JOURNAL OF MATERIALS SCIENCE 21 (1986) 2002–2006

Particle evolution during the decomposition of $CdCO_3$

Z. A. MUNIR, B. J. ASIRVATHAM
Division of Materials Science and Engineering, College of Engineering, University of California, Davis, California 95616, USA

Particle evolution during and following the decomposition of cadmium carbonate was investigated using surface area and crystallite size analyses. Surface area results of decompositions at temperatures ranging from 523 to 775 K showed a maximum corresponding to the total decomposition of the carbonate. The maxima for vacuum and air decomposition occurred at 583 and 613 K, respectively. Crystallite size analyses showed that the sizes of the CdO resulting from the air decomposition of $CdCO_3$ at low temperatures was significantly larger than the corresponding values obtained for vacuum decomposition. These observations suggest that $CdCO_3$ sinters favourably in air before decomposition, leading to larger CdO crystallites after decomposition. After complete dissociation, the evolution of CdO particles is the same for vacuum and air decomposition, indicating that the sintering of CdO is essentially the same under these two conditions.

1. Introduction

In the decomposition of many carbonates and hydroxides the structure of the product phase (oxide) is closely related to that of the precursor. In cases where the crystal structure of the product is geometrically obtained through small deformations in the angles or axes of the parent crystal, the solid–solid transformation is termed *topotactic* and is quite frequently a shear transformation process. A characteristic of these types of reaction is the independence of the crystallite size of the product of the temperature and degree of decomposition. This behaviour is in sharp contrast to the case in which the new phase is formed through the classical nucleation and growth mechanism. In the latter mechanism, the size of the crystallites of the product increases with increasing temperature. Aside from its dependence on the operative mechanism, the crystallite size of the product is influenced by evolutionary processes resulting from mass transport during sintering. At relatively high temperatures, these evolutionary processes can become the dominant considerations regarding the ultimate size of the crystallite of the product of decomposition. We report here the results of an investigation on the particle evolution during the decomposition of $CdCO_3$ under air and vacuum conditions. In the preceding paper [1] we reported the results of a thermogravimetric study of this decomposition.

Mikhail *et al.* [2, 3] investigated the decomposition of "pure" and doped $CdCO_3$ in air and reported a dependence of the specific surface area of the decomposition product on temperature and on the type of dopant. For pure $CdCO_3$, the specific surface area increased as the decomposition temperature increased from 373 to 573 K and decreased markedly as the temperature increased further. The increase in surface area was attributed to an increase in the degree of decomposition, and the subsequent decrease was explained in terms of the sintering of the resulting oxide crystallites. For partially decomposed materials, surface area measurements include the contribution of the precursor and the product phases and cannot give explicit information on the particle evolution of the product. Dumas *et al.* [4] used the method of X-ray line-broadening to determine the size and shape of CdO crystallites resulting from the decomposition of $Cd(OH)_2$. Their results showed a region of decomposition temperature over which the crystallite size of CdO is constant, indicating that the decomposition of cadmium hydroxide is topotactic. At higher decomposition temperatures, the crystallite size of CdO increased linearly with temperature. The latter observation was attributed to the sintering of the oxide crystallites.

2. Experimental methods and materials

Electronic grade cadmium carbonate listed as 99.999% pure (obtained from Johnson Matthey, London, England) was used in powder form. The highest impurity levels arising from the presence of calcium, copper, magnesium and silver were below 1 p.p.m. Scanning electron microscope imaging of the starting powder (Fig. 1 of the preceding paper [1]) showed characteristic crystallites with rhombohedral plate-like geometries. The powder is agglomerated with individual particles ranging from $< 1\,\mu m$ to slightly above $10\,\mu m$. Surface area measurements on the as-received powder of $CdCO_3$ gave a value of $3.59\,m^2\,g^{-1}$ as determined by the nitrogen adsorption (BET) method.

