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Thermoanalytic measurements with oxides at temperatures up to 2000°C

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Abstract

DTA/DSC setups by different commercial suppliers allow nowadays routine thermoanalytic investigations in different atmospheres (reductive, oxydizing, partially reactive) for $t \leq 1600$°C. Measurements at higher $t \leq 2000$°C are only possible within inert atmosphere (noble gases), as the relevant construction materials are sensitive with respect to other gases. This circumstance, together with the small palette of construction and crucible materials, reduces the possibilities for thermoanalytic measurements, especially for oxides. The paper discusses some properties of construction materials that are used for measurements in metal oxide systems. It turns out, that thermoanalytic measurements with some oxides are impossible within commercial DTA setups. In any case, TG and mass spectrometer data need a detailed discussion if obtained at high temperature, as chemical interaction of species present within the emanating gas with constructive parts of the apparatus have to be taken under consideration. © 1999 Published by Elsevier Science B.V. All rights reserved.

Keywords: DTA; TG; Mass spectrometry

1. Introduction

The choice of commercially available DTA and DSC setups drops drastically if the maximum temperature accessible upon measurement is $t_{\max} \geq 1600$°C. Beyond the not very common need for measurements at such temperatures, the restricted palette of materials that are suited for the construction of TA setups working in this "highest temperature" range is responsible for the limited choice of commercial TA setups. This paper discusses some problems that arise from the performance of thermoanalytic measurements at high temperatures. The focus will be on oxides; as the measurement of these compounds is accompanied by some severe problems, that partially cannot be solved by commercial DTA equipments.

2. Construction

Heat transport by radiation becomes important for very high t, as the heat energy flux grows proportional to t^4. Therefore, thermoanalytic equipments for the high temperature range are preferably constructed as DTA devices (Fig. 1). It is valuable to combine the measurement of the differential thermal voltage with the measurement of the mass loss (TG signal) and with the analysis of the emanating gas. This analysis can be performed by different (typically spectroscopic) methods. Mass spectroscopy proves to be suited for the

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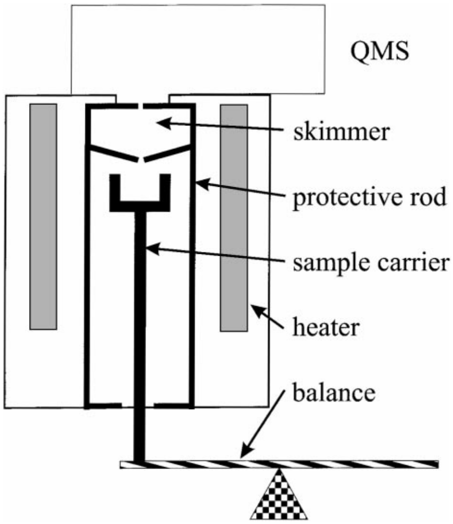

Fig. 1. Principle of a DTA apparatus for highest $T > 1600°\mathrm{C}$ with simultaneous measurement of the TG signal and coupling to a QMS via "skimmer".

analysis of inorganic substances, as often the direct measurement of m/z (mass/charge) ratios allows the determination of ions or molecules that are present in the gas. Quadrupole mass spectrometers (QMS) with measuring ranges $1 \leq m/z \leq 200$ are typical for this purpose, but nowadays upper range limits of 512 or even 1024 allow the detection of all chemical elements and of nearly all molecules that can be expected in the gas phase. High upper detection limits are for instance necessary, if evaporating organic additives to mixtures of inorganic substances have to be detected. Such additives are common for the production of ceramics to initiate the sintering process or even during crystal growth to create a protective atmosphere above the starting material.

The emanating gas has to be transferred from the sample room (pressure p typically 10^5 Pa) to the high vacuum within the QMS ($p \approx 1$ mPa). The following possibilities are common for this purpose.

Capillaries: They are made from stainless steel or fused silica. The construction of capillaries is easy and they can be fitted to nearly all DTA furnaces. Chemical reaction with the emanating gas or thermal degradation is reduced to a minimum, as the capillary itself is only heated to ca. 200–250°C to reduce condensation. No problems have to be expected, if substances with high vapor pressure (all gases, cracking products from organics, most halides) have to be detected. Unfortunately, many high melting oxides have only small vapor pressure. Here it is at least questionable, whether they can reach the QMS.

