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The decomposition of cadmium carbonate in air and in vacuum

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

Cadmium carbonate powders were decomposed isothermally in air and in vacuum over the temperature range 563 to 773 K. The decomposition rates in vacuum were higher than those in air at corresponding temperatures. When decomposed in vacuum the carbonate phase experiences a total weight loss which is higher than that based on complete dissociation of $CdCO_3$. The excess weight loss is attributed to stoichiometric deviations and the evaporative dissociation of CdO. On the basis of first-order kinetics, the activation energies for the decomposition of the carbonate in vacuum and in air were calculated as 185 and 177 kJ mol^{-1}, respectively.

1. Introduction

The decomposition of carbonates and hydroxides remains a common process for the production of oxide ceramic powders. Certain characteristics of the resulting oxide phase, e.g. particle size, are dictated by the mechanism of decomposition as well as the particle evolution processes concomitant with decomposition. The latter processes are in turn affected by the conditions under which the decomposition reaction is carried out. We have investigated the decomposition of cadmium carbonate under vacuum and atmospheric air conditions, and report here the results of a thermogravimetric study of this process. In an accompanying paper [1], we report the results of observations on the particle evolution during decomposition under the two conditions indicated above.

2. Materials and methods

Electronic grade cadmium carbonate powder, reported as 99.999% pure by the supplier (Johnson Matthey, London, England) was used in this study. The powder was analysed for cation impurities and was found to contain calcium, copper, magnesium and silver at < 1 p.p.m. X-ray analysis of this material revealed peaks belonging to $CdCO_3$ only. A scanning electron micrograph of the starting powder (Fig. 1) shows well-defined crystallites ranging in size from about 1 to 10 μm. Furthermore, Fig. 1 shows that the crystallites are in an agglomerated state. Using a gas adsorption (BET) technique, the specific surface area of the starting powder was determined as 3.59 m^2 g^{-1}.

The decomposition of $CdCO_3$ in air and in vacuum was investigated using a continuous recording electrobalance (Cahn R–1000) with a sensitivity of 10 μg. Cadmium carbonate samples were decomposed inside a 2.54 cm diameter alumina crucible, which was suspended inside a quartz tube by a 0.1 mm diameter nichrome wire. The quartz tube was situated inside a clam-shell vertical tube furnace controlled by a temperature programmer. Temperatures were measured by means of a Pt–Pt/10% Rh thermocouple, which was situated inside the quartz tube at a point 2.54 cm away from the sample. Previous calibration experiments showed that, within the experimental range of this study, thermocouple readings are within ± 1 K of those provided by another thermocouple placed in intimate contact with the sample.

The sample size in all decomposition experiments was 100 ± 0.01 mg of $CdCO_3$. When spread on the bottom of the crucible, this quantity of sample gave a thin layer with an approximate thickness of 0.1 mm. The carbonate samples were decomposed at eight temperatures ranging from 563 to 773 K. In all cases, the total duration of an experiment was 7 h including the heat-up time, which was typically 30 to 50 min. A constant heating rate of 10 K min^{-1} was used to bring the sample temperature up to the desired experimental value and, once at this level, the temperature was maintained to within ± 2 K. When the decomposition was carried out under vacuum conditions, the sample temperature was increased only after the system had been evacuated to a pressure of 7×10^{-3} Pa or lower. In these experiments, liquid nitrogen traps and baffles were used to minimize sample contamination. In experiments where the decomposition was studied under atmospheric air conditions, the system was open to the room atmosphere and only natural convection was operating.

