

THE THERMAL DECOMPOSITION OF MANGANESE CARBONATE

Thermogravimetry and exoemission of electrons

L. Biernacki and S. Pokrzywnicki

Institute of Mathematics and Physics, Technical University of Opole, ul. Ozimska 75
PL 45-370 Opole, Poland

(Received March 7; in revised form February 2, 1998)

Abstract

Results are reported on the thermal decomposition of manganese carbonate, MnCO_3 .

Thermogravimetry (TG), differential thermogravimetry (DTG), and differential thermoanalysis (DTA) curves were recorded simultaneously and depicted together with the curve of intensity of electron exoemission (EEE).

Keywords: DTA, DTG, exoemission of electrons, Gibbs energy, manganese carbonate, manganese oxides, phase change

Introduction

Carbonates have been investigated for many years among structural engineering materials.

Various carbonates are dealt with in many previous works, e.g. [1-4], DTA [2] is used in research on them, and the DTA curve can be compared with the standard atlas [14]. Carbonates either as nearly chemically pure reagents or as minerals have been subjected to DTA [5].

It appears that manganese carbonate has not yet been studied by means of TG and electron exoemission (EEE).

It is commonly known that manganese carbonate separates out from aqueous solution as hydrated $\text{MnCO}_3 \cdot \text{H}_2\text{O}$ ([3] Chapter 6). At atmospheric pressure, manganese carbonate easily loses its water at temperatures above 370 K, this process being accompanied by further decomposition:



The enthalpy of the above reaction for various temperatures has been estimated by linearization of the data in [3]:

$$\Delta H_{298}^{\circ} = 27.85 \text{ kcal mol}^{-1}$$

$$\Delta H_{700}^{\circ} = 27.02 \text{ kcal mol}^{-1}$$

It does not depend on temperature.

Investigations of manganese carbonate were carried out by: TG and EEE. The latter method is not so well known as TG, and the EEE method will therefore be briefly described here on manganese carbonate as an example.

EEE involves the non-stationary emission of low-energy particles (mainly electrons, but sometimes positively charged particles and even neutral particles as well) from a thermodynamically unstable system during its return to the equilibrium state.

The ejection of electrons from a specimen is brought about by an external influence (e.g. irradiation, quenching or mechanical deformation). Such perturbations are commonly named excitation. It is necessary to supply additional energy in order to induce electron emission, e.g. illumination by light, the most common mode of stimulation. The photostimulation in EEE is performed with light of longer wavelength than for an external photoeffect. This means that an EEE phenomenon is not the same as a classical photoeffect. EEE emission needs less external energy than a photoeffect phenomenon.

During the described EEE experiments, the specimens were both heated and illuminated. The heating or cooling of the specimen runs according to a linear regime of temperature change as a programmed function of time. The heating rate is constant.

The first investigation of the EEE phenomenon were those of Kramer [6, 7]. The phenomenon of EEE is often applied to study surface states, defect structures, dosimetry, postradiation damage, breaking of bonds in the solid state, electron hopping and so on. It has been shown that EEE can be used to investigate the thermal decomposition of some silver salts [8] and a superionic conductor [9]. EEE together with many other material features is applied in research on phase changes of either first or second order. The decomposition of salts, ion reduction and simultaneous oxidation are examples of the application of EEE to study the dynamism of phase changes or constant equilibria in chemistry.

Experimental

The thermal analysis was carried out with a Mettler Thermoanalyser TA 1, at a constant heating rate of 10 K min^{-1} . A Pt–Ir crucible was used. A Pt–PtRh10 thermocouple was utilized to measure temperature. $\alpha\text{-Al}_2\text{O}_3$ was applied as reference material.

The mass of tested samples was 0.20000 g. The temperature dependence of photostimulated EEE was measured with the air point counter described by Step-

niowski [10]. Saturated vapour of ethanol over the surface of its liquid in air was used as a quenching mixture. The counter and the ethanol were at a constant temperature of 317.5 K, thermally stabilized with a Hoeppler thermostat. The sample of manganese carbonate was applied as a layer 1 mm thick, held by a steel core as a crucible. The core was inside the heater.