Samples weighing 100 mg were decomposed in air and in vacuum at temperatures ranging from 563 to 773 K. The starting samples were placed in alumina crucibles such that the approximate depth of the

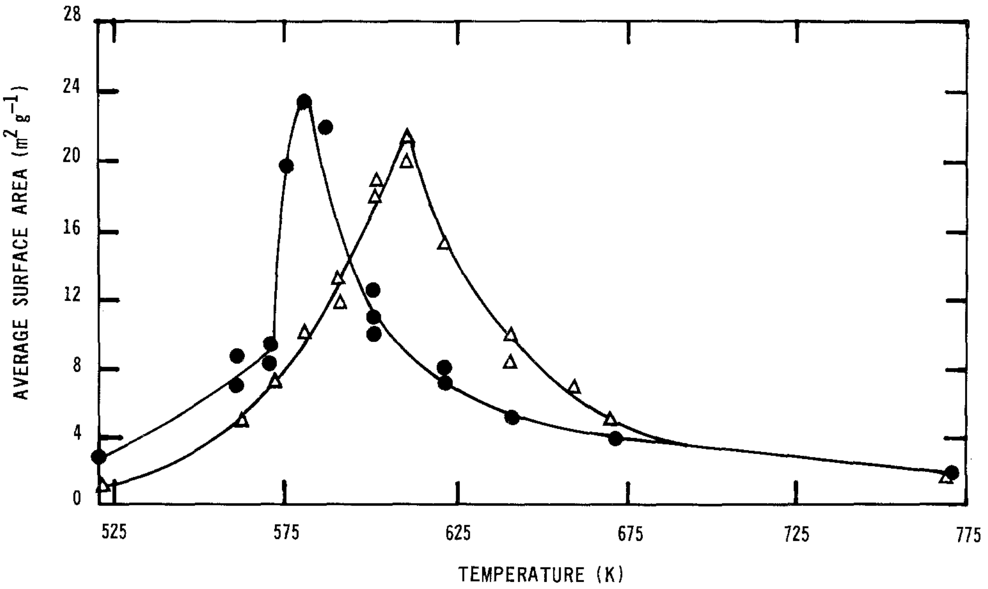

Figure 1 Temperature dependence of the surface area of the product of decomposition of cadmium carbonate in (△) air and (●) vacuum.

powder was less than 0.1 mm. Heating was maintained at a constant 10 K min^{-1} and the decomposition was carried out for 7 h with the heat-up period taking 30 to 50 min, depending on the desired final temperature. At the end of each decomposition experiment, the product was X-rayed and its BET surface area was determined. Reflections from sets of planes for the product (CdO) were used to determine the mean crystallite size through the line-broadening method. Cu$K\alpha$ radiation (λ = 0.154 05 nm) was used to obtain line-broadening data from the reflections of the (1 1 1), (2 0 0) and (2 2 0) planes. Reflections from these planes had high-intensity peaks and the results from the (2 0 0) plane were the most reliable, since the line-broadening of the others was subject to higher degrees of uncertainty due to background noise. Because line-broadening can be affected by instrument peculiarities, calibration and standard methods of correction were applied. Quartz was used as a standard before each X-ray determination to ensure the same peak intensity. Instrument-related line-broadening was determined from measurements on annealed CdO powders. A CdO sample obtained from Aldrich Chemicals and reported as 99.999% pure was annealed at 973 K for 42 h before being used for X-ray analysis. These results were used to account for instrument-related line-broadening using the Warren's correction method [5].

3. Results

3.1. Surface area analysis

The average value of a minimum of ten surface-area determinations was used to establish the dependence of the specific surface area on the temperature of decomposition. Fig. 1 depicts this dependence for $CdCO_3$ samples decomposed in vacuum and in air. As stated earlier, the specific surface area of the starting $CdCO_3$ was 3.59 m^2 g^{-1}, and as can be seen from Fig. 1 for the decomposition in vacuum this value remained unchanged until the decomposition was carried out at 563 K or higher temperatures. At 563 K only 30% of the carbonate had decomposed to CdO, yet the surface area had increased by 122% relative to the starting powder. The maximum in the surface-area curve (Fig. 1 for vacuum decomposition) was observed at 583 K, which correspond to 94% complete decomposition of the carbonate. Thus, the surface area after decomposition at this and higher temperatures is due primarily to the contribution of CdO.

When the decomposition of the carbonate was carried out in air, the dependence of the specific surface area on the decomposition temperature showed a maximum in qualitative agreement with the results obtained for vacuum decomposition. However, the maximum surface area corresponded to a decomposition at 613 K instead of 583 K as was the case for the vacuum decomposition results. Moreover, the two curves obtained under vacuum and air conditions display similar shapes beyond the maximum points but are distinctly different below them. Based on weight loss data [1], the decomposition in air is 22% complete at 563 K. It will be recalled that under vacuum conditions the decomposition is 30% complete at 563 K and is nearly complete (94%) at 583 K. The peaks of the two curves shown in Fig. 1 correspond to the temperatures at which the decomposition of $CdCO_3$ is essentially complete.