3. Results

3.1. Decomposition in vacuum

When cadmium carbonate was heated at 389 K for 7 h, a total weight loss of less than 0.1 mg was recorded. This small weight change, amounting to less than 0.1% of the initial weight of the sample, is believed to be the consequence of the desorption of volatile impurities. When heated at 563 K, the white $CdCO_3$ powder turned yellowish white in colour and became increasingly darker in colour as the temperature of decomposition was increased, finally becoming dark

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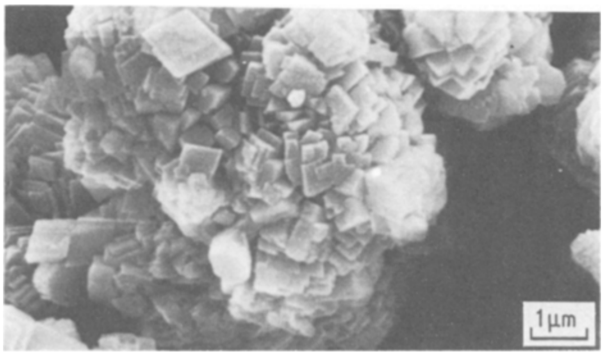

Figure 1 Scanning electron micrograph of the starting cadmium carbonate powder.

brown at the highest temperatures. Thus, the colour change is an indication of the extent of decomposition in a qualitative way. The decomposition of $CdCO_3$ proceeds according to

$$CdCO_3(s) = CdO(s) + CO_2(g) \qquad (1)$$

Starting with a 100 mg sample, complete decomposition results in a weight loss of 25.52 mg. Under a fixed duration of decomposition, 7 h, total decomposition was not achieved until the temperature was in excess of 583 K. At 583 K, the decomposition is 94.9% complete. At $T > 588$ K the observed weight loss was higher than can be accounted for on the basis of decomposition alone, i.e. Equaton 1. Decomposition experiments run in a platinum curcible gave identical results to those obtained using alumina containers. On the basis of these and other observations (to be discussed later) it was concluded that the excess weight loss was due to the evaporation of the product CdO.

Weight loss against time results are shown in Fig. 2 for the vacuum decomposition of $CdCO_3$ at temperatures ranging from 563 to 673 K. At the highest temperature, 673 K, the total weight loss was 36.0 mg, which is equivalent to a total decomposition of $CdCO_3$ (weight loss of 25.52 mg) plus the evaporation of 14.1% of the resulting oxide.

3.2. Decomposition in air

The results of the decomposition of $CdCO_3$ in air are shown in Fig. 3 as weight loss against time. These results, obtained over the temperature range 563 to 773 K, show qualitative similarities to those obtained when the decomposition was carried out under vacuum. Quantitatively, however, the two sets of results are different in two major ways. The weight loss for the air decomposition is consistently lower than that recorded for the vacuum decomposition. A more important difference, however, is in the maximum weight loss. With the exception of the data for the highest temperature, 773 K, all weight-loss results obtained in air were consistent with the maximum theoretical value as calculated from Equation 1. Furthermore, even at the highest temperature, the excess weight loss was relatively small, 3.1% above the maximum, i.e. 1.1% of the resulting oxide.

4. Discussion

The vacuum decomposition of $CdCO_3$ at temperatures higher than 583 K resulted in weight losses exceeding the theoretically calculated value for complete decomposition. On the basis of Equation 1, the observed excess weight loss must be related to the evaporation of the product, CdO. However, since this compound is an n-type semiconductor, excess weight loss can come about through small stoichiometric changes during the heating of the oxide subsequent to the decomposition of the carbonate. The extent of the possible stoichiometric changes in CdO is not established. Neither is the nature of the defects which give rise to the n-type conductivity. Both types of possible defects, cadmium interstitials and oxygen vacancies, have been reported [2–4]. Contradictory reports have also been published regarding the extent of the phase stability of this oxide [5, 6]; however, the best estimates indicate that the concentration of the excess cadmium or the oxygen vacancies is <0.1 atomic fraction [2, 3]. The observed excess weight loss is too high to be accounted for by changes in stoichiometry. If we assume cadmium interstitials as the defects in