The Fe-constantan thermocouple was situated 0.5 mm beneath the surface of the holder. An accelerating voltage of 100 V cm^{-1} was applied between the examined sample of carbonate and the counter. The samples were illuminated with unfiltered UV radiation from a quartz lamp with a Q-400 burner. Before the experiment, the samples of manganese carbonate were not subjected to radiation, deformation or any thermal decomposition. Each of the tested samples was heated at a same constant rate of 10 K min^{-1} , the same as in the TG.

The examined manganese carbonate was from Poch-Gliwice, Poland, supplied as of pure grade. The samples were investigated under atmospheric pressure in both thermal analysis and EEE measurements.

Interpretation of experimental data

Figure 1 illustrates the thermal decomposition of manganese carbonate. The experimental curves show the effects accompanying the multiphase fine structural changes.

Figure 1 reveals that the decomposition of the studied samples of manganese carbonate begins at 373 K. The loss of mass at the beginning of the process is connected both with the loss of hydrate water and the initial release of CO_2 .

These phenomena correspond to the sharp minimum at 373 K in the DTG and DTA curves and to the maximum in the EEE curve.

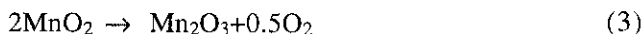
The next step is related to the further decomposition of MnCO_3 and to oxidation by oxygen from the atmosphere. This occurs close to 408 K and is accompanied by small increases in the DTG and DTA curves up to 440 K. It corresponds to a small mass loss in the TG curve. It shows the beginning of oxidation simultaneously with CO_2 loss, which is slower than the first step. This step is



In this stage, the major phase is MnO_2 besides MnCO_3 . Some intermediates are also possible, $(\text{MnO})_2\text{CO}_3$.

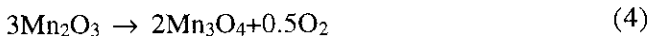
The decomposition of manganese carbonate accelerates at temperatures higher than 600 K, and the process is fastest at 691 K, as seen from the TG curve.

At 703 K, MnCO_3 decomposition is complete and the next step begins: MnO_2 reduction to Mn_2O_3 :



The reduction process is most rapid at 799 K, which corresponds to the minimum in the TG curve. This process ends at 815 K. In the temperature range 815–1150 K, Mn_2O_3 remains stable. This result can be compared with [14].

Further increase of the temperature of the sample leads to a further reaction:



This proceeds most rapidly at 1191 K. MnO is formed above 1300 K, as shown by the curves in Fig. 1.

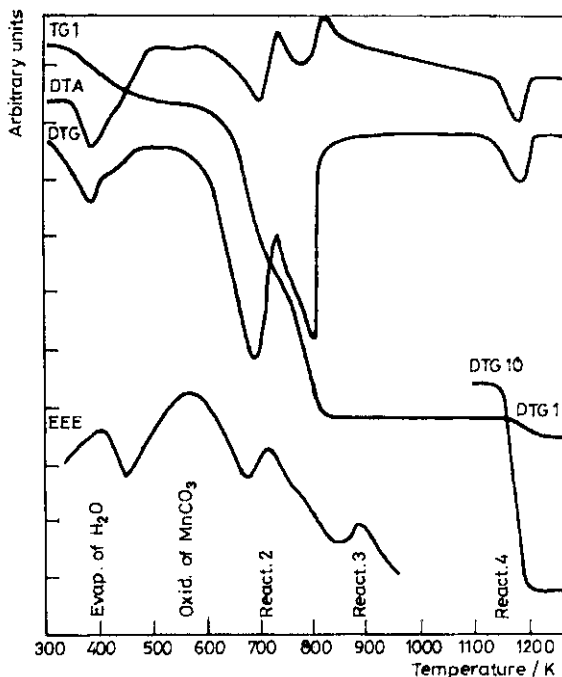
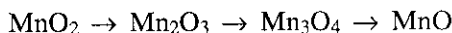


Fig. 1 TG, DTG, DTA and EEE curves vs. temperature for $MnCO_3$

The sequence of oxide formation is therefore as follows:



The most stable phase in this temperature is MnO.

During the decomposition process, a number of phenomena occur: a phase change in the solid state, the release of CO_2 , reversible oxidation and the formation of various manganese oxides. These phenomena were followed via the mass loss (TG curve) and the possibility of emission of electrons (EEE curve).

