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Thermochimica Acta 267 (1995) 129–138

thermochimica acta

Simultaneous thermogravimetry-mass spectrometry for a solid oxide fuel cell interconnect, $(La_{0.7}Ca_{0.32})CrO_3$[1]

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Received 24 November 1994; accepted 26 January 1995

Abstract

TG-MS simultaneous measurement on a nominally chromium deficient lanthanum calcium chromite, $(La_{0.7}Ca_{0.32})CrO_3$, has been made in a helium flow and the results were compared with its shrinkage behavior in air and also with TG-DTA results on related calcium chromium oxides ($n(CaO)/n(CrO_x)$ = 1:1 and 5:3) in air. In addition to evolution of water (320–920 K and 1020–1120 K) and carbon dioxide (340–1120 K), four distinct oxygen evolution peaks were observed from 900 to 1600 K; this oxygen evolution can be ascribed to the successive reduction of chromium ions in second phases which were estimated as about 1 mol% of $Ca_5(CrO_4)_3$ or 2 mol% of $Ca_3(CrO_4)_2$. With the aid of available phase diagrams, a peak of simultaneous water and oxygen evolution at 1020–1120 K was attributed to the decomposition of an intermediate reaction compound, $Ca_5(CrO_4)_3OH$. Similarly, the water evolution at 320–920 K and CO_2 evolution can be ascribed to the decomposition of hydrated calcium chromates, $CaCrO_4{\cdot}nH_2O$ and calcium carbonate which were considered to be formed as reaction products of $Ca_5(CrO_4)_3$ with water, oxygen, and carbon dioxide. These features were discussed in relation to the sintering behavior of chromium deficient lanthanum calcium chromite.

Keywords: TG-MS; Lanthanum calcium chromite; Chromium deficiency

1. Introduction

During research and development of planar solid oxide fuel cells [1,2], we found that calcium doped lanthanum chromites become air sinterable when the calcium content is

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[*] Corresponding author.

[1] Presented at the 30th Anniversary Conference of the Japan Society of Calorimetry and Thermal Analysis, Osaka, Japan, 31 October–2 November 1994.

SSDI 0040-6031 (95) 02472-7

adjusted to be slightly (2–3%) excess to the normal calcium substituted lanthanum chromite [3–7]. Such an air sinterable lanthanum calcium chromite as $(La_{0.7}Ca_{0.32})CrO_3$ always contains second phases to compensate for the chromium deficiency. At low temperatures, La_2CrO_6 is a dominant second phase, whereas $Ca_m(CrO_4)_n$ ($m > n$) becomes dominant around 1300 K [5]. In a sintering process up to 1600 K, such second phases change their chemical form finally to CaO through intermediate liquids [6]. In addition to normal factors affecting sintering characteristics, the chemical behavior of calcium chromates makes the sintering of chromium deficient lanthanum calcium chromite complicated. For example, abrupt shrinkage occurs as two steps with and without mass loss [8,9]. In view of this, careful examination of the chemical behavior of second phases during sintering will be quite important in understanding the complicated sintering of chromium deficient lanthanum chromites.

In the present study, a chromium deficient calcium doped lanthanum chromite has been investigated mainly by simultaneous thermogravimetry-mass spectrometry (TG-MS); this technique has been successfully applied to high temperature superconductors [10,11] and also to the solid oxide fuel cell cathode, $(La_{0.7}Sr_{0.3})_{0.9}MnO_3$ [12]. Since mass spectrometry is quite sensitive to detect evolution of a small amount of gasses, this is appropriate for detecting changes in the chemical form of second phases which may exist in a few per percent of the total substance. The results of TG-MS are compared with the available phase diagrams [13,14] and also with the results of sintering behavior of the chromium deficient lanthanum calcium chromite.

2. Experimental

A sample of $(La_{0.7}Ca_{0.32})CrO_3$ was prepared by the liquid mixing method; powders were co-precipitated from nitrate solution mixtures by adding an excess amount of oxalic acid and ethanol; they were dried at 573 K for 40 h and calcined twice at 1273 K for 10 h [6].