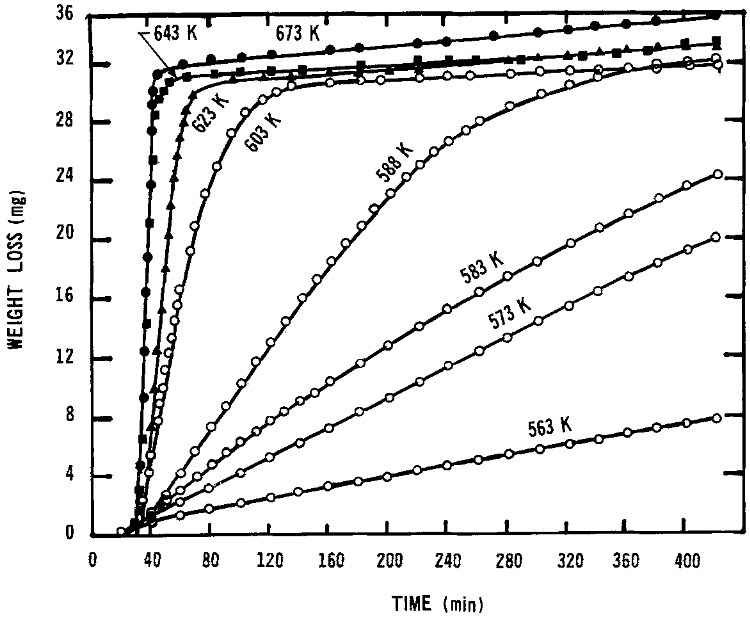

Figure 2 Temperature and time dependence of the weight loss resulting from the decomposition of $CdCO_3$ in vacuum.

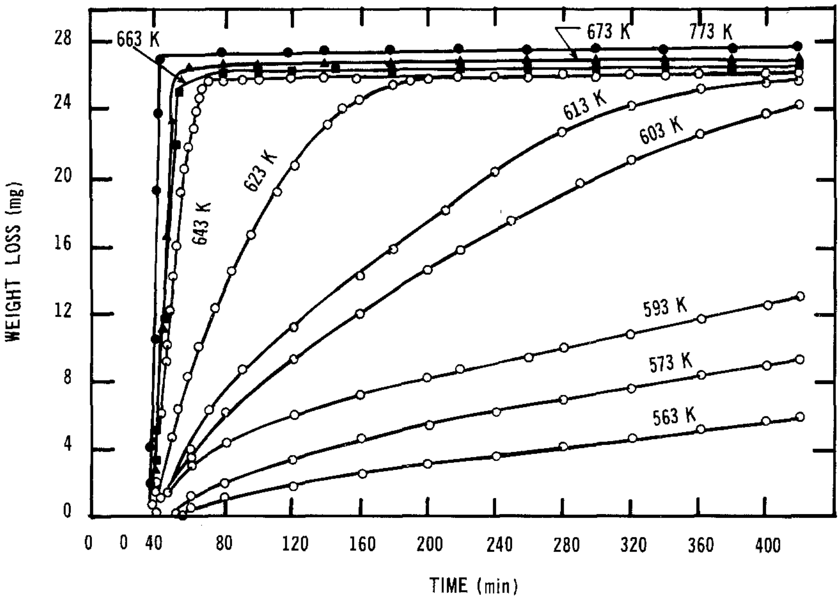

Figure 3 Temperature and time dependence of the weight loss resulting from the decomposition of $CdCO_3$ in air.