Skimmer: A skimmer is a system of two diaphragms (hole diameter ca. 70 μm) that is situated within the DTA furnace (Fig. 1). Below the first diaphragm is the atmospheric pressure that surrounds the sample; above the second diaphragm the high vacuum of the QMS. The intermediate vacuum between both diaphragms is regulated to keep the HV constant. The viscosity of gases increases with T, accordingly the intermediate vacuum has to be increased from typically 0.2 kPa at room temperature to ca. 1 kPa at 2000°C for argon. As the complete pressure reduction is performed within the "hot zone", condensation of evaporating species usually does not occur. On the other side, the possibility of chemical interaction between emanating species and the hot skimmer material has to be accounted for. Alumina ($t \leq 2000°\mathrm{C}$) or vitreous carbon ($t \leq 2000°\mathrm{C}$) are used as skimmer materials.

3. Materials and atmosphere

The choice of construction materials for furnace, protective rod including skimmer, sample carrier, crucible and thermocouples is quite big for $t \leq 1500$–$1600°\mathrm{C}$. Furnaces with heating elements made from silicon carbide, metals or alloys, with alumina parts as constructing elements and Pt/Pt–Rh thermocouples (type "S" or "B") are typical for this temperature range. Standard crucibles from alumina are easy to use and cheap, but alumina (Al_2O_3) is not stable against many hot metal oxides at elevated temperature. At least for measurements with molten oxides crucibles from noble metals should be favored. Platinum is suited for this purpose, but alloys of Pt with ca. 5%Ir ($t_{\mathrm{fus}} = 1780°\mathrm{C}$) or Au ($t_{\mathrm{fus}} = 1700°\mathrm{C}$) show a higher mechanical strength. Especially the Pt95%–Au5% alloy shows high chemical stability and can often easier be cleaned after utilization for DTA runs with molten oxides.

Crucibles and other parts made from platinum or platinum alloys and alumina are highly stable under oxidizing or at least inert (noble gas) atmosphere. The upper limit of the stability range is defined by the increased loss of tensile strength near the melting point. DTA crucibles from alumina were proved to be stable at least for $t \leq 1700°C$, from Pt95%Ir5% for $t \leq 1600°C$, and from Pt95%–Au5% for $t \leq 1450°C$. For the latter alloy a higher stability range seems to be probable but was not yet checked.

The application of the highest $t > 1700°C$ is only possible with furnaces and sample carriers containing oxygen sensitive parts: protective rods are made from vitreous carbon or graphite, and W/W–Re thermocouples are used for temperature measurement. This implies, that the measurement has to be performed within noble gas, typically argon. Standard DTA crucibles for $t > 1700°C$ are made from either graphite or tungsten. Unfortunately, these materials are not stable if in contact with many oxides.

A comprehensive overview on stability ranges of the different construction materials can be given by Ellingham diagrams [1]. These diagrams show the stability range of the different oxydation states of one element in the $Rt\ln p_{O_2}$–t plane and have linear (or nearly linear) phase boundaries. Fig. 2 shows the stability range of solid carbon (graphite) in the p_{O_2}–t plane; it was calculated on the basis of equilibrium thermodynamics (GIBBS energy minimization) using the PC program ChemSage [2]. If p_{O_2} exceeds the stability range of the solid for a given temperature, excess carbon will dissipate oxygen leading to the formation of CO and CO_2.

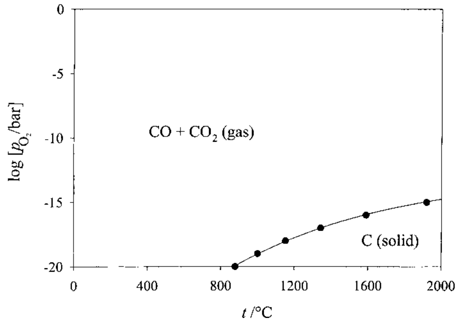

Fig. 2. Stability range of carbon (graphite) in oxygen in the log [p_{O_2}/bar]$-t$ plane.