The simultaneous measurement was made by using Shimazu TG-GC/MS(2). After dried helium gas was passed over the sample contained in an alumina crucible inside the instrument for 12 h, measurements were done under the helium flow at a heating rate of 10 K min^{-1} from room temperature to 1773 K. Since some oxygen leaked into the instrument, the actual oxygen partial pressure in the atmosphere was expected to be in the order of 10^{-5} atm or higher. Amounts of water vapor, CO_2, and O_2 detected were determined from the observed intensity of mass spectroscopy using $Na_2WO_4{\cdot}2H_2O$ and gasses with known concentration as calibration materials for water, oxygen and carbon dioxide, respectively.

Shrinkage during sintering was measured by thermal mechanical analysis (TMA320, Seiko Instruments Co. Ltd.) at heating rates of 10 K min^{-1} to 1100 K and 2 K min^{-1} for 1100–1723 K [6].

For supplemental experiments, TG-DTA measurements have been made on calcium chromate samples; powder mixtures of CaO and $CrO_{1.5}$ (mole ratio was selected as 1:1 and 5:3, respectively) were calcined at 1533 K for 10 h. After being cooled in a furnace, TG-DTA measurements were made in air at a heating rate of 5 K min^{-1}.

Table 1

Observed amount of emitted gasses from $(La_{0.7}Ca_{0.32})CrO_3$

Gaseous species	Temperature region (K)	Amount (%)
H_2O	320–920, 1020–1120	0.34
O_2	920–1770	0.48
CO_2	340–1120	0.35
Total		1.17
Result of thermogravimetry		1.22

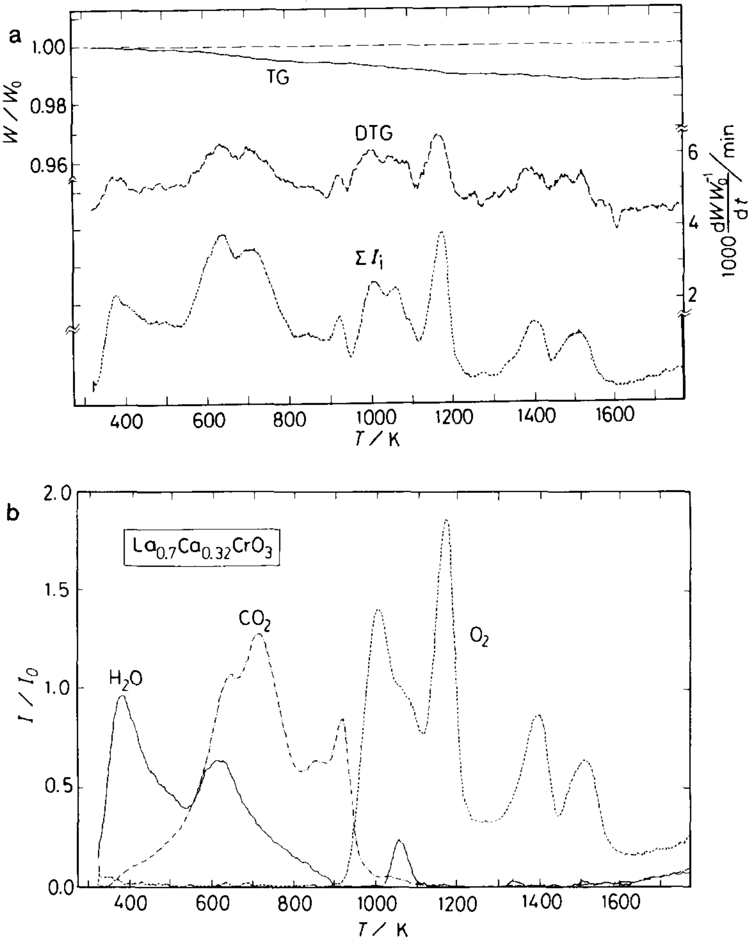

Fig. 1. Results of (a) thermogravimetry (TG), its derivative with respective to time, summation of intensities of respective gaseous species and (b) respective ion intensities of chromium deficient lanthanum calcium chromite from 298 to 1773 K at a heating rate of 10 K min^{-1} under a dried helium flow. Total amounts of emitted gasses are given in Table 1.