cadmium oxide, then the weight loss observed at 673 K would be accounted for on this basis if the initial oxide contained 16% excess (interstitial) cadmium. Since this is significantly higher than the estimated maximum value indicated above, the excess weight loss observed during the vacuum decomposition of cadmium carbonate cannot be explained totally on the basis of stoichiometric changes in the resulting oxide. Similar conclusions would be reached if the defects were assumed to be oxygen vacancies. The excess weight loss can be accounted for through the dissociation-evaporation of CdO to Cd(g) and O_2(g) [7, 8]. Extrapolating the vapour pressure data of Miller [7] to 583 K, we calculate a specific weight loss of 0.442 mg m^{-2}. On the basis of 100 mg of $CdCo_3$ as a starting sample, the calculated weight loss would be in agreement with the observed value if the CdO produced through the decomposition of the carbonate had a specific surface area of 188 $m^2 g^{-1}$. Surface area measurements reported in the following paper [1] on powders decomposed at 583 K gave a value of approximately 24 $m^2 g^{-1}$, or nearly a factor of eight lower than the calculated value. In addition, measurements of CdO crystallite size, done through X-ray line broadening [1], gave a value of about 20 nm; assuming a cubical shape for the crystallites this gives a specific surface area of 38.3 $m^2 g^{-1}$. Scanning electron microscopic observations show that the crystallites are platelet-like rather than cubic in shape (Fig. 4). This would give a higher calculated specific surface area with a magnitude depending on the aspect ratio. The specific surface area calculated to reconcile the excessive weight loss with the reported vapour pressure data, 188 $m^2 g^{-1}$, is of the same order of magnitude as has been measured in the decomposition of $Mg(OH)_2$ to MgO [9]. Specific surface areas, measured *in situ* after the decomposition of the hydroxide, had values as high as 300 $m^2 g^{-1}$.

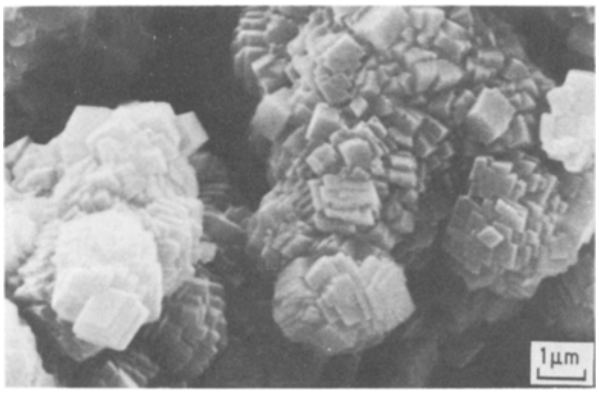

Figure 4 Scanning electron micrograph of the CdO resulting from the decomposition of $CdCO_3$.

Identification of the nature of the evaporating species was done indirectly. In experiments where excess weight loss was recorded, it was observed that a grey deposit had collected on the cooler parts of the system during vacuum evaporation, in agreement with previous reports [5]. X-ray diffraction analysis showed that the deposit was metallic cadmium. Similar observations were made when commercially available pure CdO was heated in vacuum at 973 K. Thus, it is quite likely that the excess weight loss is the result of both stoichiometric changes and dissociation of the oxide.

The results of the dissociation of $CdCO_3$ in air are in general agreement with those of Mikhail *et al.* [10]. As pointed out earlier, the decomposition in air was less favourable than in vacuum and, with the exception of the data at the highest temperature, 773 K, the total weight loss was consistent with the maximum for complete decomposition. At 773 K, the total weight loss exceeded the calculated maximum, indicating that some evaporation of CdO had taken place. Thus, the difference between the results of decomposition in vacuum and those obtained in air is due to the kinetic role of the atmosphere (air) in reducing the net flux from the evaporating surface.

The kinetics of the decomposition of $CdCO_3$ in air have been determined by Mikhail *et al.* [10] assuming a nucleation and growth process. For comparison, the results of this study are analysed to determine an activation energy for the decomposition process. In Figs 5 and 6 the undecomposed fractions of $CdCO_3$ are plotted against time for vacuum and air decomposition, respectively. On the basis of first-order

