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TA-MS for high temperature materials

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Abstract

TA-MS is also used for the characterization of solid state reactions taking place in high temperature materials. For this purpose high temperature coupling systems are preferred. Starting from a historical survey of the evolved gas analysis the technical prerequisites are described more in detail (requirements to the coupling systems and current trends in methodology). Applications in the high temperature range (carbothermal reduction of TiO_2, outgassing and sintering of hard metals) demonstrate the advantages and limitations of such techniques. © 1997 Elsevier Science B.V.

Keywords: TA-MS; High temperature applications; Coupling systems; Carbothermal reduction of TiO_2; Outgassing of hard metals; Sintering of hard metals

1. Introduction

In the production of ceramic and powdermetallurgical materials (as well as in their application) thermal processes must be utilized which affect and change the materials and their properties in various ways. Experience shows that the processes during the initial heating period are particularly important. Any "damage" done at this time is difficult to correct in subsequent process steps.

Thermal processes depend on a multitude of influencing factors with varying degrees of importance for the process itself and the development of material properties. The necessity of better process control is leading to more and more exhaustive in-situ measuring techniques, the application of which is not only important in view of reproducible technologies, but also contributes essentially to the elucidation of the actual processes involved, thus providing new and effective possibilities for process optimization. The techniques aim not only at the overall characterization (improvement of properties, reduction of scattering rate), but also at an economically efficient process management (cost cutting, stabilization of technological stages), as well as at criteria of quality management and reducing ecological risks.

Having these goals in mind, a critical assessment of all methods for the characterization of thermal behavior of materials with regard to their suitability as a possible probe for an in-situ measuring technique is needed. In this context, mention must be made of properties changing in a relevant way during the thermal production process, for example:

- Mass (dewaxing, debinding, outgassing, gas reaction,...).
- Volume and geometrical shape (shrinkage, compaction, swelling,...).
- Enthalpy (phase formation, phase transformation,...).
- Specific electric conductivity and other electrical, magnetic and optical properties.

The results of the in-situ observation of these properties during heat treatment are, apart from their

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application for temperature-programmed control, further needed for the control of the processes themselves (feedback control), taking as a basis the theoretically or empirically established set point procedures.

Research into the sintering of ceramic and powdermetallurgical materials by means of thermoanalytical methods (dilatometry, thermogravimetry, DTA, calorimetry, evolved gas thermoanalysis,...) for the simulation of corresponding process stages is yielding new result not only with respect to the elucidation of fundamental mechanisms of structure formation, but also regarding the optimization of technological steps in producing materials [1–3].

Dilatometry (measuring length changes) has always been one of the most frequently used methods for investigating sintering processes [46–50]. In the so-called "Rate Controlled Sintering" (RCS), first introduced by Palmour III [4,5], the sintering temperature is controlled in such a way that a predetermined, more or less graded, shrinkage rate profile in dependence on the shrinkage results for the sample. In this way modified non-linear temperature-time profiles may be established that optimize sintering processes with regard to cost and quality. This method exhibited (in the past) problems in establishing shrinkage rate profiles in direct correlation to materials properties or dimensions of the materials and workpieces, as well as in measuring the actual shrinkage rate, which was hindering its technological breakthrough. Yet, in spite of its shortcomings, the method possesses a high scientific-technological potential. Thus, in general, other properties that are measurable by thermoanalytic techniques may be utilized for controlling heat treatment processes. These new methods, called after Rouquerol [6,7] CRTA (controlled rate thermal analysis), are no longer methods of thermal analysis in the classical sense of the DIN 51005 [8]. A revision of the DIN seems indicated taking modern technological developments into account (cf. Section 2).

The atmosphere, its type and composition, must be considered a potential probe for CRTA methods in heat treatment processes. Thus, as a rule, the final properties of ceramic and powdermetallurgical materials are essentially determined by the quality of the atmosphere inside the sintering furnace, particularly through the interaction among sample material, furnace material, and atmosphere. During the heating period, gas reactions may occur (adsorption, absorption, desorption, evaporation, dewaxing, combustion and decomposition of organic components), as well as outgassing, oxidation and reduction, and decomposition depending on the partial pressure of individual components [9–14]. In-situ examination of these gas processes constitute the precondition for any control of the corresponding property changes and thus for the optimization of the material properties.

Such in-situ investigations may be carried out for instance by coupling a thermobalance or a simultaneous thermoanalyzer with a mass spectrometer as gas sensor [15–17]. The coupling system between thermoanalyzer and gas analyzer constitutes the most sensitive part of the whole apparatus, particularly for measurements at normal pressure (1 bar). Most coupling systems use capillaries that may be heated to 200°C connected to an adjacent orifice.

Such capillary coupling systems give sufficient results for many applications. They provide problems, however, if gas processes are to be measured and interpreted which occur at higher temperatures (e.g. evaporation of metals) or those connected with the decomposition of high molecular organic substances [18–21]. In these cases special high temperature coupling systems are required.

This paper focuses on such high temperature coupling systems that are at present routinely used for temperatures up to 1500°C and are tested up to 2000°C.

To facilitate better clarity, the salient points in the historical development of evolved gas thermoanalysis are briefly outlined below. Next, the technical preconditions and problems are critically discussed in relation to the requirements made to high-temperature coupling systems, their applications and limitations. In the final section, the efficiency of the method and of modern coupling systems is demonstrated with the help of selected application examples.

