The Kinetics of the Formation of Calcium Carbide in a Solid-Solid Reaction

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(Received January 22, 1962)

Calcium carbide is generally made from calcium oxide and carbon according to the following equation:

$$CaO + 3C = CaC_2 + CO \qquad (1)$$

Our fundamental information on the kinetics of this reaction, however, is limited.

The most extensive thermodynamic investigations into calcium carbide formation from calcium oxide and carbon have been made by the Kameyama's group[1]. They have found that the reaction of calcium oxide with carbon involves the following two main steps:

$$CaO + C = Ca + CO \qquad (2)$$

$$Ca + 2C \rightleftharpoons CaC_2 \qquad (3)$$

They concluded that the carbon monoxide pressures of Eqs. 1 and 2 were equal at 1460°C, and that the reaction of Eq. 1 was predominant in comparison with that of Eq. 2 above 1460°C.

Calcium carbide is commercially produced in the molten phase and in a complex reaction system. In order to clarify the kinetics of the reaction of calcium oxide with carbon, the corbonization of calcium oxide was, in the present study, thermogravimetrically examined in a solid-solid reaction at temperatures between 1600 and 1800°C and at various carbon monoxide pressures.

Experimental

Materials. — Calcium oxide was produced by burning precipitated calcium carbonate in an electric furnace at 1200°C for 2 hr. The carbon specimen used was charcoal which had been preheated at 1000°C for 2 hr. in order to remove volatile matters. Calcium oxide and carbon were pulverized to pass through a 200 mesh sieve and mixed at a ratio of 1 : 3 by mole. Nine grams of the mixture were compressed at about 1 ton/cm^2 into a cylindrical pellet, 20 mm. in diameter and 30 mm. in height.

Apparatus.—The apparatus used for the kinetic experiments consisted of a spring balance in a vacuum electric furnace of which the internal volume was about 150 l.[2] The pumping speed of a connected rotary pump was 1600 l./min. A graphite bucket, 45 mm. in diameter and 35 mm. in height, was suspended from the spring in the hot zone of the furnace by a fine molibdenum wire. The shrinkage of the spring by the weight loss of the sample was observed with a microscope with an eyepiece scale. The sensitivity of the spring was 0.278 g./mm. The reaction temperature was measured with a radiation pyrometer and was maintained at a desired value within ±3°C with the aid of an automatic temperature controller. The error in temperature measurement caused by the calcium vapor and the carbon monoxide atmosphere was corrected with a W/50%W-Mo thermocouple[3], which had been calibrated by an optical pyrometer in vacuo. The electric furnace was kept at the desired carbon monoxide pressure during the course of the experiments. The pressures were 50, 100 and 200 mmHg.

Procedure. — The velocity of the formation of calcium carbide was determined as follows. The reaction was stopped at a defined time, and the residual specimen was chemically analyzed for calcium carbide and for residual calcium oxide and carbon. If the formation expressed in Eq. 1 and the decomposition of the calcium carbide formed occur as main reactions in these experimental conditions, there are the following relationships among the analyzed quantities:

$$\begin{aligned}\text{Weight loss} &= \text{CO (evolved)}\\ &\quad + \text{Ca (from decomposed } CaC_2)\\ \text{Residual } CaC_2 &= CaC_2 \text{ (formed)}\\ &\quad - CaC_2 \text{ (decomposed)}\\ \text{Residual CaO} &= \text{CaO (unreacted)}\\ \text{Residual C} &= \text{C (unreacted)}\\ &\quad + \text{C (from decomposed } CaC_2)\end{aligned}$$

Each quantity was obtained from the material balance calculations in the above equations.

The notations used in Figs. 2 to 6 and in the kinetic equation are as follows:

$$\begin{aligned}\text{Reaction ratio} &= \text{Formed } CaC_2/\text{Theoretically}\\ &\quad \text{formed } CaC_2\\ \text{Decomposition ratio} &= \text{Decomposed } CaC_2/\\ &\quad \text{Theoretically formed } CaC_2\\ \text{Residual ratio (yield)} &= \text{Reaction ratio}\\ &\quad - \text{Decomposition ratio}\end{aligned}$$

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[1] N. Kameyama, "Electrochemistry: Theory and Application", Vol. III-2, Maruzen, Tokyo (1956), p. 134.

