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Thermal analysis of basic zinc carbonate. Part 1. Carbonation process of zinc oxide powders at 8 and 13°C

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Abstract

Zinc oxide powders carbonated at 8 and 13°C in an atmosphere of carbon dioxide (1 atm) and saturated water vapor were investigated by X-ray diffraction analysis and TG/DTA. Similar results were obtained for carbonation at both temperatures. Multiple phases coexisted. The predominant phase changed approximately from the oxide to the normal carbonate via a basic carbonate, as reported by Ohkuma et al. (Nihon Kagaku Kaishi, (1987) 802). Endothermic weight loss was observed at ~ 90, 220–250 and 340°C. A tentative formula was proposed for the basic carbonate; $Zn_3CO_3(OH)_4 \cdot 2H_2O$. Decomposition reactions were proposed for the first and second endothermic weight losses,

$$Zn_3CO_3(OH)_4 \cdot 2H_2O \rightarrow Zn_3CO_3(OH)_4 + 2H_2O\uparrow$$

and

$$Zn_3CO_3(OH)_4 \rightarrow 3ZnO + CO_2\uparrow + 2H_2O\uparrow,$$

respectively. The third endothermic weight loss was attributed to the decomposition of the normal carbonate.

Keywords: Basic zinc carbonate; Carbonation; DTA; TG; Thermal decomposition

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1. Introduction

Thin films of zinc oxide (ZnO) doped with a trivalent ion such as aluminum, indium, or boron, are expected to be a substitute for expensive ITO (indium tin oxide) films which are utilized as transparent electrodes for liquid crystal display devices, etc. However, doped and undoped zinc oxide films are chemically unstable as pointed out by Maniv et al. [1] The present authors reported the etching mechanism of undoped and chromium-doped zinc oxide films in hydrochloric acid and nitric acid [2]. The conductivity of the pressed oxide powders has often been observed to fluctuate remarkably even if the temperature and the humidity are maintained constant. The unstable surface obstructs the application to conductive fillers (ultra-fine powders) and gas sensors (thin films or porous bodies).

Formation of an insulating layer by carbonation of zinc oxide is one of the possible interpretations for the instability. The free energy at 25°C for the reaction $ZnO + CO_2 \rightarrow ZnCO_3$ is calculated from the thermochemical data [3] as -16.636 and $+2.760\,kJ\,mol^{-1}$ at $P_{CO_2} = 1$ and 0.004 atm, respectively, with the partial pressure of the latter corresponding approximately to ordinary air. These calculations indicate that the condition around room temperature and in ordinary air is very close to equilibrium (for example, $P_{CO_2 eq} = 0.0012$ atm at 25°C), i.e. both carbonation and decarbonation may occur depending on minute differences in the conditions.

Ohkuma et al. [4] reported the chemical change from zinc oxide powders to the normal carbonate $ZnCO_3$ (Smithonite) [5] in an atmosphere of carbon dioxide (1 atm) and saturated water vapor. A recently discovered basic zinc carbonate (chemical formula unknown), hydrozincite $Zn_5(CO_3)_2(OH)_6$ [6] and a basic zinc carbonate $Zn_2CO_3(OH)_2$, which is isostructural with Rosasite $(Cu, Zn)CO_3(OH)_2$ [7], are the predominant intermediates at 5, 10 and 20°C, respectively. We call them low-, medium- and high-temperature basic carbonate, respectively, in the present paper. Ohkuma et al. also reported [8] that the reaction was influenced by the synthetic conditions of the oxide as well as the partial pressure of carbon dioxide ($P_{CO_2} = 0.01$–1.0 atm).

In the present work, the carbonation process of zinc oxide powders was investigated at temperatures of 8 and 13°C which are different from those of Ohkuma et al. [8]. A semiquantitative analysis of the low-temperature basic carbonate was attempted by TG.

2. Experimental

2.1. Carbonation

Zinc oxide powders (purity, 99.9%; Kojyundo Chemicals Laboratory Co. Ltd.) were placed in sealed containers and maintained at 8 and 13°C in a refrigerator for 100 days. Carbon dioxide was introduced into the container every day. In order to accelerate the carbonation, a cup of water was placed in the container to provide saturated water vapor (0.011 and 0.015 atm at 8 and 13°C, respectively [9]).

2.2. Evaluation

A portion of the carbonated powders was sampled quickly for X-ray diffraction analysis at room temperature in air using a Rigaku RAD-C system with Ni-filtered Cu Kα radiation (40 kV, 45 mA). In order to confirm the phase identification, some specimens were also analyzed using a Rigaku RINT-2500 system with monochromated Cu Kα radiation (60 kV, 300 mA) and automatic phase identification software.