2. Historical survey of the evolved gas analysis

Evolved Gas Analysis [8] is defined in the DIN 51005, in its edition 11/83, in correspondence with the ICTA Nomenclature Commission [22] as a "thermoanalytical method determining type and/or quantity of volatile gaseous products emitted by samples under a heat treatment program". The latter is according to the DIN a "pre-selected sequence of time periods for heating rate, cooling rate, or constant temperature". This definition needs revising. Firstly, it should also include rate-controlled non-linear temperature programs, as is the case in CRTA. Secondly, it should allow for interaction between atmosphere and sample leading to the consumption of gas by the latter (e.g. in oxidation).

The development of evolved gas analysis has been exhaustively dealt with in numerous surveys [16,18,23–32]. It was developed simultaneously and in close connection with gas chromatography (the latter being also a thermoanalytical method), and was particularly connected with the development of suitable detectors (heat conductivity detectors, flame ionisation detectors, chemical detectors, manometers, densimeters, FT-infrared-spectrometer, mass spectrometer,...).

EGA has the following tasks:

- determination and identification of gaseous species
- quantitative determination of the same
- elucidation of gas-solid interactions

during heat treatment of sample materials.

Such analyses generally require a furnace for heating the sample. This constitutes the gas source or sink (cf. Fig. 1). Proof is achieved by means of a suitable detector, in the present case a mass spectrometer, which has been coupled to the furnace via the interface. This paper shall be concentrating on on-line couplings.

The oldest and least complicated method is the isothermic or temperature programmed pyrolysis MS in its numerous versions [23,25,28] (Curie-point pyrolysis, Knudsen-cell, electron beam evaporation, filament coating,...).

In the direct method (Direct Insertion Probe – DIP [33]) the non-volatile sample material is pyrolysed in or in the immediate vicinity of the ion source, and can thus be transferred to mass spectrometry as a directed molecular beam in the shortest possible way, in undiluted form, free from undesired interaction, and without pressure adaptation. Despite the obvious advantages of this method, a number of disadvantages in connection with material research must not be overlooked, such as:

- possible loss of components with high vapor pressures (>10–5 mbar),
- problems with the interpretation if decomposition occurs in competition with evaporation,

