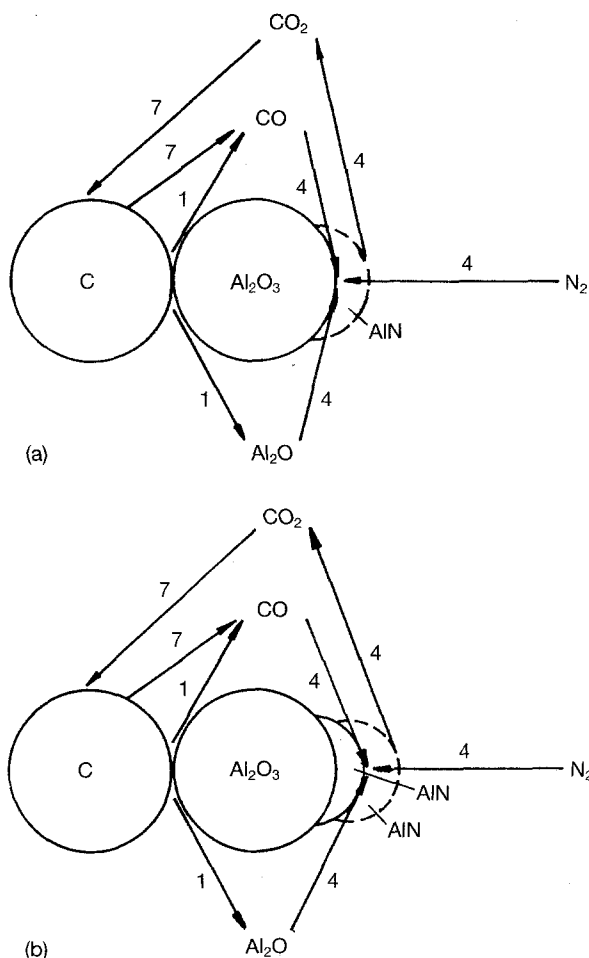


Figure 2 Reaction scheme of carbothermic nitridation: (a) nucleation stage, (b) growth stage.

between adsorbed  $\text{Al}_2\text{O}$ , CO and  $\text{N}_2$ . The Boudard reaction, Reaction 7, consists of Reactions 11 and 12[10]. Reaction 11 represents the reaction between  $\text{CO}_2$  and carbon, while Reaction 12 represents the reaction between adsorbed oxygen and carbon.

### 3.3. Reaction-rate expressions

The production rate of  $\text{Al}_2\text{O}$ ,  $[\text{Al}_2\text{O}]_{\text{s}}$  and  $[\text{O}]_{\text{c}}$  can be expressed according to the reaction mechanism shown in Reactions 8–12 as

$$\frac{d[\text{Al}_2\text{O}]}{dt} = k_1[\text{Al}_2\text{O}_{3\text{f}}][\text{C}_{\text{f}}]^2 - k_2[\text{Al}_2\text{O}][\text{solid surface}] + k_2'[[\text{Al}_2\text{O}]_{\text{s}}] \quad (13)$$

$$\frac{d[[\text{Al}_2\text{O}]_{\text{s}}]}{dt} = k_2[\text{Al}_2\text{O}][\text{solid surface}] - k_3[[\text{Al}_2\text{O}]_{\text{s}}][\text{N}_2][\text{CO}] - k_2'[[\text{Al}_2\text{O}]_{\text{s}}] \quad (14)$$

$$\frac{d[[\text{O}]_{\text{c}}]}{dt} = k_4[\text{CO}_2][\text{C}_{\text{f}}] - k_4'[\text{CO}][[\text{O}]_{\text{c}}] - k_5[\text{O}]_{\text{c}} \quad (15)$$

where  $k_1$ ,  $k_2$ ,  $k_2'$ ,  $k_3$ ,  $k_4$ ,  $k_4'$  and  $k_5$  are reaction-rate constants and  $[\text{Al}_2\text{O}]$ ,  $[[\text{Al}_2\text{O}]_{\text{s}}]$ ,  $[\text{Al}_2\text{O}_{3\text{f}}]$ ,  $[\text{C}_{\text{f}}]$ ,  $[\text{CO}]$ ,  $[\text{CO}_2]$ ,  $[\text{N}_2]$  and  $[[\text{O}]_{\text{c}}]$  are concentrations of  $\text{Al}_2\text{O}$ , adsorbed  $\text{Al}_2\text{O}$ , vacant sites of alumina, vacant sites

of carbon, CO, CO<sub>2</sub>, N<sub>2</sub> and adsorbed oxygen, respectively.