[2] H. Tagawa and H. Nakajima, This Bulletin, 35, 1239 (1962).

[3] T. Tomonari, M. Takahashi, S. Togawa and H. Arakawa, *J. Electrochem. Soc. Japan* (*Denki Kagaku*), **26**, 479 (1958); F. H. Morgan and W. E. Danforth, *J. Appl. Phys.*, **21**, 112 (1950).

Results

All curves of the weight decrease against the time were parabolic in the temperature range 1600 to 1800°C and at 50, 100 and 200 mmHg of carbon monoxide pressure. Figure 1 shows the course of the reaction at five temperatures and at 100 mmHg of carbon monoxide. The weight loss is presumed to be due to the evolution both of carbon monoxide produced in the formation of calcium carbide and of calcium vapor produced by the decomposition of the freshly formed calcium carbide. The curves of the reaction ratio vs. time, the residual ratio vs. time, and the decomposition ratio vs. time at 100 mmHg of carbon monoxide are shown in Figs. 2, 3 and 4 respectively. The reaction ratio curves are parabolic, whereas the decomposition curves are approximately linear with time. The curves of the residual ratio vs. time and of the decomposition ratio vs. time at 1760°C are shown in Figs. 5 and 6 respectively. The decomposition ratio decreases with the increasing carbon monoxide pressure at any temperature.

The reaction ratio curves were parabolic in all experiments. The rate of solid state reaction when the diffusion process is rate-determining is expressed by the following equation[4]:

$$(1-\sqrt[3]{1-x})^2=kt \tag{4}$$

where x is the reaction ratio, t the time, and k the reaction rate constant. This is derived from the reaction of a sphere of component A completely surrounded by spheres of component B. To determine whether the reaction followed the parabolic kinetics given in Eq. 4, the data in Fig. 2 were plotted as the value of $(1-\sqrt[3]{1-x})^2$ vs. time in Fig. 7. The linearity of the $(1-\sqrt[3]{1-x})^2$ vs. time curve means that the reaction is apparently diffusion-controlled. The apparent rate constant, k, in Eq. 4 was found from the slope of each line.

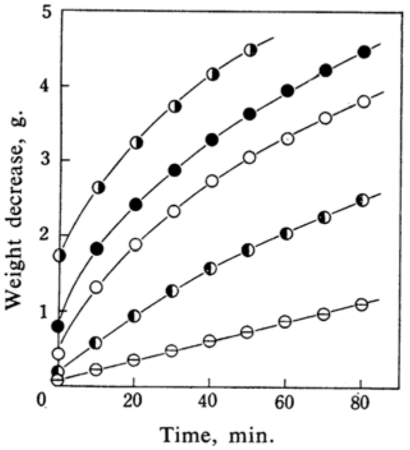

Fig. 1. Relation between weight decrease and time at 100 mmHg of CO.
◑, 1800 ●, 1760 ○, 1720 ◐, 1680 ⊖, 1640°C

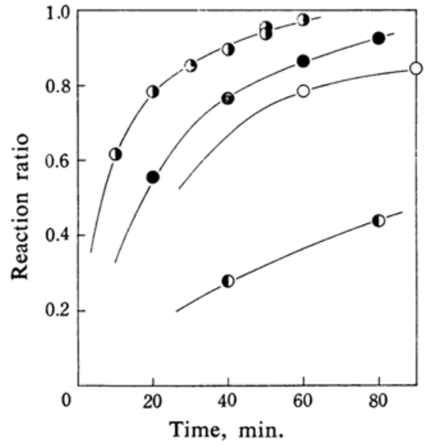

Fig. 2. Relation between reaction ratio and time at 100 mmHg of CO.

