Thermochimica Acta, 175 (1991) 13–24
Elsevier Science Publishers B.V., Amsterdam

THERMAL ANALYSIS IN THE RESEARCH AND DEVELOPMENT OF ADVANCED TECHNICAL CERAMICS.

K.A. Nielsen

Institute of Mineral Industry,
Technical University of Denmark, DK-2800 Lyngby, Denmark

ABSTRACT

The manufacture and performance of ceramics are closely related to the thermal properties of the materials. The accurate recording of these properties is strongly dependent upon the experimental conditions of the instrument for thermal analysis. A comparison shows that a modern instrument, fast and with low thermal resistance, is not superior to an old instrument when the smaller sample size in some cases cancels the better sensitivity.

Some examples have been picked from the fields of interest: Bi-Ca-Sr-Cu-O powders prepared by an oxalate route for high-Tc superconductors are calcined to yield homogeneous powders very close to the stoichiometric composition. Crystallization of glasses in the $MgO-SiO_2-Al_2O_3$ system are investigated by a fast DTA-technique but care must be taken when the data are interpreted. Production of β'-SiAlON from natural aluminosilicates, Smectite and Kaolin, by carbothermal reduction is partly a gas/solid reaction which has been studied by combined thermal analysis and mass spectrometry. The composition of the gas phase is closely related to the degree of reaction and reflects the composition of the raw materials.

1. INTRODUCTION

Thermal analysis is often used in several steps during the manufacturing of ceramics, characterization of raw materials, calcination and sintering of green bodies, characterization of the final piece of ceramic, to mention only a few. A very well-defined sample temperature is the key parameter to a variety of specific properties which could be measured on the materials. This paper is addressed towards the two techniques: Thermogravimetry (TG) and Differential Thermal Analysis (DTA), called Simultaneous Thermal Analysis (STA) when applied simultaneously on the same sample.

The sample temperature is usually measured outside the sample at the surface of the sample holder and will be accurate for the greater part of analysis, but is clearly affected by both the design of the instrument and the experimental conditions applied. To ensure a uniform temperature distribution within the sample it is desirable to reduce the sample size to a minimum set by the sensitivity of the instrument, but small samples are not always representative of the bulk material. In other words, analytical results will tell a lot about the piece of material in the present environment but very little about another piece in different environments.

To answer all questions in analytical work the instrument will therefore have to be both versatile and sensitive. In the laboratory we have at

0040-6031/91/$03.50

our disposal two sets of instruments which complement each other: one modern instrument, sensible and fast, working with small samples (90 mm^3) STANTON REDCROFT 784 (now: PL Thermal Sciences) and one old but very versatile instrument, METTLER TA1/2. Their characteristic designs are sketched in figures 1 and 2. They differ mainly in the way the temperature is controlled and recorded. The METTLER instrument records the sample-temperature and controls the furnace temperature by the same thermocouple located at the crucibles, c.p. figure 3, either located at the bottom of the reference crucible (macro crucible) or removed from both sample and reference (micro crucible & block crucible). In the former case sample temperature could be calculated by adding the signals of temperature and DTA. In the STANTON REDCROFT instrument furnace temperature is controlled by a thermocouple located at the heating element and the sample temperature is measured at the bottom of the sample crucible. Each of the heads has been designed to optimize response in a certain set of conditions, e.g. the block crucibles are designed to record DTA-signals.