TG/DTA (Rigaku 8101D) after the XRD analysis was performed in air at a heating rate of 10°C min^{-1}. The specimen's weight was measured with an ultramicrobalance (Sartorius S-4; sensitivity, 0.1 μg) before and after the thermal analysis.

3. Results and discussion

3.1. Carbonation process

The X-ray diffraction pattern for the carbonated oxide showed the oxide [10], the low-temperature basic carbonate [4] and the normal carbonate [5]. No additional phase was detected. The dependence of the diffraction intensities on the reaction time (carbonation period) is shown in Fig. 1. Similar results were observed for the carbona-

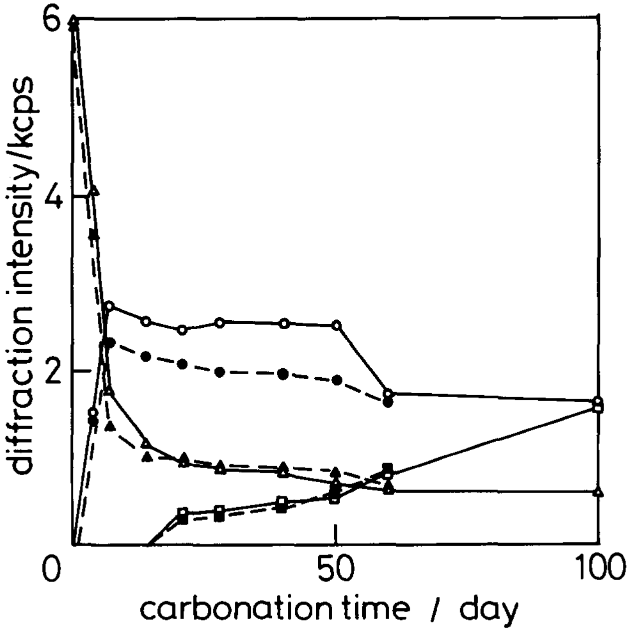

Fig. 1. Dependence of X-ray diffraction intensity on carbonation period: △, ○ and □, carbonated at 8°C; ▲, ● and ■, carbonated at 13°C; △ and ▲ zinc oxide, (002) diffraction ($2\theta = 34.4°$); ○ and ●, low-temperature basic zinc carbonate reported by Ohkuma et al. [4], unindexed peak ($2\theta = 7.6°$); and □ and ■, normal zinc carbonate, (102) diffraction ($2\theta = 32.5°$).

tion at 8 and 13°C. Multiple phases coexisted. Strict identification of the normal carbonate was difficult because the strong peaks are very close to those of the low-temperature basic carbonate. Therefore, the diffraction intensity at 32.5° might include that of the low-temperature basic carbonate. The predominant phase changed approximately from the oxide via the low-temperature basic carbonate to the normal carbonate. This result agreed with that of the needle-like oxide powders carbonated at 5°C by Ohkuma et al. [8].

3.2. Thermal analysis

The results of thermal analysis for the specimen carbonated at 8°C for 14 days are shown in Fig. 2. The oxide and the low-temperature basic carbonate were expected from the XRD analysis. Endothermic weight loss was observed at ~ 90 and 230°C. These weight loss were attributed to an evolution of water vapor and a simultaneous evolution of carbon dioxide and water vapor from the low-temperature basic zinc oxide, respectively, as will be discussed later.

The results of thermal analysis for the specimen carbonated at 8°C for 100 days are shown in Fig. 3; the oxide, the low-temperature basic carbonate and the normal carbonate were expected from the results of XRD analysis. The first and the second endothermic weight losses were attributed to the decomposition of the low-temperature basic carbonate. A third endothermic weight loss at ~ 340°C was observed which can be attributed to the decomposition of the normal carbonate; the temperature agreed with that reported by Ohkuma et al. [4].

The dependence of the DTA peak temperature on the carbonation period is shown in Fig. 4. The temperature for the first endothermic peak was constant (~ 90°C). The temperature for the second endothermic peak was constant (~ 250°C) except for the first few weeks (220–250°C). This exceptionally lower decomposition temperature can be attributed to insufficient growth of the low-temperature basic carbonate. The third endothermic peak, which is attributed to the decomposition of the normal carbonate, was observed after 100 days although the diffraction of the normal carbonate was

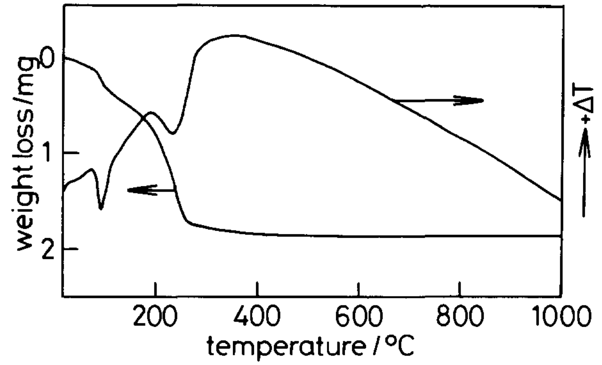

Fig. 2. Results of thermal analysis for the zinc oxide carbonated at 8°C for 14 days. Starting weight: 5.071 mg.