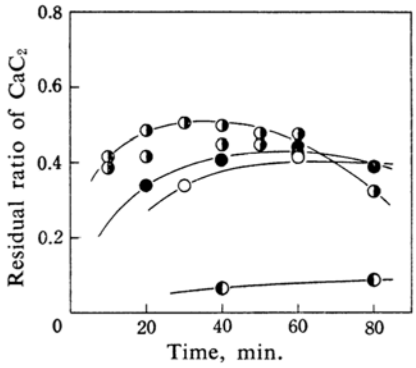

Fig. 3. Relation between residual ratio of CaC_2 and time at 100 mmHg of CO.

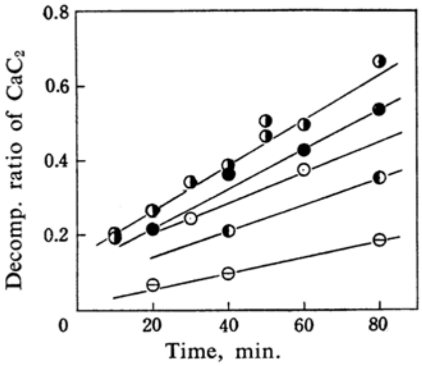

Fig. 4. Relation between decomposition ratio of CaC_2 and time at 100 mmHg of CO.

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[4] W. Jander, *Z. anorg. u. allgem., Chem.*, **111**, 78 (1927).

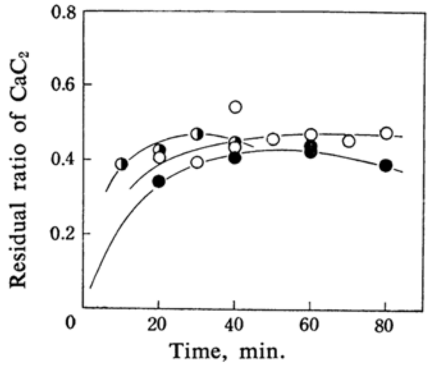

Fig. 5. Relation between residual ratio of CaC_2 and time at 1760°C.
◑, 50 ●, 100 ○, 200 mmHg

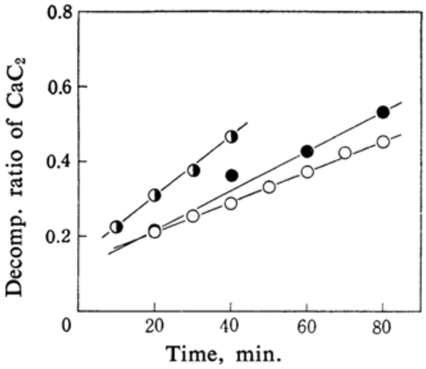

Fig. 6. Relation between decomposition ratio of CaC_2 and time at 1760°C.

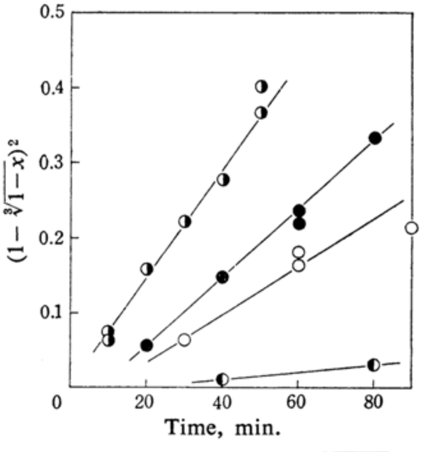

Fig. 7. Relation between $(1-\sqrt[3]{1-x})^2$ and time at 100 mmHg of CO.
◑, 1800 ●, 1760 ○, 1720 ◐ 1680°C

The logarithm of the slope was plotted against the reciprocal of the absolute temperature at 50, 100 and 200 mmHg of carbon monoxide in Fig. 8. The rate constant decreases as the pressure of carbon monoxide increases.