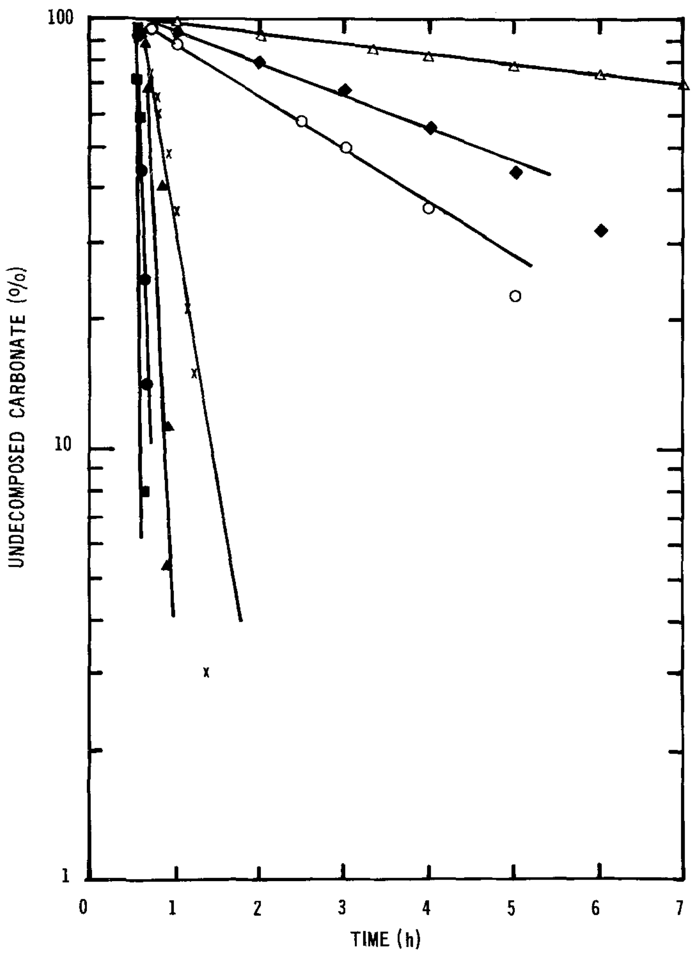

Figure 5 Time dependence of the undecomposed fraction of $CdCO_3$ (vacuum decomposition). (△) 563 K, (♦) 573 K, (○) 583 K, (×) 603 K, (▲) 623 K, (■) 643 K, (●) 673 K.