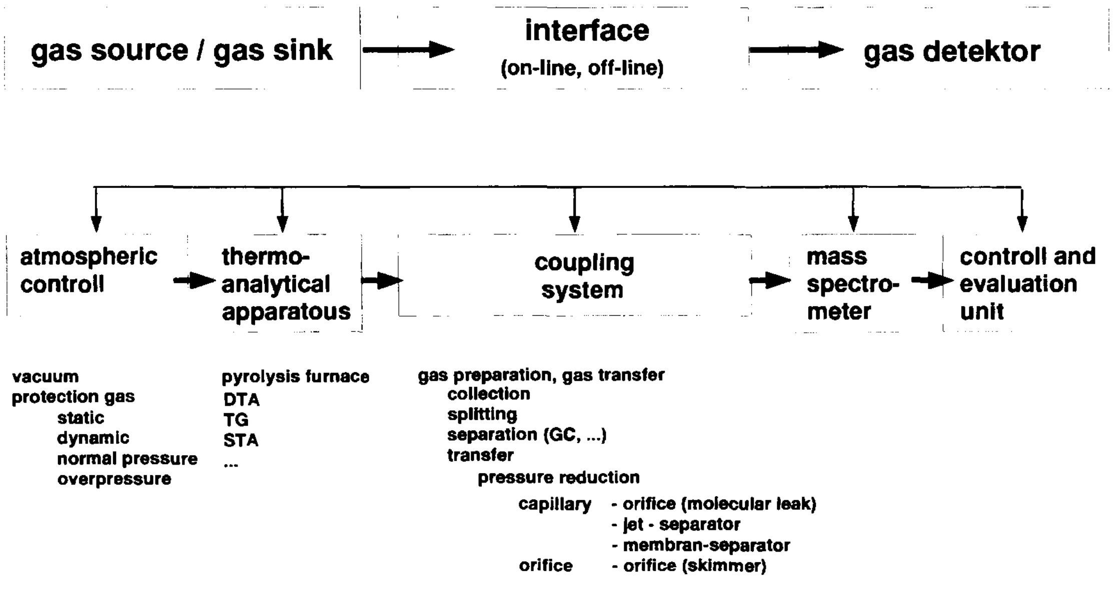
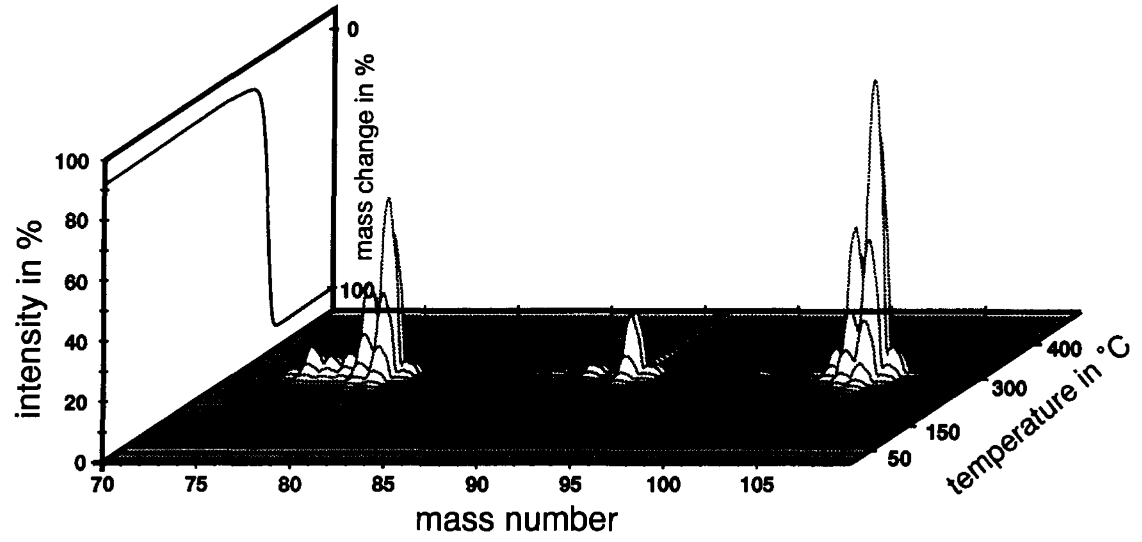
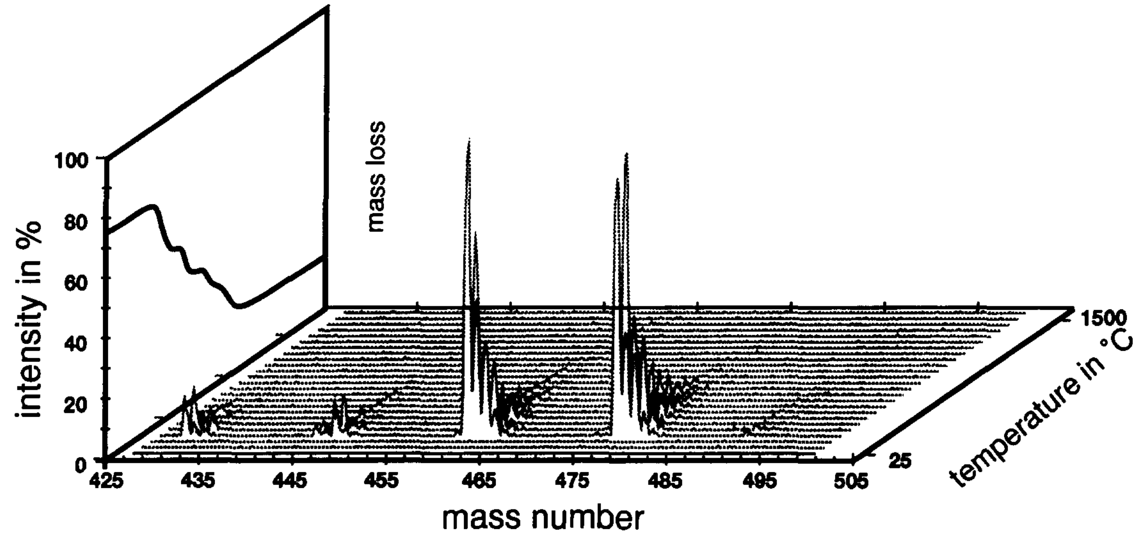


Fig. 1. Scheme of a TA-EGA system.



Pyrolysis of polystyrene



Pyrolysis of methylsilicon resin

Fig. 2. Mass change and mass spectrum of the pyrolysis of polystyrene (helium, 5 K/min, sample mass 5 mg) and methylsilicon resin (helium 10 K/min, sample mass 70 mg).

- limitation to micro and nano quantities, as well as complications in controlling, referencing, and solution of the temperature.

The indirect method already uses a separate furnace and therefore a simple TA-EGA/MS complex with a coupling system. A first experiment of this type was made as early as 1953 by Zemany [34] who slowly and gradually heated a polystyrene layer on quartz glass, channelling the decomposition products through a molecular leakage into the mass spectrometer. A spectrum was recorded in each isothermic phase. The experiment was finished after 10 days, and the main products styrene, toluene and benzene were identified in time-consuming detail work. These days, with state-of-the-art technology, such investigations take a few hours only. Fig. 2 shows a three-dimensional representation of corresponding results obtained in an apparatus using a ceramic orifice coupling system. The peaks for the molecule ion of styrene (m104) and the fragment ions for toluene (m91) and benzene (m78) are easily recognizable in the range between 300 and 400°C.

Measurements using DTA-EGA/MS coupling systems were first made in 1965 by Langer et al. [35], who were able to detect pressure-dependent reactions while working up to normal pressure.

It was Zitomer [36] who first coupled a thermobalance with a mass spectrometer in 1968. The system involved a diaphragm separator controlling the gas flow into the high vacuum. In the event of mass loss of the organic sample, mass spectrometric SCANS were recorded, i.e. accessible mass number ranges scanned.

