Some observations on the use of strontium carbonate as a temperature standard for DTA [☆]

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Abstract

The simultaneous decomposition of strontium carbonate that occurs during the solid–to–solid phase transition is a detriment to the use of this material as a high temperature standard for DTA. An atmosphere of carbon dioxide is shown to deter the reversible decomposition to much higher temperatures where it is no longer a problem.

The phase transition temperature was observed to shift during the initial heating through the transition in carbon dioxide but remain constant thereafter. Changes were also observed in the X-ray diffraction pattern during the initial heating. It is proposed that the use of this material as a DTA standard be restricted to an atmosphere of carbon dioxide using a sample that has undergone at least one temperature cycle in that atmosphere.

Keywords: DTA; Standard; Strontium carbonate; Temperature

1. Introduction

Early in the 1970s the Committee for Standardization of the International Confederation for Thermal Analysis, ICTA (now ICTAC having added "and Calorimetry") sought to establish a series of well defined, solid–to–solid, first order, phase transitions as temperature standards for DTA. The initial set of standards covered the range from

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room temperature to 1000°C [1]. These standards were established through a massive international round robin and have subsequently been marketed through NIST [2].

The highest temperature transition in this series is the rhombohedral–to–hexagonal transition in $SrCO_3$. The results of that original study recommended an extrapolated onset value of 925°C. A more recent value for that transition has been reported at 931°C [3]. Unfortunately, either temperature is above the onset temperature for the thermal decomposition of the material in normal atmospheres.

$$SrCO_3 \rightarrow SrO + CO_2 \tag{1}$$

This decomposition is readily reversible and hence the actual onset temperature depends upon the partial pressure of the product gas surrounding the sample. Consequently, when the product gas is removed by a sweep gas, the reaction will go more readily, i.e., at a lower temperature. This decomposition reaction generally begins around 900°C in the very low partial pressures of CO_2 normally encountered.

The sample is progressively destroyed as it is cycled through the transition temperature and several undesirable events occur as a result of this ill-defined extent of decomposition. The usable lifetime of the material is dramatically reduced. The SrO formed may be partially soluble in the $SrCO_3$ and thereby alter the transition temperature. The strains and defects produced in anticipation or at the onset of decomposition may also change the transition temperature. These same aspects, particularly the first, will affect the observed enthalpy of the event.

Because of the reversible nature of the decomposition it is possible to suppress the decomposition very markedly by raising the partial pressure of CO_2 in the ambient gas stream. In pure CO_2, the onset of the decomposition is not until well above 1000°C. Under these conditions it is possible to cycle indefinitely through the complete transition range without destroying or contaminating the sample. Actually this should purify the starting material by converting any hydroxide or oxide originally present to the carbonate [4]. Consequently, it is not necessary to store or package the starting material in any particular manner.

This study is intended to demonstrate these advantages and to redetermine the onset temperature of the transition in CO_2. The transition will be measured for several sources of $SrCO_3$ under a variety of conditions and compared with the earlier results [1, 3].

2. Experimental

Three sources of $SrCO_3$ were used. The first (A) was material from the original round robin [1] by ICTAC (circa 1970, stored simply in its plastic envelope in a cardboard box). Two other samples were prepared by precipitation from an aqueous solution of $Sr(NO_3)_2$ using $(NH_4)_2CO_3$. One (B) was stored in a screw-cap vial and exposed to the normal laboratory atmosphere for weeks before the reported measurements, while the second sample (C) was used very shortly after its preparation. No special sample treatments, such as selecting a particle size range or prescribed drying, were performed.

The Perkin–Elmer high temperature DTA module was used in conjunction with their System-7 control module. The DTA temperature was calibrated frequently using the melting point of gold at 1064°C. The enthalpy was not calibrated, but a multiplier of about 1.10 ± 0.05 would be suggested based upon these calibrations using the melting of gold. For DTA, nominally 20 mg samples were heated in alumina crucibles under the conditions indicated for each experiment. The gas flow rate was approximately 50 mL min⁻¹. Weights were recorded at several stages for several samples to determine the extent of decomposition.