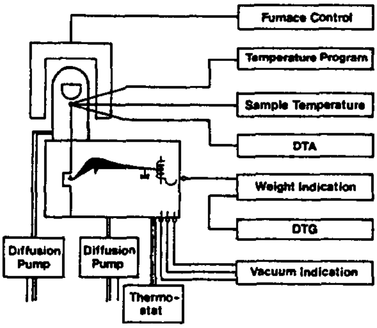

Figure 1: Schematic diagram of the METTLER TA1/2

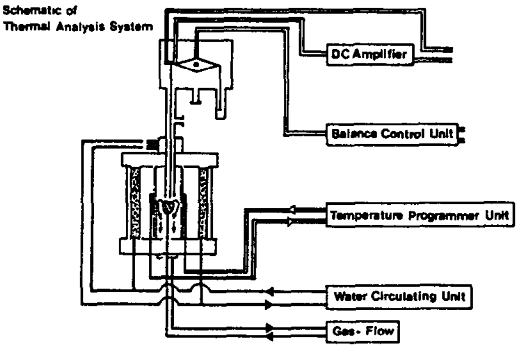

Figure 2: Schematic diagram of the STANTON REDCROFT STA 784 (now: PL Therm. Sci.)

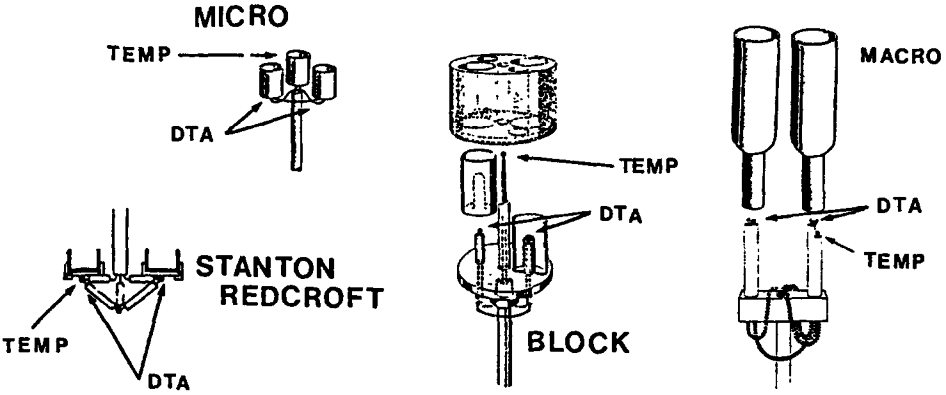

Figure 3: The crucibles and points of temperature measurement used in the METTLER TA1/2 and the STANTON REDCROFT 784.

1.1 To stress the importance of the design and the experimental conditions calciumcarbonate (analytical grade) has been heated in flowing air at a high and at a low heating rate. The TG signal is a true variable of state and in this case the weight loss is a function of both temperature and partial pressure of CO_2. Results obtained from the four STA-heads shown in figure 3 are plotted in figure 4, and evading a more detailed analysis it is clear that significant diversity is observed even at a low heating rate. The weight loss versus temperature is therefore dependent on the heating rate, the size of the sample and as seen from the block- and macro-crucibles to the design of the measuring head, all parameters that are often underestimated in reports of more complicated systems and reactions.

The accuracy of the temperature measurement has been estimated by a DTA-reference material (K_2CrO_4) for which points of extrapolated onset are listed together with points of extrapolated onset for the $CaCO_3$ in table 1. From a theoretical point of view Stanton Redcroft has got the best temperature measurement and for the decomposition of $CaCO_3$ at low heating rate records the same point of theoretical onset as does the micro crucibles.

In this case application of rate controlled thermal analysis would partly solve the problem (Paulik & Paulik 1986) because the decomposition reaction could then take place at controlled and well-defined conditions of equilibrium and the shift of conditions forced by e.g. a constant heating rate becomes negligible.

TABLE 1: Points of extrapolated onset for the decomposition of $CaCO_3$ at two heating rates and the C II -> C I transition of K_2CrO_4 at 665°C

Sample holder: (c.p. fig. 3)	K_2CrO_4 (2°C/min)	Weight of CaCO3	$CaCO_3$ (2°C/min)	$CaCO_3$ (25°C/min)
Macro (METTLER)	671°C	127,7 mg	752°C	850°C
Block (METTLER)	674°C	127,7 mg	729°C	836°C
Stanton Redcroft	668°C	21,0 mg	653°C	765°C
Micro (METTLER)	669°C	4,9 mg	650°C	721°C