After 40 years of development, the evolved gas analysis can safely be considered to belong to the established methods in the field of thermal analysis. Moreover, a steadily increasing number of publications shows that its importance is growing, particularly in combination with other thermoanalytical methods, whether as a parallel supplementation or in simultaneous coupling [32]. This holds true also for the initially stagnating field of the investigation of ceramic and powdermetallurgical materials at high temperatures.

3. Technical prerequisites

3.1. Requirements to the coupling system

The lower part of Fig. 1 shows the components of a modern modular TA-EGA-complex, comprising

- atmosphere control unit
- TA-device (TG, DTA, STA, DIL, TMA,...)
- coupling system
- detector
- evaluation and control unit

The currently satisfactory state has been greatly influenced by the rapid development computer technology has made in the last 20 years [32,37]. Nowadays a PC takes over the control of the total unit, data collection and evaluation, including library research, data administration and database management, as well as the graphical representation of the results. Similarly, both thermoanalytic devices and detectors/mass spectrometers are highly sophisticated and specialized these days.

On the other hand, atmosphere control and coupling system still present problems and therefore shall be discussed in more detail below. Many TA-devices still exhibit considerable deficits with regard to atmosphere control, particularly in connection with precision, reproducibility and automatization capability of the control of gas flow, pressure, purity, doping and mixing. Already high with conventional TA-devices, these requirements increase by a manifold in coupling with gas analytical devices.

As already mentioned, the coupling system is the most sensitive component of any TA-EGA-device. For thermoanalytical analyses under normal pressure, the most essential task of the interface lies in the transportation of the sample gas species into the ion source with simultaneous reduction of the pressure in the sample space ($\approx 10^3$ mbar) to the pressure within the HV-recipient ($\approx 10^{-5}$ mbar) of the mass spectrometer. For this purpose, mainly capillary and orifice coupling systems are used [38].

Specifically, the interface has to meet the following requirements (as regards theoretical discussion, cf. [38–40]):

- Gas sampling near to the place of the sample with a small portion of carrier gas, to a high degree independent of temperature.
- The size of the volume from which the gas sample is taken changes with the type of device used and the parameters of the individual experiment. Its temperature dependence complicates quantitative measuring. Moreover, the total gas flow has to be splitted, so that only a specific portion of it enters viscously the coupling system.

- The splitting ratio from gas flow through the coupling system to the gas flow through the outlet of the device depends among other factors on the viscosity of the gases and is thus dependent on the temperature. For instance, in a ceramic orifice system at constant pressure in the mass spectrometer, the splitting ratio is reduced between room temperature and 1500°C by one power often!
- Continuous transport with small transfer time t_F as regards heating rate and process kinetics, for the path from place of the sample to the ion source. This requires small coupling system volumes, optimal gas flow and optimal heating rates. In all common coupling systems the transfer times are in the sub-second range and thus non-critical at usual heating rates.
- Avoidance of mass discrimination, i.e. the concentration ratios in the sample gas need to be projected in a congruent way into the high vacuum. As theoretical consideration show, this requires in thermoanalytical experiments under normal pressure a two-stage pressure reduction system.
- Temperature independent transfer rate into the high vacuum. As the gas properties change noticeably with temperature – the viscosity of the inert gases used as carriers rises between room temperature and 2000°C by more than the factor of 5 – the transfer rate has to be kept constant in orifice coupling systems by controlling the intermediate vacuum.
- Small response times for gas changes, requiring among other things small volumes in the surroundings of the sample. An objective measure for the quality of the response is the blurring of mass spectrometric intensity peaks in comparison to the differentiated TG signal.
- Avoidance of condensation and other interchange effects. In order to keep interaction of the sample gas with components of the coupling system as small as possible, contact areas have to be minimized, and the coupling system components have to be kept at the current sample temperature.
- Uncomplicated installation, easy to service, and relatively inexpensive.

There is, however, no such thing as the coupling system that meets all requirements equally well. On the contrary, for each task the optimal coupling system has to be selected according to the material and problem under investigation.

For high temperature analysis of structural ceramics, functional ceramics and powdermetallurgical materials, which may contain considerable concentrations of organic components, orifice coupling systems are particularly suitable [15,37].

Orifices as gas inlet systems for all pressure ranges in vacuum technology have been known for a long time and are theoretically well understood [41]. A skimmer is in principle nothing else than an orifice. The skimmer interface, developed initially for ICP-MS, comprises two orifices specially shaped for an optimal gas flow and placed in line directly behind each other, separating sample room, intermediate vacuum and MS high vacuum. The differences in pressure are maintained by differentiated pumping. The "sampler", i.e. the first conical orifice, extracts the sample gas from the sample room. The gas expands into the intermediate vacuum ($\approx$0.1 mbar). The second, funnel-shaped orifice, the so-called skimmer dipping into the resulting compression zone produces a molecular beam transferred on the shortest possible way to the ion source. The optimized aerodynamic conditions, the short paths, and the comparable temperatures of sample and coupling system over the entire duration of the analysis provide high sensitivity also for metal vapors and samples with high boiling points.

Due to the auto-cleaning effect achieved in orifice systems, blockage of the coupling system and condensation of relevant sample gas components do not normally occur. This is of importance also in view of the analysis of materials with a high boiling point and metallic vapors, and for the reproducibility of measurement. The material of the coupling system may to a certain extent be adapted to the sample material under investigation and the corresponding temperature range, although the manufacture of orifices requires, particularly in the case of the skimmer interface, very high degrees of precision. Up to now orifices have been made of stainless steel (working temperature $T_E \leq 800°C$), quartz ($T_E \leq 900°C$), Al_2O_3 ($T_E \leq 1500°C$) and glasseous carbon ($T_E \leq 2000°C$).