3. Results

Observed amounts of gasses are given in Table 1. Fig. 1a,b shows the results of thermogravimetry (TG), its derivative (DTG) and mass spectrometry for O_2, CO_2, and H_2O. Although some chromium gaseous species [7] were expected to evolve during heating, no such species was observed by mass spectrometry or were found as recondensed substances before the mass spectrometer. The total mass loss determined by the thermogravimetric analysis is in excellent agreement with the sum of the amounts of evolved gasses determined by mass spectrometry as shown in Table 1. This is consistent with the fact that the volatilization and condensation of the chromium oxide component was negligible.

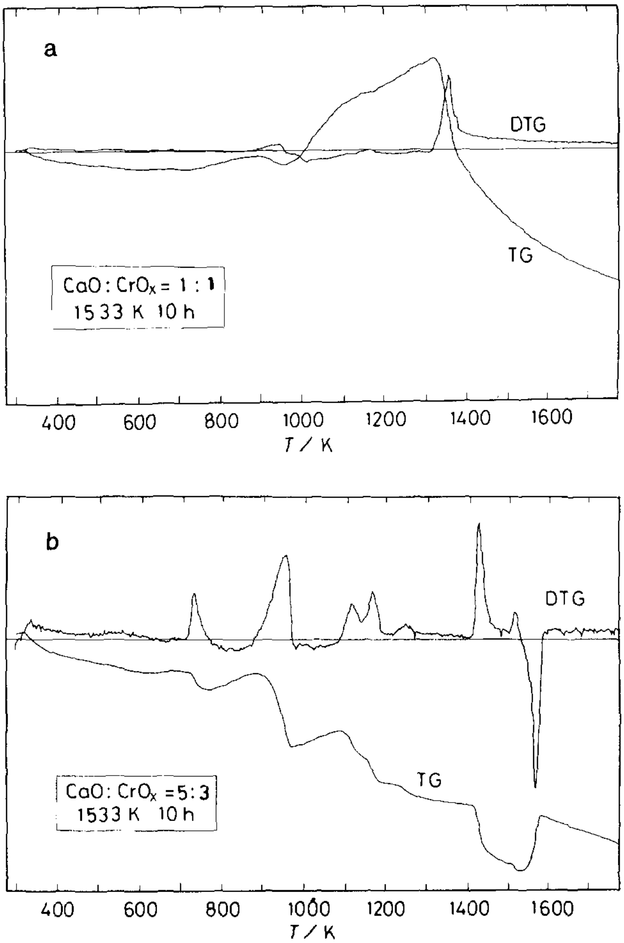

Fig. 2. Results of thermogravimetry on (a) $CaO \cdot CrO_x$ and (b) $5CaO \cdot 3CrO_x$ at a heating rate of 5 K min^{-1} in air.

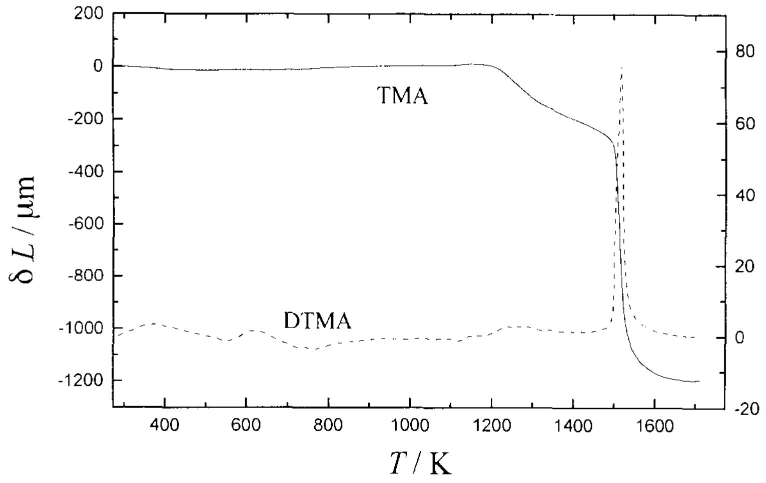

Fig. 3. Shrinkage of chromium deficient lanthanum calcium chromite in air. The initial length was 6.622 mm.