A simultaneous TG–DTA was performed in argon using the Seiko 320 high temperature system. Sample weight and flow rate were similar to those described in the previous paragraph. A Scintag PAD5 powder diffractometer with CuK_α radiation was used to determine the X-ray diffraction patterns.

3. Results and Discussion

Overlap of the thermal decomposition with the phase transition is clearly evident in Fig. 1, which presents the simultaneous TG–DTA curves for a sample A heated in argon. The solid state transition near 925°C is well into the decomposition. Any heating cycle that would include the full DTA peak would also lead to approximately 30% decomposition. The use of CO_2 as an atmosphere, however, shifts this decomposition to well above 1000°C so that it does not occur simultaneously with the phase transition. Consequently, the transition can be observed without any degradation. This is seen clearly in Fig. 2 for sample C that has been heated repeatedly in CO_2. The baseline has
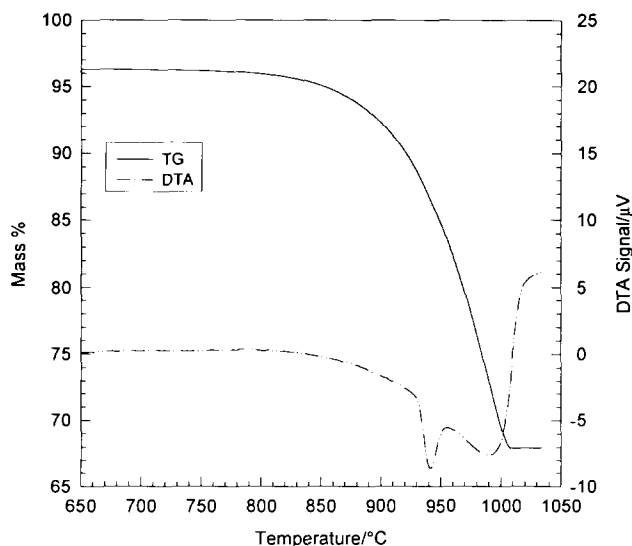

Fig. 1. Simultaneous TG–DTA plot of 7.322 mg $SrCO_3$ (sample A) in argon at 10°C min⁻¹.
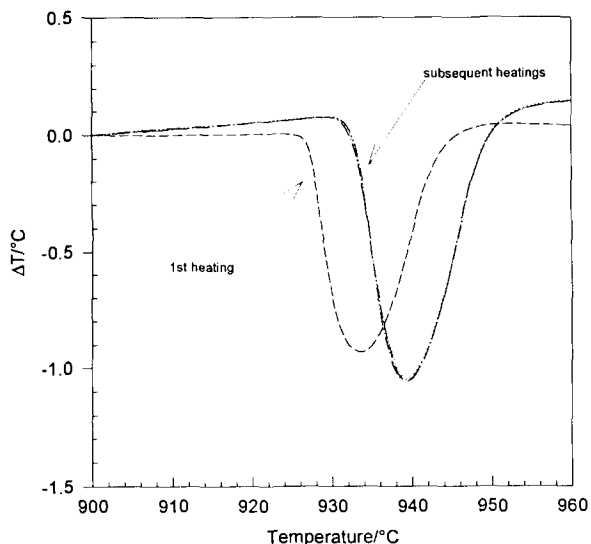
Fig. 2. Four DTA heating cycles of 13.78 mg of $SrCO_3$ (sample C) in CO_2 at $10°C\,min^{-1}$.

a slight exothermic drift and the peaks do not diminish in size during this repeated temperature cycling.