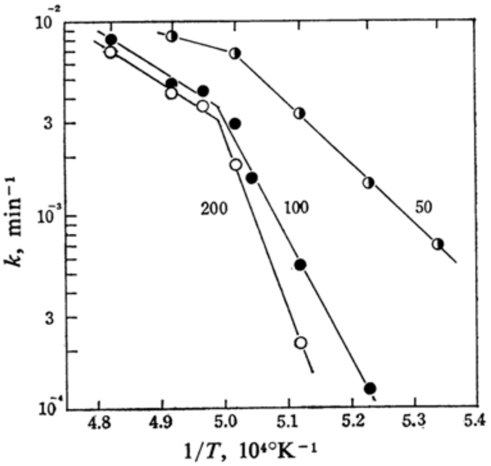

Fig. 8. Relation between logarithm of reaction velocity and the reciprocal absolute temperature at 50, 100 and 200 mmHg of CO.

Discussion

The formation of calcium carbide in a solid state reaction has been studied by Kameyama et al.[1] and by Mukaibo and Yamanaka[5]. Kameyama has found that calcium carbide is formed by the following successive reactions.

$$CaO + C = CaO\cdot C \text{ (Interdiffusion state)} \quad (5)$$

$$CaO\cdot C \text{ (Interdiffusion state)} = Ca + CO \quad (6)$$

$$Ca + 2C = CaC_2 \quad (7)$$

It has been found that the interdiffusion between calcium oxide and carbon occurs at temperatures above 1000°C. Although the reactions of 5 and 6 are determined by diffusion, the kinetics of $CaO+C=Ca+CO$ is described as a zero-order reaction because the products of the reaction of calcium oxide with carbon vaporized from the surface of the reactants[2,5]. The activation energy of the reaction was 147 kcal./mol.[2]

The formation of calcium carbide is apparently expressed by the following equation: $(1-\sqrt[3]{1-x})^2=kt$. In this kinetics, the following steps are considered to be rate-determining:

1) Diffusion of carbon into calcium oxide, and vice versa.
2) Diffusion of carbon monoxide through the product layer.

The apparent activation energy at 50 mmHg of carbon monoxide obtained from Fig. 8 was 143 kcal./mol., while that above 100 mmHg was more than 200 kcal./mol. The effect of the varied carbon monoxide pressure on the

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[5] T. Mukaibo and Y. Yamanaka, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kōgyō Kagaku Zassi*), **58**, 643 (1955).

activation energy may be involved in the pressure term of the kinetics equation, but the general formula of this kinetics has not yet been determined. From the fact that the velocity, k, depends on the pressure of carbon monoxide and that the activation energy is close to that of the first step of the carbide formation at about 1400°C, the rate-determining step may be the diffusion of gas through the product layer as well as that of solids into the solid and product layer. As the calcium carbide formed simultaneously enters upon consecutive decomposition, the reaction velocity, k, is considered to be not an absolute measure, but a relative one.

The apparent reaction rate vs. the reciprocal absolute temperature curves have a break point at about 1700°C. It is considered that reactions expressed in Eqs. 8 and 9, besides the reaction of $CaO+3C=CaC_2+CO$, occur at higher temperature, above 1700°C:

$$m\mathrm{CaC_2} + n\mathrm{CaO} = m\mathrm{CaC_2}\cdot n\mathrm{CaO} \qquad (8)$$

$$m\mathrm{CaC_2}\cdot n\mathrm{CaO} = (m-1)\mathrm{CaC_2}\cdot(n-2)\mathrm{CaO} + 3\mathrm{Ca} + 2\mathrm{CO} \qquad (9)$$

Summary

The kinetics of the formation of calcium carbide in the solid state reaction of calcium oxide with carbon has been examined by using a thermobalance in the temperature range 1600 to 1800°C and at 50, 100 and 200 mmHg of carbon monoxide. The reaction ratio vs. time curves were parabolic in all experimental runs, and the reaction followed parabolic kinetics: $(1-\sqrt[3]{1-x})^2=kt$. On the other hand, the decomposition of calcium carbide as a successive reaction occurred from the specimen surface and was described as a zero-order reaction. As the reaction velocity depended strongly on the pressure of carbon monoxide, it is considered that the reaction rate is governed by the diffusion process of gas through the product layer, as well as that of solids into the solid and product layer.

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