3.2. Crystallite size determination

The crystallite size, D_{200}, of CdO and its dependence on the decomposition temperature is shown in Fig. 2 for the decomposition in air and in vacuum. As stated earlier, the (2 0 0) peak was the most intense and its broadening was used to calculate the crystallite size over the entire temperature range of this study. Results from the (1 1 1) and (2 2 0) peaks were limited to the upper temperature range and are shown in Figs 3a and b for vacuum and air decomposition, respectively. The results from these peaks are in general agreement with those obtained from the (2 0 0) peak over the applicable temperature ranges. Fig. 2 shows that changes in the crystallite size, D_{200}, of CdO are relatively modest when the oxide is prepared under vacuum decomposition. In contrast, the D_{200} for CdO

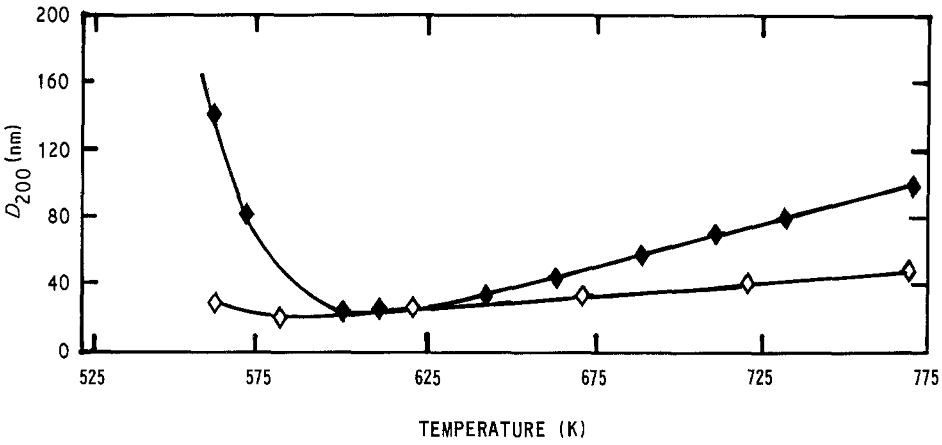

Figure 2 Dependence of the crystallite size, D_{200}, of CdO on the temperature of decomposition of cadmium carbonate in (♦) air and (◇) vacuum.

resulting from the decomposition of $CdCO_3$ in air shows marked changes over the entire experimental range. A dramatic decrease of D_{200} between 563 and 613 K is observed: a decrease from 140 to 20 nm in the size of the CdO crystallites. Above 613 K, D_{200} increases steadily to 100 nm at 773 K.

4. Discussion

In general, the increase in surface area of partially decomposed $CdCO_3$ powders corresponds to the degree of decomposition, i.e. to the amount of oxide. This is valid for decomposition in vacuum and in air. In both cases, the highest surface area obtained corresponds to the complete (or nearly complete) decomposition of the carbonate. The subsequent decrease in surface area is the result of the sintering of the product oxide. These general observations emphasize only the similarities between the results under the two experimental conditions. Of more interest, however, are the differences between the results obtained under these conditions.

Between 523 and 613 K the increase in surface area for powders decomposed in air is more gradual in comparison with similar results obtained for vacuum decomposition. As pointed out above, in this temperature range the degree of decomposition increased from zero to 98%, and thus the measured surface area represents the sum of the contributions of the