The effects on the DTA for the thermal decomposition, during continued cycling of sample A after having switched the purge gas to argon, are shown in Fig. 3. The
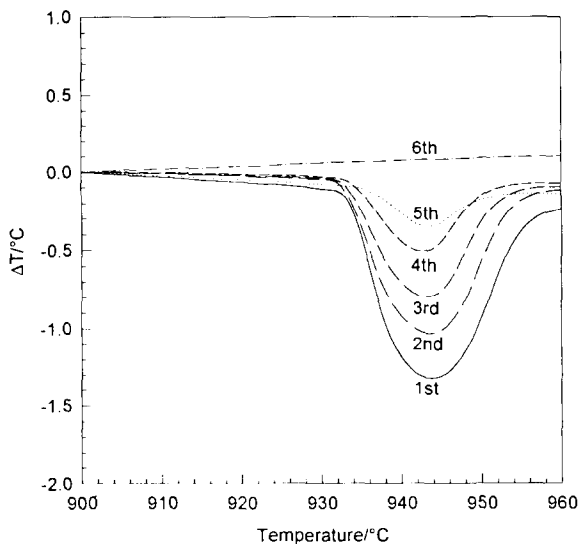

Fig. 3. Six DTA heating cycles of 24.26 mg of $SrCO_3$ (sample A) in argon at $10°C\,min^{-1}$.

transition peak was seen to diminish with each cycle and actually vanish after the fifth heating. The sample weight at the end of these cycles corresponded to that predicted for complete conversion to SrO.

The reversible nature of the decomposition allows for the reformation of the $SrCO_3$ by simply changing the atmosphere from argon back to carbon dioxide and reheating. The residue of sample A from Fig. 3 was reheated in the DTA several times in CO_2 and its behavior was found to be exactly the same as that of sample C (Fig. 2). Clearly $SrCO_3$ reformed during the first reheating in CO_2.

Besides the decomposition and reformation reactions, Fig. 2 shows how the onset of the transition temperature increases by several degrees between the first and second heating cycle. This is true for all three samples (A, B, and C) of $SrCO_3$. Table 1 shows the exact temperature shifts. At the top of the table 24.26 mg of Sample A was taken through four heating cycles in CO_2. The temperature shift between the first and second cycles is clearly evident. At this point, the sample was reweighed at 23.95 mg and cycled

Table 1
DTA measurements for successive heating cycles of strontium carbonate

Source of sample	Initial mass; purge gas	Onset temperature/°C	$\Delta H/\mathrm{J\,g}^{-1}$
ICTA–NIST (Sample A)	24.26 mg; CO_2	928.2	97.8
		934.0	98.6
		933.5	99.0
		933.5	99.4
	23.95 mg; argon	933.4	106.5
		932.9	86.0
		933.0	57.8
		933.7	30.9
		935.7	20.0
	16.68 mg; CO_2	927.5	79.5
		932.0	112.7
		931.9	113.6
		931.9	116.4
Precipitated and stored for 12 weeks (sample B)	22.02 mg; argon	927.5	101.6
		936.8	53.9
		938.2	14.9
	15.16 mg; CO_2	928.0	127.5
		931.9	133.9
		931.8	134.6
		931.8	134.3
As sample B, freshly prepared	19.99 mg; argon	927.8	98.9
		937.0	46.4
(Sample C)	13.78 mg; CO_2	927.2	116.8
		932.7	138.3
		932.6	139.6
		932.9	139.0

through the transition in argon five times. These are the five curves illustrated in Fig. 3. There is no increase in the transition temperature this time because the sample has already been previously exposed to thermal treatment in CO_2. In fact, the transition temperature shows a decreasing trend as the carbonate is converted to the oxide. After the cycling in argon, the sample (now SrO) was reweighed at 16.68 mg and subjected to four more heating cycles in CO_2. $SrCO_3$ is formed during the first cycle and the transition temperature increases in the second cycle similarly to the initial heating in CO_2.

The remaining portions of the table show the results from heating samples B and C first in argon then reweighing the remaining oxide and reheating in CO_2. The aforementioned temperature shift is present in both the initial heating of the carbonate in argon and in the subsequent heating of the oxide in CO_2. It should be noted that this shift was also noticed by Charsley et al. in nitrogen and attributed to the decomposition [3]. While this appeared reasonable, it cannot be the explanation for the increase that occurs during the initial heating in CO_2. In CO_2 a shift occurs even though any amount of SrO is being decreased, i.e., reverse decomposition.