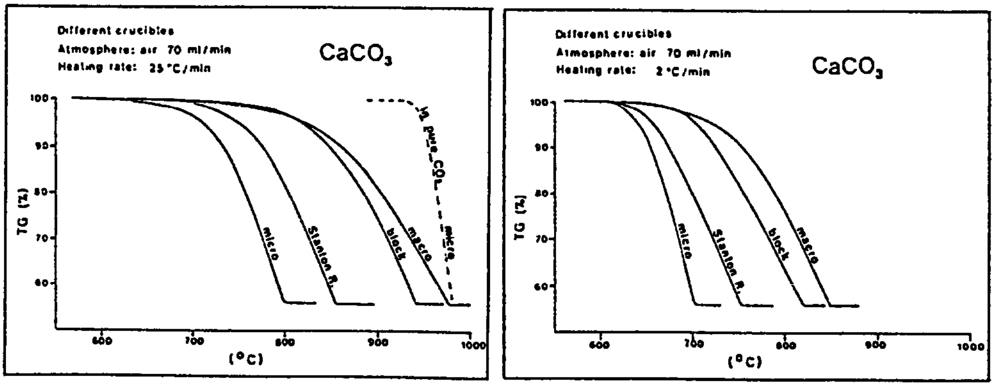

Figure 4: The weight loss (%) of $CaCO_3$ versus temperature at two heating rates measured in four different STA-heads (c.p. fig. 3)
Sample weights are listed in table 1.
Results showed by a dotted line were taken from Mettler, tech. bull. T-106

1.2 Graduate students shall by means of X-ray diffraction (XRD) and thermal analysis (DTA) determine the relative amount of quartz in pieces of tile that have been fired at a rather low temperature and at different higher temperatures. (The quartz will disappear on firing). The samples for XRD and for DTA are typically 150 mm^3 and 90 mm^3 respectively and the peak areas of curves are determined by the students with mean deviations of 2 % (SiO_2) for XRD analysis and 6 % (SiO_2) for DTA analysis*). This makes the diffraction analysis the most reliable of the two. Care is taken to make the test samples representative, but the results are disappointing. Results from the two methods should fit on a straight line and is shown in a plot on figure 5. But it is seen that the results from the DTA analysis (circles) have almost no significant connection to the results from the diffraction analysis. The experimental error is shown as a shaded area. Making similar DTA-experiments using larger samples (900 mm^3) in the METTLER TA1/2 instrument the mean deviation on area determination will be 8 % (SiO_2) but the final results fit somewhat better to the diffraction results as can be seen on figure 5 (triangles). Some of the determinations made by the Stanton Redcroft instrument are far below the expected values and might reflect a poor thermal contact between the crucible and the measuring thermocouple, but results stress the need for homogeneity of the samples prior to analysis.

---

*)Careful analysis will reduce this rather large standard deviation to below 1 % (SiO_2).

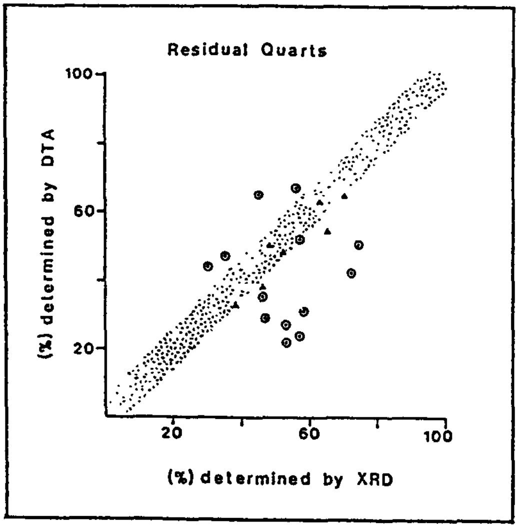

Figure 4: Two methods, XRD and DTA, used for the determination of the amount of quarts in samples of tiles fired at higher temperatures relatively to the amount of quartz in the same samples fired at a low temperature. The results are expected to lie within the mean deviation on the area determinations of the DTA and XRD analyses, which has been indicated as a shaded area.
Circles represent results from small DTA-samples (90 mm^3)
Triangles represent results from larger DTA-samples (900 mm^3)