The following are worthy of note. (i) Below 970 K, water vapor evolved in two steps; peaks were observed at 370 K and 610 K. This behavior is rather common among perovskite related materials [10–12]. An interesting point about the H_2O evolution is that an additional peak was observed at 1160 K. At that temperature, CO_2 did no longer evolved, while oxygen evolved as one of many distinct peaks. (ii) Oxygen evolution shows quite sharp peaks. The major peaks are 1010, 1170, 1400 and 1520 K.

Fig. 2 shows the results of TG on samples of $n(\mathrm{CaO})/n(\mathrm{CrO}_x) = 1{:}1$ and 5:3, respectively. For the 1:1 sample, namely, $\mathrm{CaO{\cdot}CrO}_x$, mass gain was observed from 1000–1320 K. This may be due to a quenting effect; it seems that oxygen did not fully react with the sample after its preparation at 1533 K. Above 1320 K, a large mass loss was observed; this can be ascribed to the melting of $CaCrO_4$ and the successive reduction of chromium ions. For the 5:3 sample, namely, $\mathrm{5CaO{\cdot}3CrO}_x$, complicated mass changes were observed above 720 K including some mass gain stages in addition to many mass loss stages.

Fig. 3 shows the shrinkage behavior of $(\mathrm{La}_{0.7}\mathrm{Ca}_{0.32})\mathrm{CrO}_3$ in air. When compared with a result reported elsewhere [6], the present sample was more homogenized, resulting in a steeper shrinkage around 1500 K.

4. Discussion

4.1. Oxygen evolution

The oxygen partial pressure during the present experiment was estimated to be in the order of 10^{-5} atm. This suggests that the observed oxygen evolution from the present sample is not due to changes in the oxygen stoichiometric number of the perovskite phase but due to chemical reductions of the second phases. Since 0.48 mass% of oxygen evolved totally, this amount corresponds to 0.032 mol of oxygen relative to 1 mol of the chromium component. This suggests that about 0.043% of the chromium component was already oxidized to the hexa valence state before the present experiment. The chemical equilibria calculation and X-ray diffractometry showed that the second phase around 1300 K is calcium oxychromates. If this can be assumed to be $Ca_5(CrO_4)_3$, the present sample can be represented as a mixture of $0.01Ca_5(CrO_4)_3 + 0.97(La_{0.722}Ca_{0.278})CrO_3$; for another case of the $Ca_3(CrO_4)_2$ formation as a second phase, the starting material can be calculated as a mixture of $0.02Ca_3(CrO_4)_2 + 0.96(La_{0.729}Ca_{0.271})CaO_3$. Since the estimated atomic ratio of the chromium component existing in the second phases is 0.03 and 0.04 for the above cases, respectively, this is consistent with the observed value of 0.043. This confirms that the amount of evolved oxygen is consistent with the extent of the chromium deficiency of the present sample.

According to phase relations in the $CaO–CrO_x$ system determined by Panek and others [13,14], it is expected that the reduction of calcium oxychromates occurs in several steps with increasing temperature. For example, $5CaO{\cdot}3CrO_x$ undergoes the following transformations in air:

$$3CaCrO_4 + 2CaO + 1/2H_2O = Ca_5(CrO_4)_3OH + 3/4O_2(g) \text{ at } 1073\text{ K} \tag{1}$$

$$Ca_5(CrO_4)_3OH = 3/2Ca_3(CrO_4)_2 + 1/2CaO + 1/2\ H_2O(g) \text{ at } 1173\text{ K} \tag{2}$$

$$3/2Ca_3(CrO_4)_2 + 1/2CaO = Ca_5(CrO_4)_3 + 1/4O_2(g) \text{ at } 1393\text{ K} \tag{3}$$

$$Ca_5(CrO_4)_3 + lO_2(g) = nCaO + m \text{ oxychromate melt at } 1548\text{ K} \tag{4}$$

Eqs. (1)–(4) should be compared with the result of Fig. 2b for $n(CaO)/n(CrO_x) = 5/3$. The mass loss observed at 1410 K should correspond to Eq. (3); the mass gain at 1570 K is to correspond to Eq. (4); for this purpose, Eq. (4) is written as an oxygen evolving reaction, although it has not been clarified yet. However, it is not surprising that the valence number of chromium ions may increase on melting. Furthermore, twin peaks between 1100 and 1200 K can be ascribed to Eqs. (1) and (2). Therefore, the thermal behavior of this sample in air is consistent with the available phase relations except for the peaks at 710 and 950 K.