We assume that the above scheme (reactions (1)–(4)) is the only decomposition process under the given conditions. If it is assumed that only the simple de-

composition process took place according to reaction (1), then after taking into account that $\Delta G = \Delta H - T\Delta S$ in this reaction equals zero, we can calculate a value of $T_{\text{decomp.}}$, i.e. the temperature of the decomposition of MnCO_3 . This gives $T_{\text{decomp.}} = \Delta H / \Delta S = 625 \text{ K}$ (calculated from data in [4]). The decomposition could go to completion at this temperature without any outside influence.

The above phase change needs energy to break one of the three C–O bonds in MnCO_3 . The oxidation phenomenon involves part of the energy in the system. The temperature at which the free Gibbs energy is zero should be regarded as the thermodynamic temperature of the decomposition reaction which occurs without oxidation of manganese(II) [2, 3]. In the presented experiment, the decomposition process was carried out under irreversible conditions. For example, in the main reaction of manganese carbonate decomposition, see (1), when $\Delta G < 0$. Then, at 691 K, $\Delta G = -17 \text{ kcal mol}^{-1}$. This means that the reaction will proceed rapidly.

A comparison of the temperature regions of existence of the various manganese oxides with the curve $\Delta N / \Delta t = f(T)$ (e.g. the intensity of EEE as a function of temperature) reveals that the EEE comes from a newly created phase. The broken bonds are the centres of sputtering; after supply of the lower energy levels, the energy comes from the usual external photoeffect.

During the experiment, it was observed that hydrated manganese carbonate undergoes facile thermal decomposition to anhydrous manganese carbonate and four oxides. These processes are in dynamic equilibrium in the short period of time. The oxygen pressure over the crucible can change the ratios of the intermediates of the interphases in the dynamic equilibrium state.

A clear EEE response from the specimen and a good correlation between TG and EEE as a function of temperature for multiphase changes in manganese carbonate and manganese oxides has been found in this work.

Nevertheless, further studies can be made of the intensity of EEE in correlation to the thermodynamic category.

Research on this subject is continuing.

References

- 1 K. H. Stern and E. L. Weise, High Temperature Properties and Decomposition of Inorganic Salts, Part 2. Carbonates. NSRDS-ABS 30, National Bureau of Standards U.S., November 1969.
- 2 W. W. Wendlandt, Thermal Analysis, Wiley – Interscience, New York 1986.
- 3 H. Remy, Lehrbuch der Anorganischen Chemie, Akademische Verlagsgesellschaft, Geest & Portig, K. G. Leipzig 1961, B. 2.
- 4 I. B. Barin, O. Knacke and O. Kubaschewski, Thermochemical Properties of Inorganic Substances, Springer-Verlag, Berlin, Heidelberg, New York.
- 5 D. W. N. Ivanova, Ticrmogramy minerallov – Zapiski Vsesojuznogo Mineralnogo Obščestva, Leningrad, 1961.
- 6 J. Kramer, Zs. Phys., 125 (1949) 739.

- 7 J. Kramer, *Der Metallische Zustand*, Vandenhoeck – Ruprecht, Getyngen, 1950.
- 8 T. Górecki, Cz. Górecki and L. Biernacki, *Thermochim. Acta*, 130 (1988) 329.
- 9 Cz. Górecki, T. Górecki and L. Biernacki, *Solid State Ionics*, 2 (1988) 125.
- 10 I. Stępniewski, *Acta Phys. Polon.*, 30 (1966) 163.
- 11 T. Górecki and B. Sujak, *Acta Phys. Polon.*, A 42 (1972) 487.
- 12 F. A. Cotton and G. Wilkinson, *Basic Inorganic Chemistry*, John Wiley and Sons, Inc. New York, 1976.
- 13 L. Biernacki and S. Pokrzywnicki, *J. Thermal Anal.*, 47 (1996) 1759.
- 14 L. Biernacki, Cz. Górecki and T. Górecki, *Jap. J. Applied Phys.*, 24 (1986) 116.
- 15 G. Liptay, *Atlas of Thermodynamical Curves*, Akadémiai Kiadó, Budapest 1977.