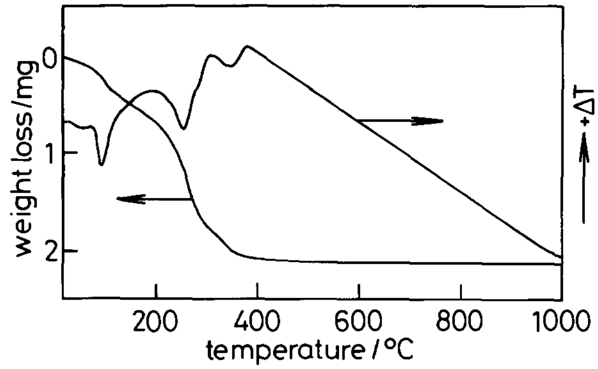

Fig. 3. Results of thermal analysis for the zinc oxide carbonated at 8°C for 100 days. Starting weight: 5.245 mg.

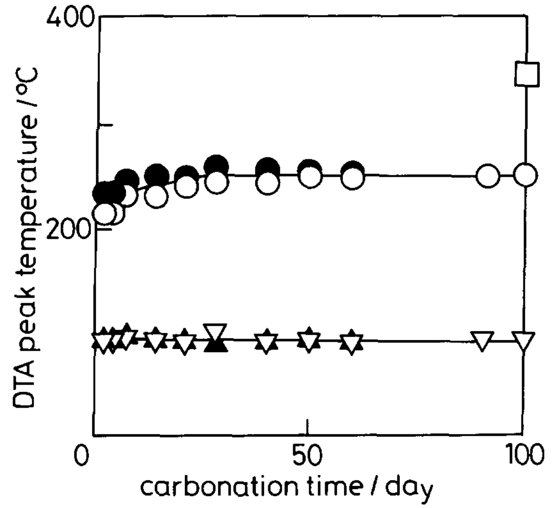

Fig. 4. Dependence of DTA peak temperature on the carbonation period. ∇, ○ and □, carbonated at 8 °C; ▲ and ●, carbonated at 13 °C; ∇ and ▲, the first endothermic peak at ~ 90°C; ○ and ●, the second endothermic peak at ~ 220–250 °C, □, the third endothermic peak at ~ 340 °C.

detected at 20 days. This inconsistency can be explained as follows: as mentioned above, the diffraction peak for the normal carbonate (at $2\theta = 32.5°$) duplicated that of the low-temperature basic carbonate; or else the normal carbonate formed at the early stage of the carbonation was unstable and decomposed at the lower temperature, i.e. no clear endothermic peak was observed.

3.3. Composition of the low-temperature basic carbonate

The chemical formula of the low-temperature basic carbonate was not reported because the pure phase was not obtained. The formula was tentatively estimated in the present work from the specimens carbonated for 0–7 days during which only the low-temperature carbonate and the oxide were detected by XRD analysis. The specimens with longer carbonation periods (14 days or more) were not considered because the normal carbonate was detected by XRD analysis as well as the low-temperature basic carbonate and the oxide.

First, a relative weight loss R_1 (%) is defined as (the first weight loss at ~ 90°C)/(the weight of the oxide after the thermal analysis). R_2 and R_3 are also defined as (the second weight loss at ~ 220–250°C)/(the weight of the oxide after the thermal analysis) and (the third weight loss at ~ 340°C)/(the weight of the oxide after the thermal analysis), respectively. R_1, R_2 and R_3 are plotted against the carbonation period in Fig. 5. Increasing R_1 and R_2 can be interpreted as formation of the lower-temperature basic carbonate for the first 7 days when the peak intensity of the XRD for the low-temperature carbonate was increasing while that for the oxide was decreasing. R_1 and R_2 increased up to approximately 14.8 and 32.8%. These values correspond to the decomposition reactions

$$Zn_3CO_3(OH)_4 \cdot 2H_2O \rightarrow Zn_3CO_3(OH)_4 + 2H_2O\uparrow \qquad (1)$$

and

$$Zn_3CO_3(OH)_4 \rightarrow 3ZnO + CO_2\uparrow + 2H_2O\uparrow \qquad (2)$$

respectively. Reaction (1) satisfies the results reported by Ohkuma et al. [4] that the evolved gas during the first weight loss mainly consists of water vapor. They reported

