Decomposition of Co_2TiO_4 Spinel below 1000 K

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Co_2TiO_4 spinel was found to decompose to the mixture of $CoTiO_3$ ilmenite and Co_3O_4 spinel below 1000 K. The decomposition rate was the larger for the sample ground for the longer period. It showed a maximum around 870–920 K which seemed to appear from the balance between the rate increase by diffusion and the decrease of nucleation probability with temperature. The thermodynamical consideration supported the experimental results.

Introduction

In the previous paper (*1*), we found that the submicron particles of TiO_2 and Co_3O_4 reacted at about 700°C to form the $CoTiO_3$ ilmenite, and then at 800°C to form the Co_2TiO_4 spinel as a consequence of the reaction between $CoTiO_3$ and Co_3O_4. This experimental result might suggest that the Co_2TiO_4 spinel may be less stable than the mixture of $CoTiO_3$ ilmenite and Co_3O_4 spinel below 800°C. The formation of spinel type titanates, including Co_2TiO_4, have been studied thermodynamically (*2, 3*).

In the present work, the decomposition of Co_2TiO_4 spinel below 800°C was studied kinetically and discussed thermodynamically.

Experimental and Results

The original Co_2TiO_4 spinel sample was prepared by heating the stoichiometric mixture of Co_3O_4 and TiO_2 at 1200°C in air for 24 hr. The heating was repeated twice. It was identified from its X-ray powder pattern as a single phase of spinel.

The original Co_2TiO_4 spinel thus prepared was ground in an agate mortar in air for 4, 20, and 40 hr. The sample ground longer time seemed to be strained more strongly, because of the broadening of the diffraction lines and

of the large value of effective Debye parameter B_{eff} (*4*). The values of B_{eff} for the original, 4-hr, 20-hr and 40-hr ground spinel were 0.42, 0.84, 1.53, and 2.27 Å^2, respectively.

The four samples, original and ground, were heated at 550, 600, 650, 700, and 800°C for 1–30 days and quenched into water. The $CoTiO_3$ ilmenite was supposed to be formed by the following decomposition reaction

$$Co_2TiO_4 + (1/6)O_2 \rightarrow$$
$$CoTiO_3 + (1/3)Co_3O_4. \qquad (1)$$
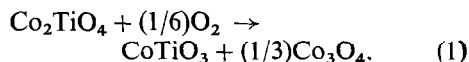
The amount of $CoTiO_3$ ilmenite, p, was determined from the diffraction intensity ratio between spinel (220) ($2\theta = 34.8°$) and ilmenite (104) ($2\theta = 38.2°$) lines. The smallest value of p which can be detected by the present technique was estimated as less than 2%. The diffraction lines of Co_3O_4 spinel were also observed after heating below 700°C.

The changes of the amount of $CoTiO_3$ ilmenite formed with heating time are shown as the Jander's plot in Fig. 1. For the original sample, the decomposition rate is very slow, only 26% after 30 days at 600°C, and difficult to find dependence on temperature. For the ground samples, however, the decomposition rate is much faster than that of the original; the longer the grinding time of the sample, the faster the decomposition at a given temperature between 550 and 700°C. The ground
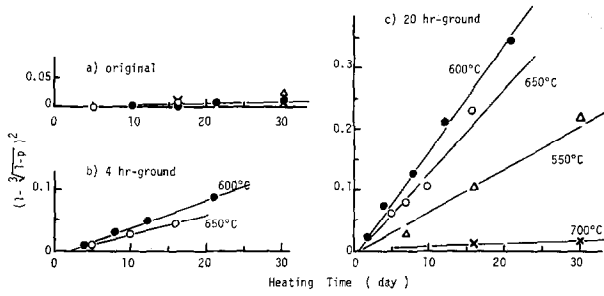
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FIG. 1. Changes of the amount of $CoTiO_3$ ilmenite formed, p, with heating time.

samples show the dependence of the decomposition rate on temperature as shown for the 20-hr ground sample in Fig. 1c. In Fig. 2 the decomposition rate k, which is the slope of the straight line in Fig. 1, is plotted as a function of the reciprocal of decomposition temperature for four samples.

At 800°C, no decomposition of the Co_2TiO_4 spinel was observed even after the heating for 30 days. On the partly decomposed samples, the amount of $CoTiO_3$ ilmenite decreased by heating at 800°C. For example, on the sample which was obtained by heating the 20-hr ground sample at 600°C for four days and has the p-value of 61%, the p-value decreased down to 18% by heating at 800°C for one day.

Discussion

As shown in Fig. 2, the decomposition rate k is the larger for the sample ground for the longer period and shows a maximum around 870–820 K. The increase in decomposition rate by grinding is caused from the increase in the points nucleated the decomposition.
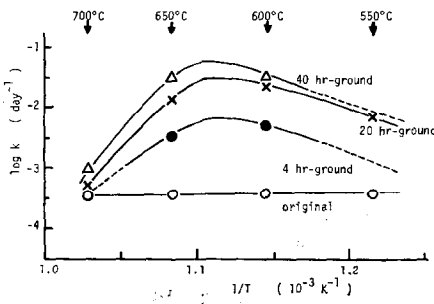
The maximum in the dependence of decomposition rate on temperature seems to appear from the balance between the rate increase by diffusion and the decrease of nucleation probability with temperature. The boundary between the stable regions of Co_2TiO_4 spinel and the mixture of Co_3O_4 spinel and $CoTiO_3$ ilmenite is supposed to be around 1000 K.

The free energy changes for the elemental reactions among CoO, TiO_2, and O_2, and that for the reaction (1) which is calculated from the elemental reactions are shown in Fig. 3. On some reactions, the free energy changes below 1070 K is not available and so it is estimated by the linear extrapolation as shown in Fig. 3 by the broken lines. The free energy change for the decomposition reaction (1) is found to become negative below 1000 K. This thermodynamical estimation agrees with the experimental results shown above. The instability of Co_2TiO_4 spinel below 1000 K
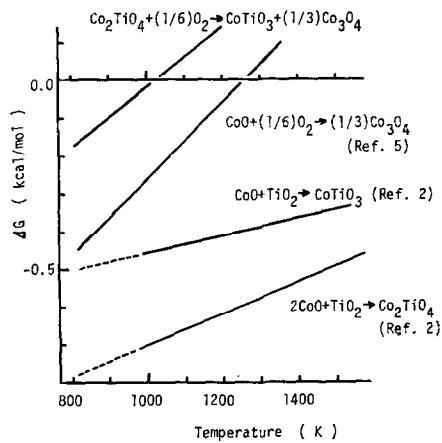

FIG. 2. Changes of the decomposition rate k with reciprocal of decomposition temperature.

FIG. 3. Free energy changes for various reactions.

may be closely related to the fact that Co_3O_4 is more stable than CoO at low temperatures (5).

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