On the other hand, $5CaO{\cdot}3CrO_x$ undergoes as follows in a reductive atmosphere at $p(O_2) = 10^{-6}$ atm:

$$3CaCrO_4 + 2CaO + 1/2H_2O = Ca_5(CrO_4)_3OH + 3/4O_2(g) \text{ at } 943\text{ K} \tag{1'}$$

$$Ca_5(CrO_4)_3OH = 3/2Ca_3(CrO_4)_2 + 1/2CaO + 1/2H_2O(g) \text{ at } 963\text{ K} \tag{2'}$$

$$3/2Ca_3(CrO_4)_2 + 1/2CaO = 1/4Ca_6Cr_{12}O_{27} + 7/2CaO + 9/8O_2(g) \text{ at } 1083\text{ K} \tag{5}$$

$$1/4Ca_6Cr_{12}O_{27} + 7/2CaO = 3/2CaCr_2O_4 + 7/2CaO + 3/8O_2(g) \text{ at } 1273\text{ K} \tag{6}$$

Eqs. (1′), (2′), (5) and (6) should be compared with the present result of TG-MS measurement under a helium atmosphere. Since the water evolution was observed around 1060 K, this can be ascribed to Eq. (2′). This means that there is about 100 K difference in reaction temperature between the present results and the phase diagram by Panek [13]. This leads to the following identification; the oxygen evolution peak at 1000 K should be due to Eq. (1′), the oxygen evolution peak at 1180 K being Eq. (5). The oxygen evolution from 1300 to 1600 K may be due to Eq. (6). The compound, $Ca_6Cr_{12}O_{27}$, can be regarded as the same compound as that found and regarded as a room-temperature phase of $CaCr_2O_4$ by Sakurai and Nishino [15]. According to Panek, this compound is reduced to $CaCr_2O_4$ as given in Eq. (6).

Since two oxygen evolution peaks between 1300 and 1600 K were observed, one of them can be attributed to a reaction of calcium chromates with perovskite to increase the calcium content in the perovskite:

$$\begin{aligned}&(La_{1-x}Ca_x)CrO_3 + nCa_3(CrO_4)_2 =\\ &\quad (1-x+2n)[La_{(1-x)/(1-x+2n)}Ca_{(x+2n)/(1-x+2n)}CrO_3] + nCaO + n/2O_2(g)\end{aligned} \tag{7}$$

At present, the proper identification of respective oxygen evolution peaks is difficult.

The amount of water emitted around 1070 K is about 6% of total emitted water; since the total mole number of emitted water is 0.04 mol for 1 mol of the chromium component, this means that about 0.24 mol of water evolved for 1 mol of $Ca_5(CrO_4)_3$.

According to Eq. (2′), a half mole of water should be emitted if the second phase was all converted to $Ca_5(CrO_4)_3OH$. This suggests that about a half of calcium oxychromates were actually converted into $Ca_5(CrO_4)_3OH$ in the present experiment. This seems reasonable in view of the fact that the present measurement was made under dried helium and water is available only as a result of decomposition which took place at lower temperatures.

Sakurai and Nishino [15] reported that the analogous carbonate, $Ca_{10}(CrO_4)_6CO_3$, can be formed from $CaCO_3$ and $CaCrO_4$ under carbon dioxide flow around 1073 K:

$$4CaCO_3 + 6CaCrO_4 = Ca_{10}(CrO_4)_6CO_3 + 3CO_2 + 1.5O_2 \tag{8}$$

This compound will decompose in a similar way to Eq. (2) as follows:

$$Ca_{10}(CrO_4)_6CO_3 = 3Ca_3(CrO_4)_2 + CaO + CO_2(g) \tag{9}$$

Since there appeared a high temperature tail in the CO_2 evolution peaks about 1000 K, it cannot be excluded that a small amount of this compound was present in the present sample. Even so, the simultaneous evolution of CO_2 and O_2 suggested by Eq. (8) was not observed so that there is no information about how this compound, if any, was formed.