Catalytic interaction is marginal due to the small contact areas in relation to the thickness of the orifice. A further advantage is obviously the relative ease with which the apparatus may be converted for measurements carried out below normal pressure (10^2–10^{-4} mbar) simply by removing one or both of the orifices.

A disadvantage is that orifices are complicated and therefore expensive systems which moreover perform heavy-duty work. Another problem is that gas sampling and its temperature dependence is complex and not yet fully understood.

A further processing of the gas, e.g. through the column of a chromatograph, is not possible with orifice coupling systems on-line before the MS-detector. Such analyses require the use of the splitted, strongly diluted gas portion. The capillary itself works, on the other hand, like a gas chromatographic column. This has an advantage as to the separation of component mixtures, but a dominant disadvantage with respect to time and temperature resolution.

The results shown in Section 4 were obtained exclusively by using apparatus with orifice and skimmer coupling systems, respectively. Measurements were taken under gas flow and at normal pressure. Commonly a ceramic orifice system (Al_2O_3, $T_E \leq 1500°C$) and a stainless steel skimmer system ($T_E \leq 850°C$) were used, while a high-temperature skimmer system for temperatures of up to 2000°C is currently being tested. The basic structure of the coupling systems used is shown in Fig. 3 (after [38]). Principally quadrupol mass spectrometers were used as mass spectrometrical gas analyzers.

3.2. *Current trends in methodology*

A further methodological development in thermoanalysis/evolved gas analysis (by means of mass spectrometry) is to be expected particularly in the fields of atmosphere control and coupling systems (cf. Fig. 1).

Aims are

- quantitative partial pressure measurements,
- kinetic interpretation,
- elucidation of solid–gas interaction.

There is no doubt that the requirements as to atmosphere will rise. This involves higher purity, better reproducibility, and higher variability in the composition of the atmosphere by defined addition of oxidising, reducing, carburising, and nitriding components in a wide range of concentrations.

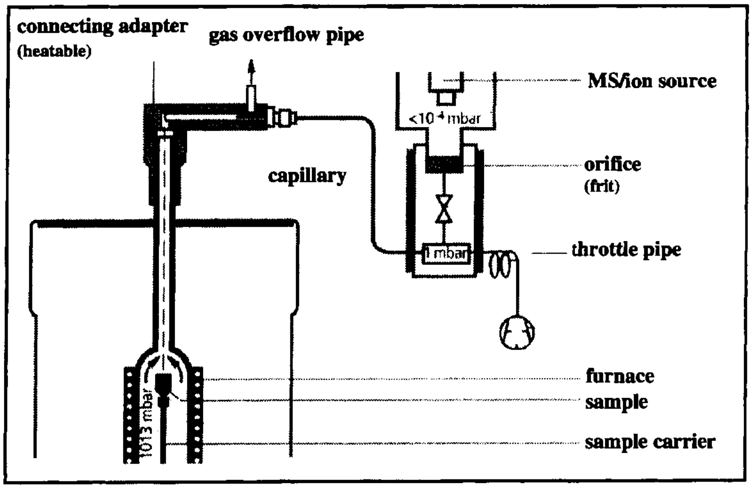
Preparation and execution of experiments (gas filling, gas exchange, pressure changes,...) should be automated.

In the coupling system with gas sampling, a better theoretical understanding is needed as a prerequisite for quantitative measurements. In this context, computer simulations of aerodynamic conditions, as well as basic experimental research into suitable gas and temperature sensors are the obvious choices.

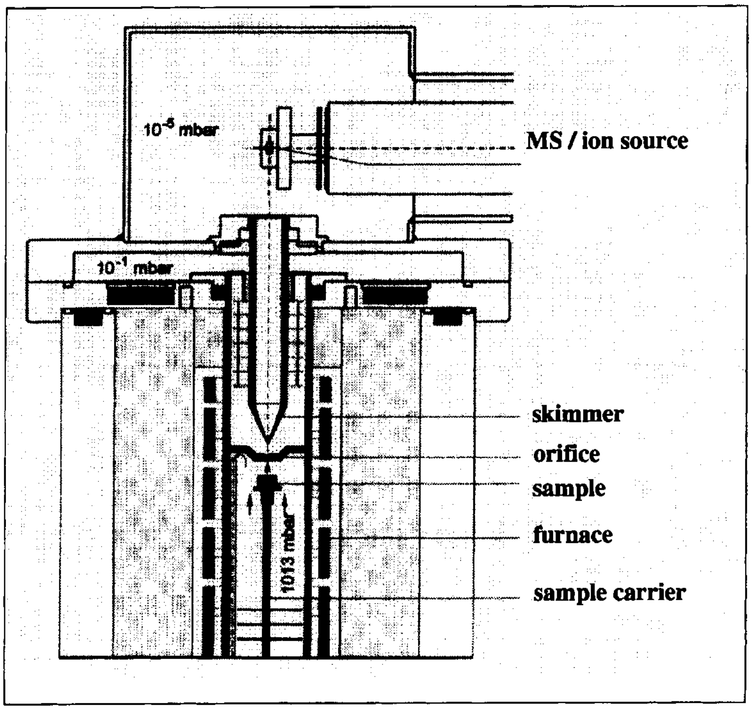
Specific adaptations of the coupling systems to concrete materials and specific technological problems are to be expected also in the future. This regards, for example, the choice of materials for both furnace and coupling system, as well as the process window for pressure (pressure sintering of high-tech ceramics) and temperature (measurements around and above 2000°C).