At steady state, the production rate of the intermediates can be assumed to be nil.

$$\frac{d[\text{Al}_2\text{O}_3]}{dt} = \frac{d[[\text{Al}_2\text{O}_3]_s]}{dt} \quad (16a)$$

$$= \frac{d[[\text{O}]_c]}{dt} \quad (16b)$$

$$= 0 \quad (16c)$$

Substituting Equations 16a–c into Equations 13–15, respectively, the expressions of the concentrations of Al<sub>2</sub>O, [Al<sub>2</sub>O]<sub>s</sub> and [O]<sub>c</sub> can be calculated and expressed as follows

$$[\text{Al}_2\text{O}] = \frac{k_1[\text{Al}_2\text{O}_{3f}][\text{C}_f]^2 + k'_2[[\text{Al}_2\text{O}]_s]}{k_2[\text{solid surface}]} \quad (17)$$

$$[[\text{Al}_2\text{O}]_s] = \frac{k_1[\text{Al}_2\text{O}_{3f}][\text{C}_f]^2}{k_3[\text{N}_2][\text{CO}]} \quad (18)$$

$$[[\text{O}]_c] = \frac{k_4[\text{CO}_2][\text{C}_f]}{k_5 + k'_4[\text{CO}]} \quad (19)$$

The total concentration of active sites [C<sub>t</sub>] equals the sum of those of vacant sites and adsorbed oxygen

$$[\text{C}_t] = [\text{C}_f] + [[\text{O}]_c] \quad (20)$$

The expression of [C<sub>f</sub>] is obtained following a substitution of Equation 19 into Equation 20 and rearranging.

$$[\text{C}_f] = [\text{C}_t] \left/ \left\{ 1 + \frac{k_4[\text{CO}_2]}{k_5 + k'_4[\text{CO}]} \right\} \right. \quad (21)$$

The total concentration of active sites on Al<sub>2</sub>O<sub>3</sub>, [Al<sub>2</sub>O<sub>3t</sub>], equals the sum of those of vacant sites and adsorbed Al<sub>2</sub>O

$$[\text{Al}_2\text{O}_{3t}] = [\text{Al}_2\text{O}_{3f}] + m[[\text{Al}_2\text{O}]_s] \quad (22)$$

where *m* is the fraction of Al<sub>2</sub>O adsorbed on to the Al<sub>2</sub>O<sub>3</sub> surface.

After substituting Equation 18 into Equation 22 and rearranging, one obtains the expression for [Al<sub>2</sub>O<sub>3f</sub>]

$$[\text{Al}_2\text{O}_{3f}] = [\text{Al}_2\text{O}_{3t}] \left/ \left\{ 1 + \frac{mk_1[\text{C}_f]^2}{k_3[\text{CO}][\text{N}_2]} \right\} \right. \quad (23)$$

and the consumption rate of Al<sub>2</sub>O<sub>3f</sub> can be expressed as

$$\begin{aligned} \frac{d[\text{Al}_2\text{O}_{3f}]}{dt} &= \frac{d[\text{Al}_2\text{O}_{3t}]}{dt} \\ &= -k_1[\text{Al}_2\text{O}_{3f}][\text{C}_f]^2 \\ &\quad - k_2[\text{Al}_2\text{O}]m[\text{solid surface}] \\ &\quad + k'_2m[[\text{Al}_2\text{O}]_s] \end{aligned} \quad (24)$$

On substituting Equations 17, 18, 21 and 23 into Equation 24, the consumption rate of Al<sub>2</sub>O<sub>3</sub> can be expressed as

$$\frac{d[\text{Al}_2\text{O}_3]}{dt} = -(1+m)k_1[\text{Al}_2\text{O}_{3t}][\text{C}_t]^2 \left/ \left( \left\{ 1 + \frac{mk_1[\text{C}_f]^2}{k_3[\text{N}_2][\text{CO}]} \right\} \times \left\{ 1 + \frac{k_4[\text{CO}_2]}{k_5 + k'_4[\text{CO}]} \right\}^2 \right) \right. \quad (25)$$