Any $(m+1)$ valent oxide $MeO_{(m+1)/2}$ has a dissociation oxygen partial pressure according to the redox equilibrium reaction

$$2MeO_{(m+1)/2} \Leftrightarrow 2MeO_{m/2} + \frac{1}{2}O_2 \tag{1}$$

and will be reduced to the m valent state under the presence of carbon, if this dissociation oxygen partial pressure is larger than$p_{O_2}(t)$ given in Fig. 2. Table 1 (also calculated with ChemSage) gives for a selection of oxides the critical temperature, where the oxide starts to be unstable in presence of carbon or carbon monoxide, respectively. If not hindered kinetically, chemical reactions similar to

$$CaO + C \Leftrightarrow Ca + CO\uparrow, \tag{2}$$

$$CaO + 3C \Leftrightarrow CaC_2 + CO\uparrow, \tag{3}$$

proceed for $t > t_{red}^{C}$ *or* $t > t_{red}^{CO}$, respectively. In some cases the reduction proceeds over an extended equilibrium range; in such cases the approximate onset of reduction is given. It is obvious, that graphite crucibles are not suited for the performance of DTA measurements with many oxides at $t \leq 2000°C$.

Tungsten crucibles are also not stable against many oxides, as the electronegativity of W is (with ca. 1.7) lower as the electronegativity of many other metals. Any iron oxides (hematite Fe_2O_3, magnetite Fe_3O_4, wustite FeO) are e.g. not in equilibrium with metallic W.

Experiments with Ir crucibles (electronegativity: 2.2) were partially successful. A part of the binary phase diagram Al_2O_3–Tb_2O_3 with liquidus temperatures up to 1930°C could be measured using conical Ir crucibles ($V = 0.05$ ml) and a NETZSCH tungsten high temperature sample carrier [3]. However, problems arise here from the different coefficient of thermal expansion for both metals. For $25°C \leq t$

Table 1
Calculated equilibrium temperatures t_{red}^{C} for the reduction of oxides by carbon and t_{red}^{CO} for the reduction by carbon monoxide under a total pressure of 101 kPa

Oxide	CaO	Al_2O_3	Ga_2O_3	SiO_2	GeO_2	Fe_2O_3	FeO	P_4O_{10}
t_{red}^{C} (°C)	1826	1918	1006	1512	655	117	759	ca. 600
t_{red}^{CO} (°C)	ca. 1400	ca. 1600	1006	ca. 1200	655	117	759	ca. 700

$\leq 2000°C$ an average value $\alpha_W = 7.1 \times 10^{-1}\ K^{-1}$ can be found for tungsten [4]; for iridium the higher value $\alpha_{Ir} = 9.31 \times 10^{-6}\ K^{-1}$ was reported [5]. After crossing a temperature range of $\Delta t = 2000$ K during DTA measurements the geometrical dimensions of sample carrier and crucible show a difference of $(\alpha_{Ir} - \alpha_W)\ \Delta t = 0.44\%$ that obviously often leads to tight fitting of the crucible within the sample carrier. It occurred in such cases, that crucible or even sample carrier were damaged upon removing the crucible after the measurement.

An alternative material for crucibles seems to be tantalum. Although the electronegativity of this metal is not very high (ca. 1.5) it is reported to exhibit good chemical stability in the high temperature range. However, Ta crucibles were not yet tested by the author.

The performance of DTA measurements in nominally inert noble gas atmosphere is sometimes problematic. Fig. 3 shows two TG curves that were obtained from identical mixtures of 42.23% $SrCO_3$, 39.90% GeO_2, and 17.87% Ga_2O_3 powders (mass%) under the same heating rate of 10 K/min (NETZSCH STA 409C). The full line denotes a measurement with 106 mg mixture under argon and with a vitreous carbon protective rod; the dashed line denotes a subsequent measurement with 59 mg mixture under air and with a alumina protective rod. In both cases the observed mass loss up to ca. 1100°C due to thermolysis of the carbonate (12.62%) is close to the theoretical loss (12.59%), but two peculiarities are obvious:

1. The mass loss during the measurement under Ar proceeds faster.
2. After the measurement under air the mass loss is finished at ca. 1100°C (pronounced stage of the dashed line). The mass loss upon measurement within Ar proceeds after the stage until the end of the measurement. In Fig. 3 this additional mass loss reaches 0.83%, but it depends slightly from the experimental conditions (Ar flow rate, crucible with or without lid).