2. TYPICAL APPLICATIONS OF STA

2.1 Calcination is a very important operation and maybe the process most frequently followed by STA. Calcination of a High-T_c superconducting material prepared by an oxalate route is the chosen example because decomposition of the mixed oxalates is easily interpreted by comparing the decomposition reactions of the pure Me-oxalates. Preparation of the precursors for the Bi-Ca-Sr-Cu-O powders was done by Stenstrop et al. (1989) by mixing stock solutions of the Me-nitrates with partly hydrolyzed diethyloxalate from which a fast coprecipitation of oxalates leads to a homogeneous and fine grained product. The slurry was stirred for 2 days at room temperature to allow complete hydrolysis of the diethyloxalate and diluted with ethanol to reduce the solubility of the oxalates, finally washed and dried. The recovery of metals are very close to 100%. Calcination of both the separate Me-oxalates and the coprecipitated precursor were studied by heating samples in air to 800°C at a heating rate of 2°C/min. From figure 6 will be seen that oxalates of the more electronegative metals, Bi and Cu, decompose to oxides at low temperatures within a narrow range of temperature and that decomposition of the oxalates of the more electropositive metals, Ca and Sr, takes place at well separated steps at different higher temperatures. Calcination of the precursor is shown in figure 7 and the steps of weight loss correspond to a sequential rather than a combined decomposition of the coprecipitated oxalates as outlined in figure 6. Crystal water is removed below 150°C and from 240 - 300°C oxalates of Bi and Cu decompose to the corresponding oxides. The weight loss from 380 - 480°C corresponds to decomposition of the Ca- and Sr-oxalates to carbonates and finally calciumcarbonate decomposes to calciumoxide at 600 - 700°C.

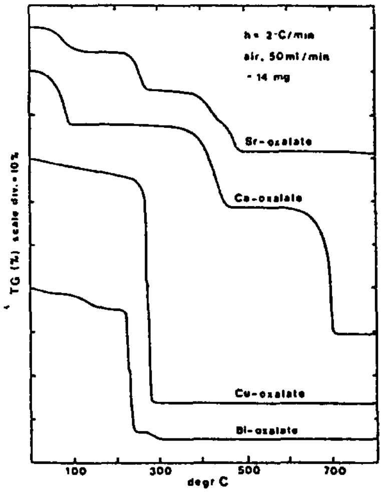

Figure 6: Calcination of the separate Bi-, Ca-, Sr, and Cu-oxalates, studied by heating samples in air to 800°C at a heating rate of 2°C/min.

Decomposition of $SrCO_3$ to SrO has not started until 780°C but a prolonged heat treatment at low partial pressure $p(CO_2)$ is necessary because release of CO_2 during the final sintering of the ceramic above 800°C will cause undesirable porosity.

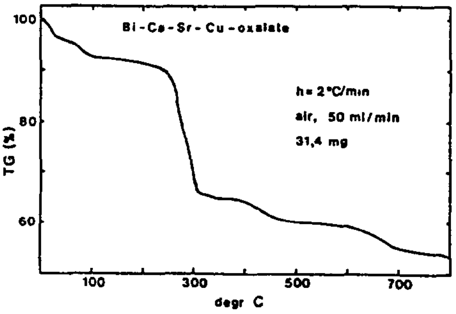

Figure 7: Calcination of the coprecipitated precursor for Bi-Ca-Sr-Cu-O High-T_c superconductor, studied by heating samples in air to 800°C at a heating rate of 2°C/min.

2.2 Crystallization of glasses in the $MgO-SiO_2-Al_2O_3$ system has been studied by non-isothermal DTA technique which is fast and requires only small amounts of sample. The results have been analysed on a theoretical base and as an example illustrates many problems common to an exact use of DTA signals in analytical work. Models of conceptual and mathematical simplicity has been preferred to more complex expressions required to model the heterogeneous crystallization taking place.