If the solid–solid reaction between alumina and carbon, Reaction 8, is very slow which controls the overall rate, *k*<sub>1</sub> approaches zero. Furthermore, Reaction 12 will be assumed to be substantially slower than Reaction 11 [10] such that *k*<sub>5</sub> ≪ *k*<sub>4</sub> and *k*<sub>5</sub> ≪ *k*'<sub>4</sub>. Equation 25 can then be simplified to

$$\begin{aligned} \frac{d[\text{Al}_2\text{O}_{3t}]}{dt} &= \\ &= -(1+m)k_1[\text{Al}_2\text{O}_{3t}][\text{C}_t]^2 \left/ \left\{ 1 + \frac{k_4[\text{CO}_2]}{k'_4[\text{CO}]} \right\}^2 \right. \end{aligned} \quad (26)$$

The concentrations of total active sites of carbon [C<sub>t</sub>] and alumina [Al<sub>2</sub>O<sub>3t</sub>] are proportional to the molar concentrations of carbon [C] and alumina [Al<sub>2</sub>O<sub>3</sub>]

$$[\text{C}_t] = k'[\text{C}] \quad (27)$$

$$[\text{Al}_2\text{O}_{3t}] = k''[\text{Al}_2\text{O}_3] \quad (28)$$

Replacing [C<sub>t</sub>] and [Al<sub>2</sub>O<sub>3t</sub>] in Equation 26 by Equations 27 and 28, combining *k*<sub>1</sub> and *k*'<sup>2</sup> into *k*<sub>a</sub> and rearranging, Equation 26 can be written as follows

$$\begin{aligned} \frac{d[\text{Al}_2\text{O}_3]}{dt} &= \\ &= -(1+m)k_a[\text{Al}_2\text{O}_3][\text{C}]^2 \left/ \left\{ 1 + \frac{k_4[\text{CO}_2]}{k'_4[\text{CO}]} \right\}^2 \right. \end{aligned} \quad (29)$$

where *m* is a function of soaking time. During the initial stage, no AlN is present in the solid sample, Al<sub>2</sub>O only is adsorbed at the Al<sub>2</sub>O<sub>3</sub> surface, and then *m* approaches 1. During the growth stage, most Al<sub>2</sub>O is adsorbed at the AlN surface, and *m* approaches zero. The nucleation stage is observed from the experimental results [5] to be rather short. Thus we can assume that *m* approaches zero in our experimental system. Equation 29 can therefore be rearranged and written as follows

$$\begin{aligned} \left\{ \frac{[\text{Al}_2\text{O}_3][\text{C}]^2}{d[\text{Al}_2\text{O}_3]/dt} \right\}^{0.5} &= \\ &= - \left( \frac{1}{k_a} \right)^{0.5} - \frac{k_4}{k_a^{0.5} k'_4} \frac{[\text{CO}_2]}{[\text{CO}]} \end{aligned} \quad (30)$$

If the assumptions and the derivation presented above are true, a plot of  $[[\text{Al}_2\text{O}_3][\text{C}]^2 / \{d[\text{Al}_2\text{O}_3]/dt\}]^{0.5}$  against [CO<sub>2</sub>]/[CO] would produce a straight line with a slope of *k*<sub>4</sub>/*k*<sub>a</sub><sup>0.5</sup>*k*'<sub>4</sub> and an intercept of  $-(1/k_a)^{0.5}$ . The experimentally obtained molar ratios of CO<sub>2</sub>/CO are depicted in Fig. 1. The concentrations of Al<sub>2</sub>O<sub>3</sub> and C with various soaking times and various temperatures are shown in Figs 3 and 4, respectively. The plots of  $[[\text{Al}_2\text{O}_3][\text{C}]^2 / \{d[\text{Al}_2\text{O}_3]/dt\}]^{0.5}$  against [CO<sub>2</sub>]/[CO] with different temperature are shown in Fig. 5. These plots are clearly good straight lines. This validates the mechanism, Reactions 8–12, and the assumptions made.