It must be concluded, that the additional mass loss is due to the reduction $Ga_2O_3 \rightarrow Ga_2O$ and/or $GeO_2 \rightarrow Ge$ that was performed by the carbon protective rod. The reduction process becomes possible, as already traces of other gases present within the Ar (e.g. H_2O) are according

$$C + H_2O \Leftrightarrow CO + H_2, \tag{4}$$

in equilibrium with other species as CO and H_2 that can perform the reduction of the oxides to metals. The equilibrium reaction

$$CO_2 + C \Leftrightarrow 2CO, \tag{5}$$

is responsible for the acceleration of the strontium

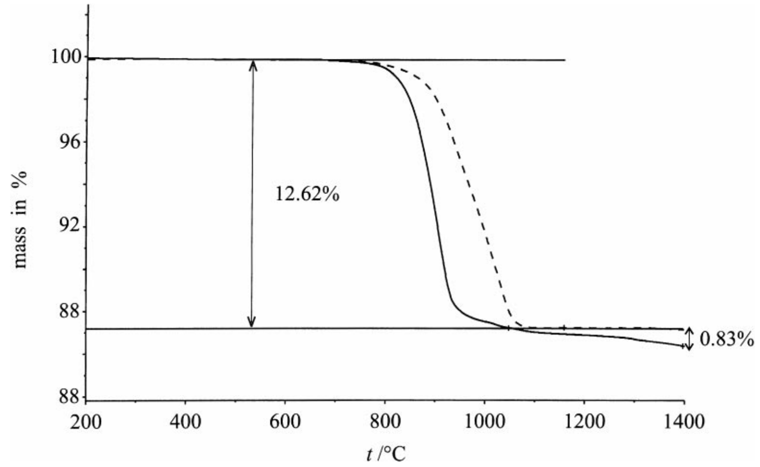

Fig. 3. TG curves of identical mixtures of $SrCO_3$, GeO_2, and Ga_2O_3 in Pt95%–Au5% crucibles without lid (heating rate 10 K/min). Solid line: Measurement in Ar atmosphere (5N) using graphite furnance and graphite protective rod. Dashed line: Measurement in air using SiC furnace and alumina protective rod.

carbonate decomposition

$$SrCO_3 \Leftrightarrow SrO + CO_2\uparrow, \tag{6}$$

as Eq. (5) removes the carbon dioxide from the equilibrium Eq. (6). The mass loss of the Ar measurement exceeds 12.6% (the limit value of the mass loss in air) at 1030°C. It can be assumed that this temperature marks the onset of Ga^{3+} or Ge^{4+} reduction. As long as the thermolysis Eq. (6) proceeds, the reduction of the oxides is prohibited by the produced CO_2.

The reductive atmosphere can not only lead to the described unexpected TG effects that can be accompanied by DTA effects too, but in some cases even to the destruction of crucibles and/or sample carriers. After a long DTA run of 70 mg $GaPO_4$ (cycling between 500°C and 1200°C with 16, 8, 4, and 2 K/min performed within Ar using a vitreous carbon protective rod) within Pt95%–Au5% crucibles the crucible bottom was found to be damaged. Besides the crucible was welded to the thermocouple sitting directly below the crucible bottom. In this case, the gallium phosphate containing Ga^{3+} and P^{5+} was destroyed by the reduction of the P^{5+} (cf. Table 1). Elementary phosphorus is known to alloy very easily to platinum.

Most of the severe problems described in this chapter result from the circumstance, that commercial thermoanalytic equipments for $t \leq 1600$–1700°C allow only the performance of measurements within nominally inert, but practically reductive atmosphere. Unfortunately, with many oxides measurements within such atmosphere are completely impossible.

Another problem that shall not be discussed here in detail is the lack of accurate calibration materials for high t measurements with oxides: As most of the measurements must be performed within crucibles from noble metals (Pt, Ir), the calibration should be done with noble metal crucibles too. Unfortunately, the calibration substances for $t > 1000$°C [6] are metals that alloy easily with the crucible material.

4. Interpretation of high temperature QMS results

The most common gaseous species emanating during DTA measurements of oxides at higher temperatures are:

oxygen that can be produced from higher valent oxides upon transformation to lower valent oxides or even to the element,
carbon dioxide that is a product of the thermolysis of carbonates (Fig. 3),
water that can result either from the thermolysis of hydroxides or from adsorbed water that is desorbed at elevated temperatures.