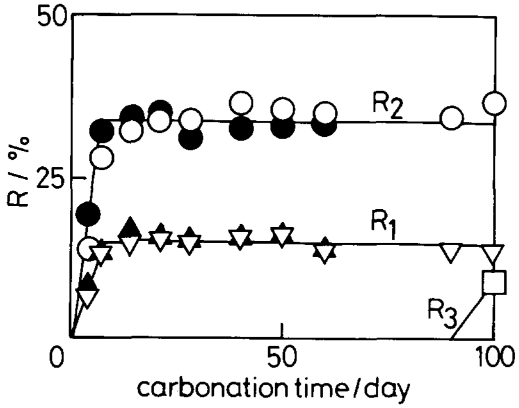

Fig. 5. Dependence of relative weight loss R on the carbonation period: ▽ and ▲, relative weight loss R_1(%) = (the first weight loss at ~ 90°C)/(the weight of the oxide after the thermal analysis); ○ and ●, relative weight loss R_2(%) = (the second weight loss at ~ 220–250°C)/(the weight of the oxide after the thermal analysis) and □, relative weight loss R_3(%) = (the third weight loss at ~ 340°C)/(the weight of the oxide after the thermal analysis); ▽, ○ and □, carbonated at 8°C; and ▲ and ●, carbonated at 13°C.

that a small amount (approximately 4%) of carbon dioxide was detected in the evolved gas. This can be attributed to the adsorbed carbon dioxide. Reaction (2) satisfies the result by Ohkuma et al. [4] that the evolved gas during the second weight loss consists of carbon dioxide and water vapor in the ratio of 1:2. The estimated molar ratio $[CO_2]/[ZnO]$ for the low-temperature basic carbonate $Zn_3CO_3(OH)_4 \cdot 2H_2O$ (0.33) is smaller than those of the medium-temperature basic carbonate $Zn_5(CO_3)_2(OH)_6$ (hydrozincite [6]) and high-temperature basic carbonate $Zn_2CO_3(OH)_2$ (0.40 and 0.50, respectively). The estimated molar ratio $[H_2O]/[ZnO]$ for the low-temperature basic carbonate (1.33) is larger than those of the medium and high-temperature basic carbonate (0.60 and 0.50, respectively).

R_1 is plotted against R_2 in Fig. 6. A strong correlation for the first 7 days ($R_1 < 14.8\%$ and $R_2 < 32.8\%$) indicates that the first weight loss at ~ 90°C (evolution of water vapor) is proportional to the second weight loss at 220–250°C (evolution of carbon dioxide and water vapor). This supports the hypothesis that the first weight loss is attributed to the stoichiometric water (crystalline water) while Ohkuma et al. [4] interpreted this as adsorbed water which is non-stoichiometric. The gradient (0.46) agrees approximately with that ($0.45 = 14.8\%/32.8\%$) expected from the above-mentioned decomposition reactions (1) and (2).

4. Conclusions

Zinc oxide powders were carbonated at 8 and 13°C in an atmosphere of carbon dioxide (1 atm) and saturated water vapor. The carbonation process was investigated using X-ray diffraction analysis and thermal analysis.

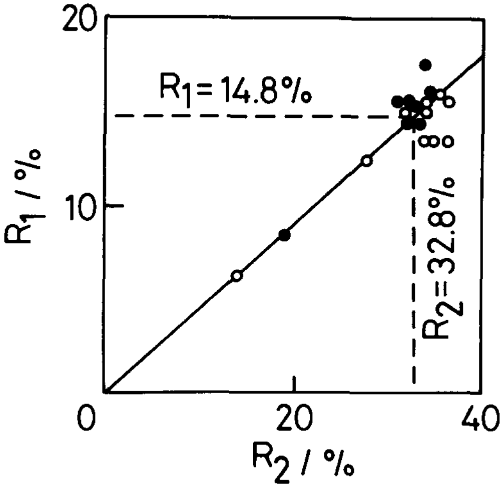

Fig. 6. Relation between R_1 and R_2: ○, carbonated at 8°C; and ●, carbonated at 13°C. R_1 and R_2 are defined in the figure caption of Fig. 5.

Similar results were obtained for the carbonation at both temperatures. Multiple phases coexisted. The predominant phase changed approximately from the oxide via what we call the low-temperature basic carbonate to the normal carbonate.

Endothermic weight loss was observed at ~ 90, 220–250 and 340°C. A tentative formula was proposed for the low-temperature basic carbonate, $Zn_3CO_3(OH)_4 \cdot 2H_2O$. A decomposition reaction was proposed for the first and second endothermic weight loss

$$Zn_3CO_3(OH)_4 \cdot 2H_2O \rightarrow Zn_3CO_3(OH)_4 + 2H_2O\uparrow$$

and

$$Zn_3CO_3(OH)_4 \rightarrow 3ZnO + CO_2\uparrow + 2H_2O\uparrow$$

The third endothermic weight loss was attributed to the decomposition of the normal carbonate.

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