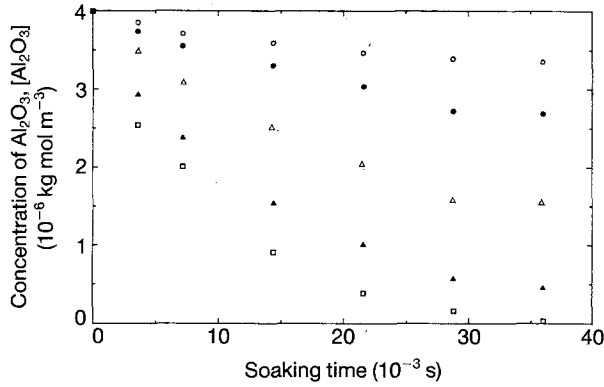


Figure 3 Plot of the concentration of  $\text{Al}_2\text{O}_3$  against soaking time; the effect of reaction temperature: (○) 1648 K, (●) 1698 K, (△) 1748 K, (▲) 1800 K, (□) 1825 K.

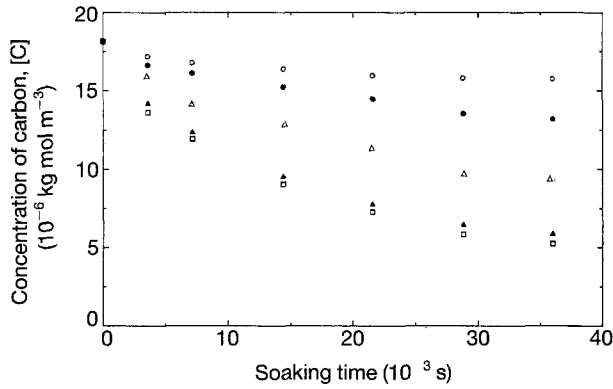


Figure 4 Plot of the concentration of carbon against soaking time; the effect of reaction temperature: (○) 1648 K, (●) 1698 K, (△) 1748 K, (▲) 1800 K, (□) 1825 K.

The expressions for  $k_a$  and  $k_4/k'_4$  obtained are as follows

$$k_a = 143.88 \exp(-290580/RT) \quad \text{m}^3 \text{s}^{-1} \text{kg}^{-1} \text{mol}^{-1} \quad (31)$$

$$k_4/k'_4 = 5.83 \times 10^{14} \exp(-427497/RT) \quad \text{m}^3 \text{s}^{-1} \text{kg}^{-1} \text{mol}^{-1} \quad (32)$$

where  $R = 8.314 \text{ kJ kg}^{-1} \text{ mol}^{-1} \text{ K}^{-1}$ . The Arrhenius plots are shown in Fig. 6. If Equations 31 and 32 are substituted back into Equation 29, the consumption rate of  $\text{Al}_2\text{O}_3$  can be written as

$$\frac{d[\text{Al}_2\text{O}_3]}{dt} = -143.88(1+m) \exp(-290580/RT) [\text{Al}_2\text{O}_3] [\text{C}]^2 / \left\{ 1 + 5.83 \times 10^{14} \exp(-427497/RT) \frac{[\text{CO}_2]}{[\text{CO}]} \right\}^2 \quad \text{kg mol s}^{-1} \text{m}^{-3} \quad (33)$$

By a similar method, the consumption rate of carbon and the production rate of  $\text{AlN}$  can be obtained as follows

$$\frac{d[\text{C}]}{dt} = -409.504 \exp(-254500/RT) [\text{Al}_2\text{O}_3] [\text{C}]^2 /$$

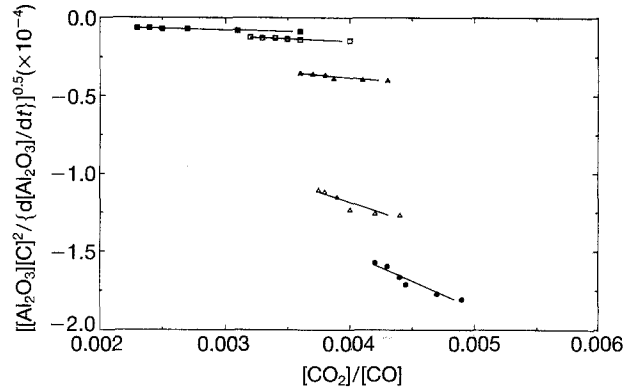


Figure 5 Plot of  $[[\text{Al}_2\text{O}_3][\text{C}]^2 / \{d[\text{Al}_2\text{O}_3]/dt\}]^{0.5}$  against  $[\text{CO}_2]/[\text{CO}]$  with several reaction temperatures: (●) 1648 K, (△) 1698 K, (▲) 1748 K, (□) 1800 K, (■) 1825 K.