Considering the signal (ΔT) a function of the enthalpy flux e.g. of crystallization, dH/dt, the heat capacity of the sample (including its holder), C, the heating rate, h, the apparatus constant, $K = f(T)$, and the difference in heat capacities of sample and reference, ΔC, it will consist of three terms (Holba 1975):

$$\Delta T = (DTA) = - K^{-1} (dH/dt + C\, d(\Delta T)/dt - \Delta C h) \qquad (1)$$

where the first is proportional to the enthalpy flux, the second to the thermal inertia of the sample and its holder and the third to the change in baseline during heating. The equation (1) is suitable for converting the DTA signal into the true enthalpy flux (Nevriva et al. 1975) shown at figure 8, where a typical DTA curve from crystallization is converted. The correction for change in baseline is done as shown, and the correction for thermal inertia includes determination of the heat capacity of the sample plus holder (assumed constant during the process) and use of the first derivative of the DTA curve. The converted curve will not have the same T_p as the measured curve.

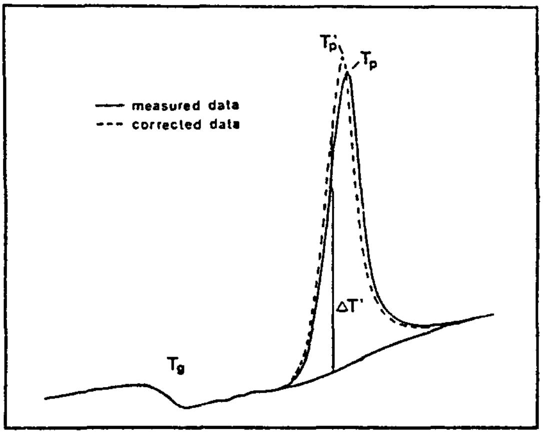

Figure 8: A typical DTA peak as measured for crystallization of a glass and the peak converted into true enthalpy flux by addition of the thermal inertia of the sample and its holder. The variables are listed in table 2.

Most analytical methods for calculating thermodynamic data from a crystallization process have started from the assumption that the rate of the process can formally be described by a Johnson-Mehl-Avrami (JMA) equation and therefore be expressed as a function of only three - or in som cases two - variables: the degree of conversion, x, the temperature, T, and the order of reaction, n, in the form:

$$- dx/dt = A \exp(-E/RT)(1-x)^n \tag{2}$$

where A is the pre-exponential factor, E, the activation energy.

The JMA-expression is based on one of the following assumptions that are true only for very simple systems:

i) The crystal growth rate has an Arrhenian temperature dependence and the nucleation rate is negligible.

ii) Both the crystal growth and the nucleation frequency have Arrhenian temperature dependencies

However, results are usually fitted well by this model at least within the limited ranges of crystallization. It should not lead to the conclusion that the JMA-expression is a true description of the process, Yinnon & Uhlmann (1983), Holba (1987), but that the dominant factors of crystallization processes - even heterogeneous - often could be quantified this way.

Among the relations for non-isothermal analysis, c.p table 2, those derived by Augis & Bennet (1978) and Marotta & Buri (1978) can be used to calculate both a numerical constant, n, which characterizes the crystallization mechanism and the crystal growth activation energy, E_G. Assumption i) was taken as valid for this glass composition and the overall activation energy, E, is then equal to E_G when using the equation of Augis & Bennett (1978). By the method of Marotta & Buri (1978) the constants can be evaluated from slopes of straight lines, which in turn are plotted from measured values, T, ΔT and T_P. The additional assumptions implied in applying this method are that the reaction rate (dx/dt) at a certain temperature is proportional to the temperature difference, ΔT, and that a change in temperature has much greater influence on ΔT than on the crystallized fraction, x.

TABLE 2: Expressions used in the DTA-evaluation of glass crystallization kinetic parameters.