The investigation of gas–solid interaction is supported by a further processing of the coupled gases, e.g. by chromatographic separation or by using tandem mass spectrometry. The use of special ion sources is also conceivable. Currently high-temperature experiments predominantly use hard electron impact ionisation and open sources. With regard to the problems mentioned above, improvements are to be expected by using closed ion sources or soft ionisation methods.

Finally, a further direction in future developments may be seen in the combination of the TG/EGA/MS complex with other thermoanalytic or gasanalytic methods. Such simultaneous methods may, for instance, be heat flux DSC, thermoconductometry, thermomagnetometry, thermophotometry, or emanation thermoanalysis [42]. Similarly, the use of further gas-specific detectors must be taken into consideration. However, any increase in information gained by simultaneous use of different methods will be curtailed by loss of sensitivity, greater susceptibility to interference within the complex device, and higher technical and economic costs, so that there will be limitations in this respect.



capillary coupling system



skimmer coupling system

Fig. 3. Basic types of coupling systems TG-MS [38]. (a) Capillary coupling system; (b) skimmer coupling system.

A topical issue with a promising future is the in-situ control of heat treatment and atmosphere by partial pressure change rates in selected gas species. An example for experiments in this direction is given in Rouquerol et al. [7]. However, any technological application will require further basic laboratory research aiming at process optimization through gas-phase control on the one hand, and the transfer of such results into the technological field (upscaling) on the other [43].

4. Application examples

4.1. Pyrolysis

A wide field of applications opens up for systems with thermobalance – mass spectrometer coupling for the characterization of thermal decomposition of organic basic, additional, and auxiliary materials.

Two examples shall suffice here. Fig. 2 shows the mass changes and mass spectrum for the pyrolysis of polysterene under inert conditions (helium, 5 K/min; sample mass 5 mg). The three-dimensional representation of the mass spectrometrical intensities in relation to mass number and temperature shows that at temperatures between 300 and 400°C polysterene is completely decomposed (mass loss 100%), releasing gaseous components such as the molecular ion of styrene (m104), the fragment ions of toluene (m91), and benzene (m78).

The second example in Fig. 2 refers to the thermal decomposition of a methylsilicon resin emulsion in water and petrol, also under inert conditions (helium, 10 K/min; sample mass 70 mg). Remarkable in this example is the determination of volatile organic fragments with relatively high ion masses. The quadrupol mass spectrometer is capable of detecting mass numbers of up to m512.

4.2. Determination of metal vapors

It is important for the validity of measurements as well as the comparative evaluation of the analytical method and the coupling system, whether or not, and to what degree, metal vapors may be transferred through the orifice at sample temperature, and to identify them by means of mass spectrometry. Furthermore, this question is of great practical value in view of current materials developments and also for environmental problems (e.g. waste combustion). Fig. 4 shows the results of the evaporation of lead out of a lead melt under inert conditions (helium, 5 K/min; sample mass 7 mg). Up to a temperature of 1050°C more than half of the sample mass is evaporated. The manner in which the mass spectrometer intensities for mass numbers m208, m207, and m206 rise with mass loss is clearly to be seen. As intensity relations prove, these are unequivocally lead isotopes m208 (relative abundance 52.3%), m207 (relative abundance 22.6%), and m206 (relative abundance 23.6%). This offers, for example, the possibility of optimising the sintering regime of PZT ceramics through the gaseous phase for cases in which extreme geometrical shape of parts result in increased lead evaporation. Similar results as for lead were obtained for zinc, silver, titanium (cf. Fig. 5), which