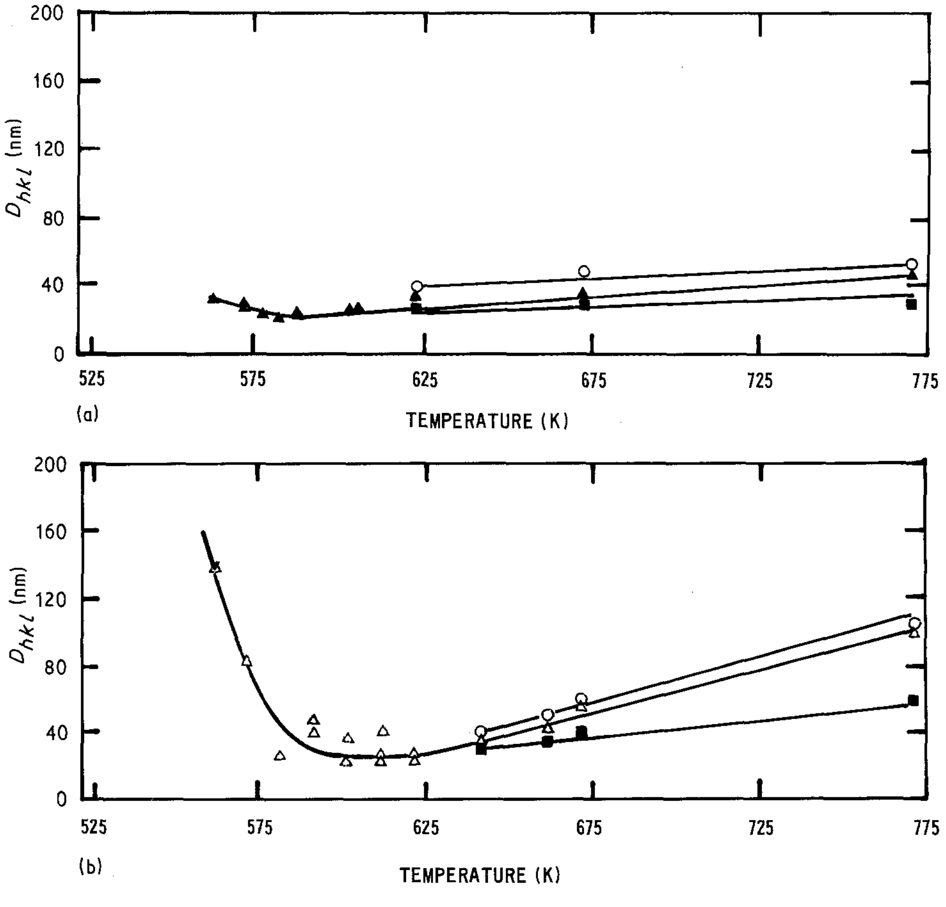

Figure 3 (a) Dependence of the crystallite size of CdO on the temperature of decomposition of cadmium carbonate in vacuum. (○) D_{111}, (▲) D_{200}, (■) D_{220}. (b) Decomposition in air: (○) D_{111}, (△) D_{200}, (■) D_{220}.

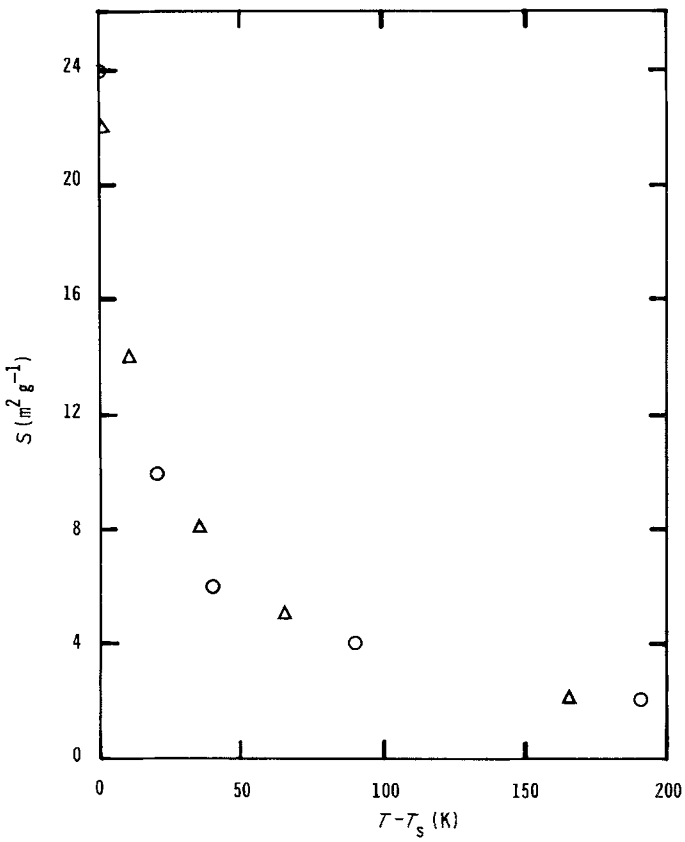

Figure 4 Dependence of surface area, *s*, of the product of decomposition of $CdCO_3$ on the normalized temperature: (△) air, (○) vacuum.