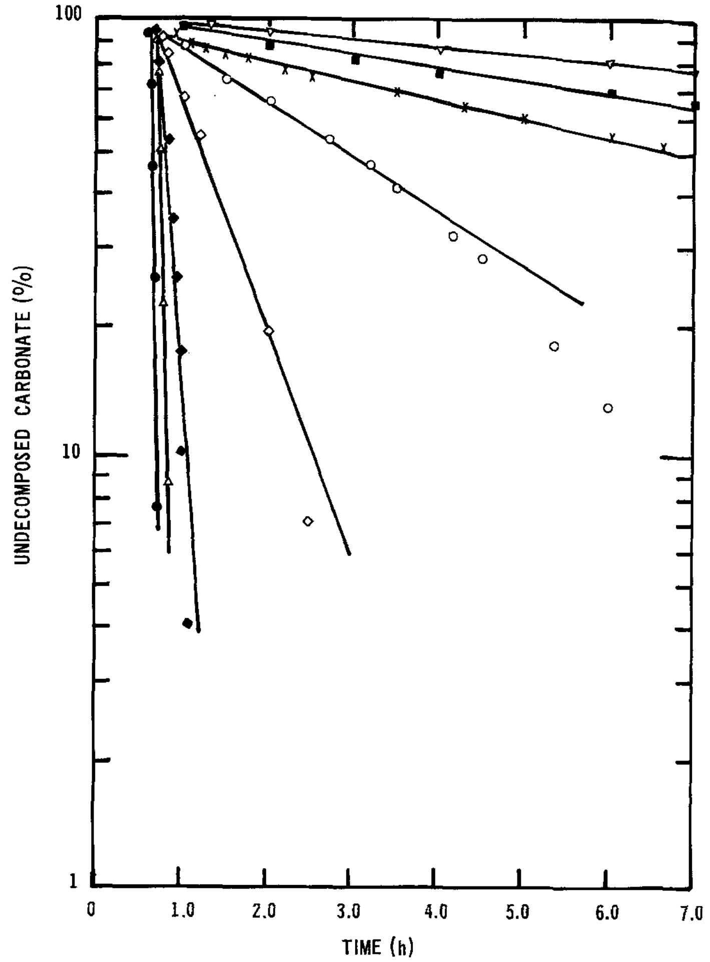

Figure 6 Time dependence of the undecomposed fraction of $CdCO_3$ (air decomposition). (▽) 563 K, (■) 573 K, (×) 593 K, (○) 603 K, (◇) 623 K, (♦) 643 K, (△) 673 K, (●) 773 K.

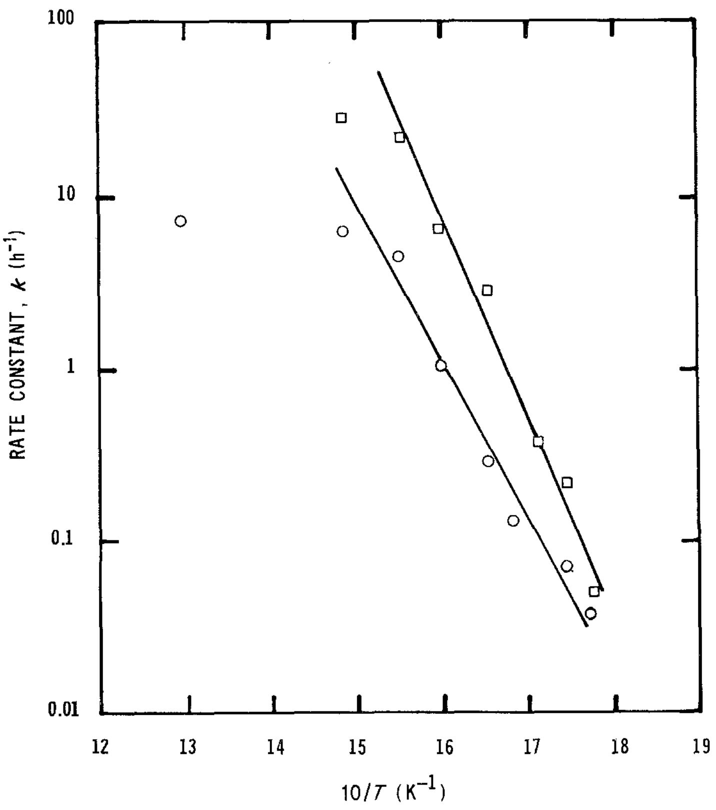

Figure 7 Temperature dependence of the rate constants for decomposition of $CdCO_3$ in (○) air and (□) vacuum.

kinetics, the slopes of the linear lines on these semi-log plots represent the rate constants. The temperature dependences of the rate constants for air and vacuum decomposition are shown in Fig. 7. From this figure, activation energies of 185 and 177 kJ mol^{-1} were calculated for the vacuum and air decomposition, respectively. Prodan and Pavlyuchenko [11] reported an activation energy of 150.6 kJ mol^{-1} for the decomposition of $CdCO_3$ under vacuum, and a corresponding value of 121.3 kJ mol^{-1} was reported by Criado [12]. For decomposition in air, Mikhail *et al.* [10] calculated a value of 94.1 kJ mol^{-1} for pure $CdCO_3$. However, their results showed a strong temperature dependence for doped $CdCO_3$ even at the lowest level (1 at %). For these samples the activation energy ranged from 184 kJ mol^{-1} at the lowest temperatures of decomposition ($T < 673$ K) to as low as 17 kJ mol^{-1} for higher temperatures (733 to 833 K). Moreover, these authors observed excess weight loss when the decomposition was carried out in air at $T \geqslant 733$ K.

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