The X-ray diffraction patterns of all three materials were virtually identical. Although the pattern matches that reported for rhombohedral $SrCO_3$, the lines were broad and there was a distinct scrambling of the peaks near a 2θ value of $35°$, as seen in Fig. 4. The patterns associated with likely impurities such as strontium oxides or hydroxides do not seem to be responsible for this effect. After having been heated in
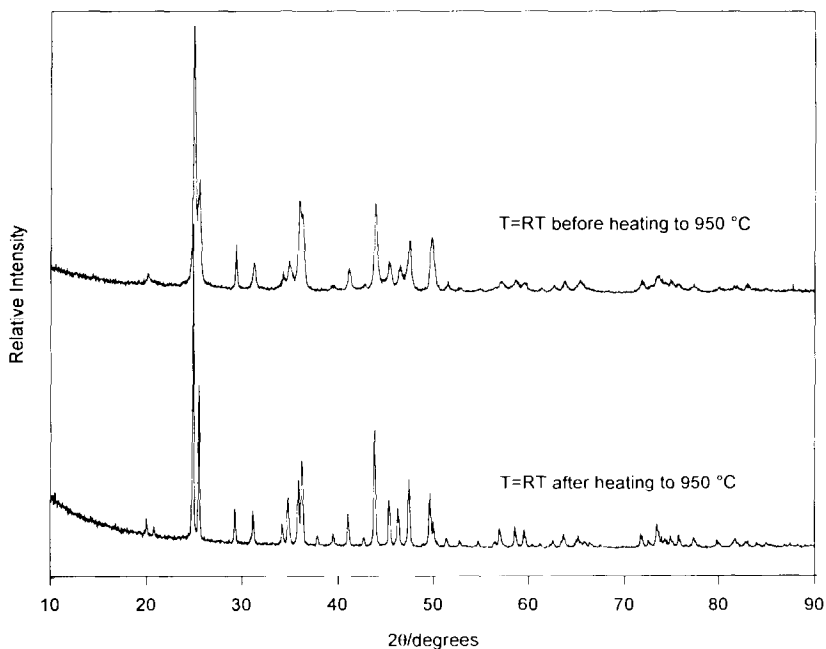

Fig. 4. X-ray diffraction patterns for $SrCO_3$ (sample A) before and after annealing at 950°C.

CO_2 to 950°C once and cooled in CO_2, the pattern sharpens and matches perfectly that reported for the room temperature form of $SrCO_3$ [4].

It now appears that some form of stress or defects are alleviated during the initial transition unrelated to the decomposition. Consequently, rather than use the first heating as originally proposed [3], it seems advisable to cycle the sample at least once through the phase transition (in an atmosphere of CO_2, of course) prior to recording the temperature for calibration purposes.

From the data in Table 1, it appears that a transition temperature of 932.7 ± 0.8°C would be correct for this heating rate. Interestingly this value, also obtained during subsequent heatings, is in near perfect agreement with the value observed during the *initial* heating by Charsley et al. [3]. Both are well above the earlier value of 925°C [1, 2]. The value for the initial heating in this work, however, agrees reasonably well with that earlier value of 925°C. The precision within individual samples or subsets is better than the range of ± 0.8°C given above. This may be attributed to sample inhomogeneities, particle size, packing, etc.

The observed values of enthalpy show a significant increase, simultaneous with the increase in temperature, between the first and subsequent cycles in CO_2. Since the enthalpy represents the minimum possible activation energy for the process, this trend is in the expected direction. This increase in enthalpy would also be consistent with the release of strain energy during the phase transition in the initial cycle.

The enthalpies listed in Table 1 for the experiments in argon are based on the starting weights and are good estimates of the extent of decomposition during each cycle. The absolute values in CO_2, however, show very large changes, from 99 to $139\,Jg^{-1}$. The trend is that the value decreases with storage time. The higher range for the fresher samples is in agreement with the value of $133\,Jg^{-1}$ given in Barin's compilation [5]. The much older sample A has much lower and more varied values.

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