undecomposed $CdCO_3$ and the product oxide. The contributions of these phases to the total surface area depends not only on their relative abundance but also on the sintering between the crystallites. The maximum surface area obtained during air decomposition, 21 m^2 g^{-1}, is slightly lower (by about 12%) than the maximum value obtained during vacuum decomposition. Since both maxima correspond to the complete (or nearly complete) decomposition of the carbonate, it can be assumed that the CdO particles had not experienced a significant degree of sintering. This conclusion is supported by the results of the crystallite size analysis. The D_{200} values corresponding to the temperatures at which the maximum surface areas were observed, are the lowest for both vacuum and air decomposition. These considerations lead us to conclude that the difference in the decomposition process under the two conditions examined in this work is primarily due to the sintering of the carbonate phase prior to decomposition.

To test this assumption, we annealed two samples of $CdCO_3$ at 523 K, one in air and the other in vacuum for 7 h. At this temperature no measurable decomposition was detected [1], and thus surface-area changes are due entirely to the sintering of the carbonate phase. The surface area of the sample which was heated in air was 1 m^2 g^{-1} and that of the sample heated in vacuum was 2.8 m^2 g^{-1}. Since the surface area of the starting material was 3.59 m^2 g^{-1}, sintering was significant in samples annealed in air. This process manifests itself in two ways: it causes a reduction in the total surface area and, apparently, it influences the crystallite size of the product. Comparing the crystallite size results for the two sets of data (air and vacuum decomposition), it is evident (Fig. 2) that much larger crystallite sizes of CdO are produced at the lower temperatures when the decomposition is carried out in air as compared with those resulting from vacuum decomposition. This observation suggests that the crystallite size of CdO is directly correlated with that of the precursor, $CdCO_3$. Sintered, and presumably larger, $CdCO_3$ particles produced larger CdO crystallites. At higher temperatures the decomposition process takes place at such a high rate that the sintering of the $CdCO_3$ is not realized and thus the crystallite size of the resulting CdO is small. At $573 < T < 613$ K the crystallite size of CdO resulting from the decomposition in air has the lowest value, about 20 nm. Corresponding results from the vacuum decomposition show that the smallest crystallite sizes of CdO are obtained at the temperature where the decomposition is nearly complete.

Beyond the point at which the surface area is maximum (583 K for vacuum decomposition and 613 K for air decomposition) the surface area decreases and the crystallite size increases with increasing temperature. This decrease, which results from the sintering of CdO, has basically the same temperature dependence for the results obtained under the two experimental conditions. This is shown in Fig. 4 in which the surface area is plotted against $T - T_s$, where T_s is the temperature at which the surface area is maximum. The evolution of CdO particles appears to be the same regardless of the conditions under which they were formed. In the study by Dumas *et al.* [4] on the decomposition of $Cd(OH)_2$ it was observed that the mean crystallite size of CdO depended on the partial pressure of H_2O under which the decomposition was taking place. Since there were no reported thermogravimetric and surface area data in the cited paper, it is not possible to determine whether water vapour influences the sintering of the precursor $Cd(OH)_2$, or the sintering of the product CdO.

In this work, at the lower temperatures the sintering of $CdCO_3$ is a major factor influencing the particle size of the oxide product. In addition, sintering of the carbonate phase is expected to retard the decomposition process due to the reduction in surface area [6] and the concomitant reduction of the ease of escape of the gaseous product, CO_2. We believe that this is the reason for the shift of the temperature corresponding to complete dissociation from 583 to 613 K as the condition changes from vacuum to air.

Acknowledgements

This work was supported by a grant from the Office of Basic Energy Sciences, the Department of Energy, Contract No. DE–AT03–ATET10708.

References

1. B. J. ASIRVATHAM and Z. A. MUNIR, *J. Mater. Sci.* **21** (1986) 1997.
2. R. S. MIKHAIL, D. DOLLIMORE, A. M. KARNEL and N. R. EL-NAZER, *J. Appl. Chem. Biotechnol.* **23** (1973) 419.
3. *Idem, ibid.* **23** (1973) 431.
4. P. DUMAS, N. EA, J. C. NIEPCE and G. WATELLE, *J. Solid State Chem.* **27** (1979) 317.
5. B. D. CULLITY, "Elements of X-ray Diffraction", 2nd Edn (Addison-Wesley, Reading, Massachusetts, 1978) p. 284.
6. Z. A. MUNIR and P. G. COOMBS, *Met. Trans.* **148** (1983) 95.

Received 15 July
and accepted 12 August 1985