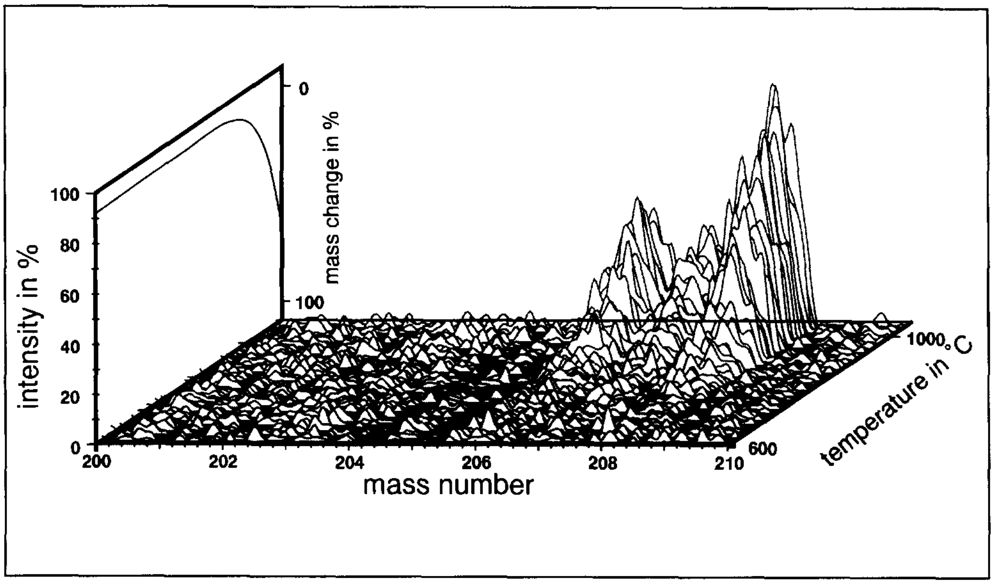
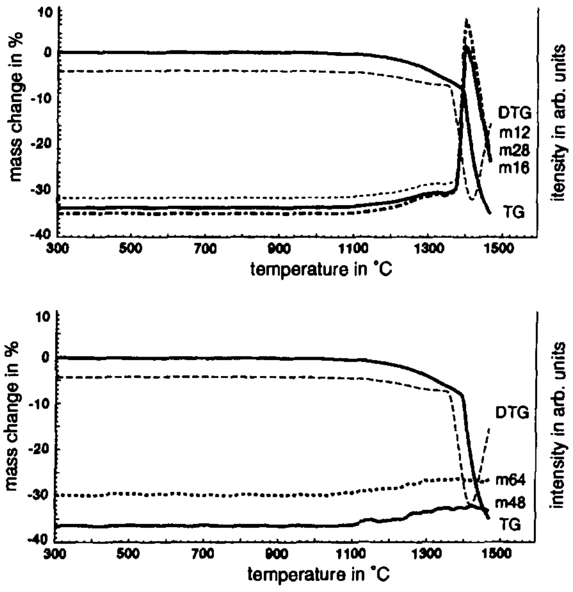
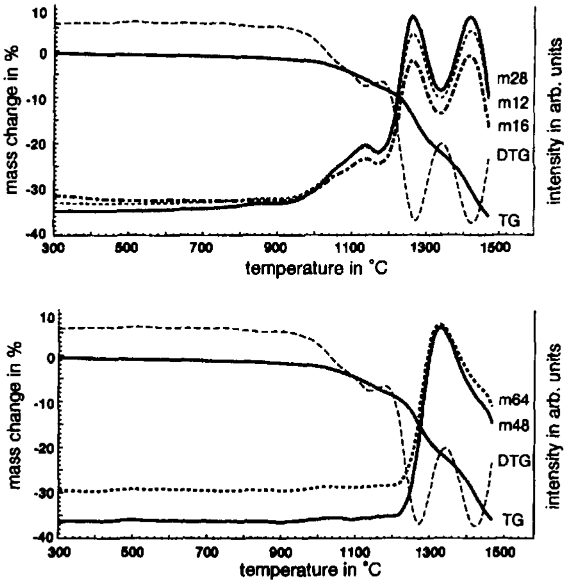


Fig. 4. Mass change and mass spectrum of the evaporation of lead out of a lead melt (argon, 10 K/min, sample mass 7 mg).



a) carbothermal reduction of TiO_2 by graphite



b) carbothermal reduction of TiO_2 by highly activated carbon

Fig. 5. Mass change and MS intensities for mass numbers m28, m12, m16 (carbon monoxide) and m48 (Ti) and m64 (TiO) (helium, 10 K/min, sample mass 50 mg). (a) Carbothermal reduction of TiO_2 by graphite; (b) carbothermal reduction of TiO_2 by highly activated carbon.

impressively demonstrates the efficiency of orifice coupling systems.

4.3. Preparation of TiC by carbothermal reduction of TiO$_2$

Titaniumcarbide is an interesting hard material with a very high melting point (>3000°C), high hardness, resistance to wear and corrosion. One method of preparing it is the carbothermal reduction of TiO$_2$ [44] according to the reaction

$$TiO_2 + 3C = TiC + 2CO$$

The selection of the initial materials, in this case of the type of carbon to be used, and the control of the thermal process provide the possibility to adjust definite grain sizes of the hard material over a wide range. Knowledge about the course of the reaction is an essential precondition for this. Among other methods, the STA-EGA/MS method (helium, heating rate 10 K/min) was used. Fig. 5 shows the corresponding analyses. Fig. 5(a) represents the results using inactive furnace soot (specific surface according to BET measurements 8 m^2/g). The moderate mass loss ($m/m_0 \approx 8\%$) between 1100 and 1400°C is due to the formation of Ti$_3$O$_5$. After this further reduction occurs in a rapid sequence, leading to the formation of TiC. A dominant mass loss curve and sharp peaks for carbon monoxide (m28, m12, and m16) is characteristic for this process. Relevant intensity changes for titanium and its oxides, as well as carbides, could not be found.

A different picture arises (cf. Fig. 5(b)) if highly activated carbon (BET value 1000 m^2/g) is used. The reduction begins already below 1000°C, and the formation of Ti$_3$O$_5$ is finished at 1250°C. The DTG-curve (differentiated TG-curve: mass loss rate) and the intensity curve for carbon monoxide show a multiple stage course of the subsequent reactions. Remarkable peaks in the intensity curves for Ti (m48) and TiO (m64) are found. This gives indications as to the probable reaction course, with porosity at micro level playing a major part [44].