4.2. Water and carbon dioxide evolution

As discussed above, the oxygen evolution can be interpreted by assuming that a small amount of calcium chromates are present in the present sample. This makes it reasonable to interpret the water and CO_2 evolution in terms of the same substances, namely, the calcium chromates. Since the respective amounts of emitted carbon dioxide and water are 0.017 mol and 0.040 mol relative to 1 mol of the chromium component, it is most likely that 0.02 mol of $Ca_3(CrO_4)_2$ may react with oxygen, water (0.04 mol) and carbon dioxide (0.02 mol) to form a mixture of $0.04CaCrO_4{\cdot}H_2O + 0.02CaCO_3$, although the observed amount of CO_2 is slightly lower than that required for this reaction.

Recently, Ito et al. [16] have measured the dehydration of $CaCrO_4$ by acoustic emission (AE) and TG-DTA-MS methods. They found that the dehydration occurs in four steps and that their starting temperatures do not depend on the atmosphere (air, nitrogen or argon). When compared with their results, the present second peak of water evolution around 600 K can be ascribed to their stage III; this means that in the present profile, their stages III and IV are combined to form one step. Although the present amount of emitted water during the lower temperature stages (stages I and II) is larger than theirs, this can be due to the difference in the total amount of hydrated water.

The decomposition temperature of $CaCO_3$ is about 1150 K under a carbon dioxide atmosphere; however, below this temperature, almost all CO_2 evolution occurred in the present experiment. When $CaCO_3$ reacts with other substances to emit CO_2, the CO_2 evolution temperature should be lowered. Even so, it is not easy to find a proper reaction for the present case.

4.3. *Possible effects due to lanthanum chromates*

Since La_2CrO_6 appeared in powders especially prepared at a lower temperature, there may be some possibilities that phases originated from La_2CrO_6 may exist at room temperature; the most plausible compounds are $La_2(CrO_4)_3{\cdot}7H_2O$ and $La_2(CO_3)_3{\cdot}8H_2O$. The thermal decomposition behavior of such compounds has been investigated by many authors [17–25]. However, there is no clear indication for the presence of such lanthanum oxide based second phases.

4.4. *Comparison with sintering behavior*

The results by TG-MS should be compared with the sintering behavior given in Fig. 3. Shrinkage starts moderately from 1200 K and steeply from 1500 K. A similar two-stage shrinkage has been observed by Chick et al. [8,9]. These two temperatures happen to be in good agreement with the present second and fourth oxygen evolution peaks, respectively. However, the present TG-MS was made in helium and direct comparison cannot give correct information. Therefore, we discuss the results on $n\mathrm{CaO}{\cdot}m\mathrm{CrO}_x$ in air.

From observations by TMA, SEM/EDAX and Auger Electron spectroscopy (AES) and also calculated results for complicated chemical equilibria, Sakai et al. [6] concluded that sintering is assisted by the calcium oxychromates which become in the liquid state and their composition changes to a CaO-rich side with increasing temperature. Usually, the final steep shrinkage around 1500 K is considered due to the liquid formation. When compared with Fig. 2(b) for $5CaO{\cdot}3CrO_x$ in air, the main shrinkage occurred in the same temperature region as melting of the calcium chromate.

Normally, the TG-MS measurement cannot be made easily in air so that it is hard to know, from the present TG-MS results, exactly what chemical processes happen during the main shrinking states. Even so, the present results revealed that almost all gas evolving processes are related to the calcium chromates existing as second phase. In other words, to explain the present gas evolution, we need to assume that the calcium chromates reacted with water and carbon dioxide to form hydrated calcium chromate and calcium carbonate. This should be important from the viewpoint of material processing, because such reactions may change grain size, dispersion and chemical reactivity of second phases in powders to be sintered, leading to different sintering characteristics.

5. Conclusive remarks

The most important result of the present investigation is that the calcium chromates at a CaO-rich composition, which existed as second phases in the chromium deficient lanthanum calcium chromite, are the major source for gaseous evolution from 300 to 1773 K. It is most likely that the room temperature chemical form of such second phases depends on a high temperature preparation process, the cooling process and also the process of keeping at room temperature from water and carbon dioxide. This may be the most important factor which gives rise to non-reproducible sintering behavior. Although only one measurement was made in the present investigation, TG-MS results, if accumulated, may provide useful information for characterizing powders in which second phases in a small content dominate the sintering properties.

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