If capillaries are used for the connection between sample room and QMS, these gases can expected to be found within the spectrometer. The same results, if the skimmers and the other hot parts of the DTA setup are made from alumina that is usually specified for $t \leq 1600$°C. The reduction of Al_2O_3 by CO starts at this temperature (cf. Table 1) and no chemical reaction occurs with H_2O or O_2 in an even higher extended temperature range. Thus the three gases can be identified easily within the QMS. Unfortunately, alumina skimmers cannot be used for $t > 1600$°C.

Different equilibria exist between the three gases and the vitreous carbon of the skimmer and the protective rods for highest temperatures. The two most important equilibria are already given in Eqs. (4) and (5). For $t \leq 800$°C carbon is with water (and thus hydrogen too) even methane in equilibrium according

$$C + 2H_2 \Leftrightarrow CH_4 \tag{7}$$

and can be found by QMS. Fig. 4 gives a quantitative graphical representation of the existing equilibria for $100°C \leq t \leq 2000°C$ at atmospheric total pressure (101 kPa).

For $t > 1000$°C the emanating gases that one usually would expect are only in minor amounts in equilibrium with the excess carbon (CO_2, H_2O) or almost completely absent (O_2). Carbon monoxide is for $t > 1000$°C the main species indicating emanating CO_2, H_2O, or O_2. It should be remarked, that the CO signal has the same $m/z = 28$ as N_2. The parallel occurrence of CO and H_2 ($m/z = 2$) indicates, that H_2O has emanated from the sample. At $t > 1600$°C the dissociation of the hydrogen molecule into atoms starts at atmospheric pressure.

All chemical equilibria mentioned in this chapter are shifted by the total pressure p. As p reduces drastically from the sample room to the QMS, a continuous "adjustment" of the gas composition should be expected. However, no considerable devia-

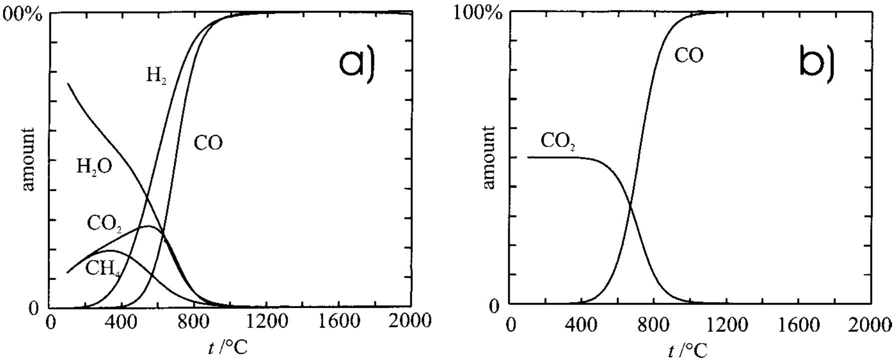

Fig. 4. Calculated equilibria (p = 101 kPa) between excess carbon and minor additives of (a) H_2O (b) O_2 or CO_2. Complete reaction of the additive is set to 100%.

tions from the calculated ratios (Fig. 3(a, b)) could be found during experimental studies. Obviously, the transport of the gas from the hot sample room to the cold QMS proceeds quick enough to freeze the equilibrium that was obtained at atmospheric pressure.

5. Summary and conclusion

Contemporary thermoanalytic equipment allows the performance of routine measurements even at very high temperatures $t > 1600$–1700°C. Due to constructive restrictions, all measurements within such thermoanalytic setups have to be performed under noble gas atmosphere. This atmosphere, together with crucibles or other parts made from carbon, leads to highly reductive conditions during the measurements. Especially for thermoanalytic investigations with many oxides, these conditions are unsuited, as reduction occurs. Whenever possible (this means at least for $t < 1600$°C) such measurements should be performed using alternative setups and oxidizing atmosphere (e.g. air).

Spectroscopic analysis of gaseous species emanating during DTA measurements enhances considerably the possibility for explanation of TG signals. Carbon skimmers that can be used up to 2000°C for the transport of emanating gas to QMS. For the interpretation of QMS signals it has to be considered, that the composition of the analyzed gas often depends on t and p dependent equilibria between emanating gas and the skimmer material.

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