4.4. Outgassing and sintering of hard metals

The ceramic orifice system was used at a heating rate of 10 K/min under flowing helium for the analysis of dewaxing, outgassing, and sintering of a conventional WC-Co hard metal with paraffin as compaction aid.

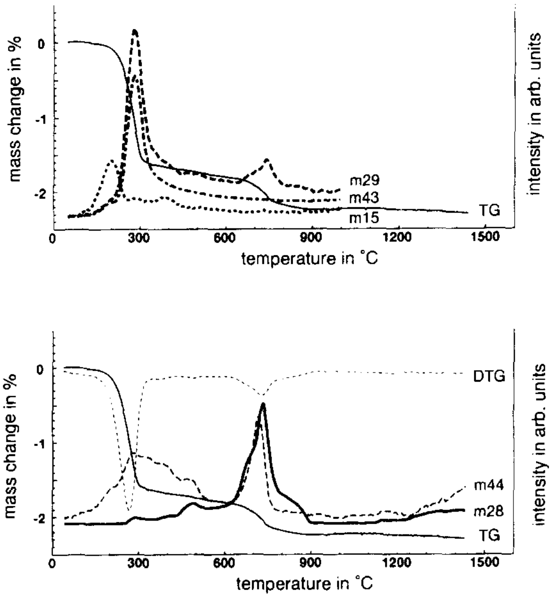


Fig. 6. Mass change and MS intensities for mass numbers m15, m29, m43 (organic decomposition products) and m28 (CO) and m44 (CO$_2$) during outgassing and sintering of a standard hard metal WC–6 wt% Co mit 2 wt% paraffin (helium, 10 K/min, sample mass 50 mg).

The results obtained are represented in Fig. 6, showing the mass loss curve (TG), the mass loss rate (DTG), and intensities of selected mass numbers, all in relation to the temperature.

At the mass loss step ($m/m_0 \approx 2\%$) with temperatures slightly below 300°C, pyrolysis of the organic binder occurs [1,45]. The peaks of the mass numbers m15, m29, and m43 are typical for the low-molecular hydrocarbons produced in this process. The different temperatures of the peaks and their fine structure indicate that the process is not a simple one (evaporation, decomposition, recombination).

The small peaks for mass numbers m28 and m44 in the temperature range around 500°C are due to the formation of carbonoxides through reduction of oxide impurities in the cobalt by the carbon of the mixture itself. Mass changes are very small in this range. The oxide impurities in the WC proper, introduced with the initial material and by its previous technological treatment (as for example, mix grinding of the basic blend) are reduced between 700 and 800°C. This process is connected with a mass loss stage (≈0.4%) and distinctive peaks for CO (m28) and CO_2 (m44).

Other hard metals may for various reasons (e.g. inhibition of grain growth) contain additions of further carbides. These introduce further oxide impurities which will be reduced at other, often higher temperatures by the carbon of the mixture. For example mixed carbide (W, Ti)C contains other impurities which are reduced only at temperatures above 900°C [45]. With the consumption of carbon present in the mixture arises an increasing disturbance of the carbon balance in the hard metal. As carbon balance and the technical properties of the sintered hard metal are directly connected, the optimization of the outgassing and sintering processes demand an exact knowledge of the carbon reactions during the production process of the hard metal, and this requires the in-situ characterization of the relevant gaseous species (CO, CO_2,...), in order to be able to influence and control the sintering process.

5. Summary

Complex devices combining classical thermoanalytical apparatus (especially thermobalances) and gas analytical measuring devices (besides FTIR-spectrometers predominantly mass spectrometers) by means of suitable coupling systems have become an integral part of modern physical and chemical analysis. Possibilities and limitations, as well as tendencies in the development of this technique are discussed.

There are numerous solutions for coupling systems, which prove to be the most sensitive part of the total device. Optimal versions may be selected taking material, problem, and financial considerations into account. For high-temperature analysis of ceramic and powdermetallurgical materials the obvious choice are orifice coupling systems.

The performance and efficiency of these orifice coupling systems are demonstrated by means of application examples (pyrolysis of organic components, determination of metallic vapors). In the simulation of technological processes (e.g. carbothermal reduction of TiO_2) or process sequences (e.g. outgassing and sintering of hard metals), using such devices produces results by the help of which processes and technologies may be optimized. Of increasing value are developments leading to the process optimization by gas-phase control. Transfer of these findings into the industrial field (upscaling) is a further main issue in current research and development.

List of symbols

BET	measuring method for determining specific surface
CRTA	controlled rate thermal analysis
DIP	direct insertion probe
DIL	dilatometry
DSC	differential scanning calorimetry
DTA	differential thermal analysis
DTG-curve	differential TG-curve (mass change curve)
EGA	evolved gas analysis
ICP-MS	inductively coupled plasma mass spectrometry
ICTA	International Confederation on Thermal Analysis
MS	mass spectrometer
RCS	rate controlled sintering
STA	simultaneous thermal analysis
TA	thermal analysis
T_E	working temperature
t_F	transfer time
TG	thermogravimetry
TG-curve	mass change curve
TMA	thermomechanical analysis

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