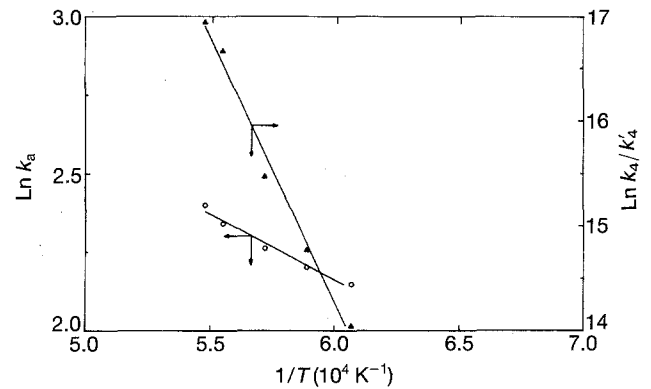


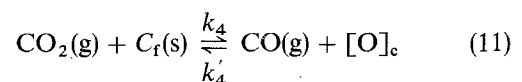
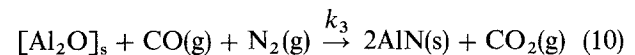
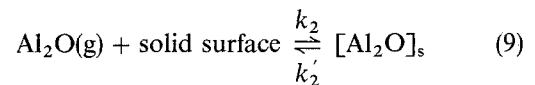
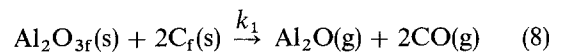
Figure 6 Arrhenius plots of  $k_a$  and  $k_4/k'_4$ .

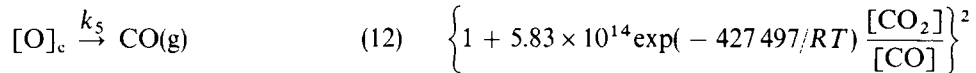
$$\left\{ 1 + 5.83 \times 10^{14} \exp(-427497/RT) \frac{[\text{CO}_2]}{[\text{CO}]} \right\}^2 \quad \text{kg mol s}^{-1} \text{m}^{-3} \quad (34)$$

$$\frac{d[\text{AlN}]}{dt} = 53.24(1+m) \exp(-290580/RT) [\text{Al}_2\text{O}_3] [\text{C}]^2 / \left\{ 1 + 5.83 \times 10^{14} \exp(-427497/RT) \frac{[\text{CO}_2]}{[\text{CO}]} \right\}^2 \quad \text{kg mol s}^{-1} \text{m}^{-3} \quad (35)$$

#### 4. Conclusions

The mechanism of the reduction of a carbon/alumina powder mixture in a flowing nitrogen stream was confirmed from the experimental results to be





Reaction 8 was observed to be rather slow and became a rate-limiting step. The rate of forward and reverse reactions of Reaction 11 were also observed to be substantially higher than that of Reaction 12.

The consumption rates of  $\text{Al}_2\text{O}_3$  and carbon and the production rate of  $\text{AlN}$  were found to be

$$\frac{d[\text{Al}_2\text{O}_3]}{dt} = -143.88(1+m)\exp(-290580/RT)[\text{Al}_2\text{O}_3][\text{C}]^2 \left\{ 1 + 5.83 \times 10^{14} \exp(-427497/RT) \frac{[\text{CO}_2]}{[\text{CO}]} \right\}^2 \text{ kg mol s}^{-1} \text{ m}^{-3} \quad (33)$$

$$\frac{d[\text{C}]}{dt} = -409.504\exp(-254500/RT)[\text{Al}_2\text{O}_3][\text{C}]^2 \left\{ 1 + 5.83 \times 10^{14} \exp(-427497/RT) \frac{[\text{CO}_2]}{[\text{CO}]} \right\}^2 \text{ kg mol s}^{-1} \text{ m}^{-3} \quad (34)$$

$$\frac{d[\text{AlN}]}{dt} = 53.24(1+m)\exp(-290580/RT)[\text{Al}_2\text{O}_3][\text{C}]^2$$

$$\text{kg mol s}^{-1} \text{ m}^{-3} \quad (35)$$

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