Reference	Mathematical expression
Augis & Bennett (1978)	$\ln(h/(T_P-T_0)) = -E/(RT_P) + C$ $n = 2.5\ RT_P^2/bE$
Marotta & Buri (1978)	$\ln(\Delta T) = -nE_G/(RT) + C$ $\ln(h) = -E_G/(RT_P) + C'$
Bansal & Doremus (1984)	$\ln(T_P^2/h) = \ln(E/R) - \ln(A) + E/RT_P$

Meaning of the variables:

b - full with at half maximum of the peak
ΔT - The deviation from baseline
T_P - DTA peak temperature
T - The temperature corresponding to a given value of ΔT
T_0 - Room temperature
h - Heating rate
E - The overall crystallization activation energy.
E_G - The activation energy for crystal growth
A - Frequency factor
R - Gas constant
C,C' - Constants
m - Constant characterizing crystallization mechanism
n - n=m when nucleation rate is zero, n=m+1 when nucleation rate is non-zero

In the aim of producing Enstatite reinforced glass ceramics (De-Chun 1990) crystallization of glasses in the $MgO-SiO_2-Al_2O_3$ system was altered by addition of TiO_2 as a nucleating agent. From a glass of the composition: SiO_2(53,6%), Al_2O_3(17,1%), MgO(20,2%), TiO_2(9,1%) a number of different phases were formed, MAT-phase ($Mg_xAl_{2-2x}Ti_{1+x}O_5$), Enstatite, Cordierite, High-Quarts, Cristobalite and Mg-Petalite. The crystallization process is therefore heterogeneous and can not formally be described by any of the models used for evaluation. However, the activation energies were fitted by correlation coefficients better than 90 % and varied only 10 % among the individual models, c.p table 3. An example of the plots is shown in figure 9. Evaluation of the present data by comparison with literature data of activation energies was impossible because no such were found

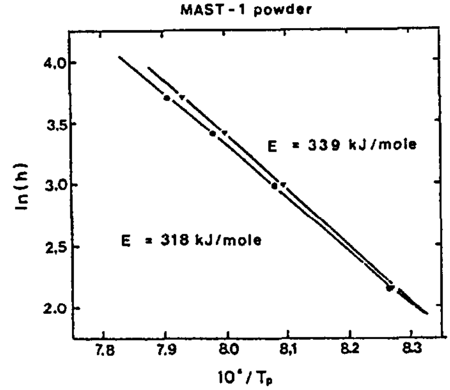

Figure 9: Apparent activation energy (E_G) for crystallization of MAT+oEn+MgP in the glass powder as evaluated from the major exothermic DTA peak according to Marotta & Buri (1978)
Circles represent uncorrected data.
Triangles represent data, corrected for thermal inertia of the sample.

Both corrected and uncorrected sets of data are compared because usually calculations are based on uncorrected data. By correcting the data as explained above activation energies will change only 6-7 %, which is not significant compared to the overall accuracy of the calculations. A correction of the data will change the order of crystallization, n, from 3.5 till 3.9 which in systems of homogeneous crystallization would indicate a different mechanism. In this case "n" is the overall constant for the heterogeneous crystallization process and has no kinetic sense.

The results illustrate that this three-parameter model is very useful because it will fit data even when used for numerical evaluation in cases where the material does not meet the assumptions of the model and to some extent they justify the widespread use of uncorrected data, at least for calculation of activation energies.

TABLE 3: Activation energies for crystallization in a glass evaluated by different models.

Model	Measured data	Corrected data
Marotta & Buri (1978)	318 kJ/mol	339 kJ/mol
Augis & Bennett (1978)	304 kJ/mol	324 kJ/mol
Bansal & Doremus (1984)	297 kJ/mol	319 kJ/mol

3. APPLICATIONS OF STA/MS

Coupling of thermal analysis to mass spectrometry (MS) makes it possible to characterize the gas phase both qualitatively and quantitatively and thereby obtaining detailed information on decomposition reactions and gas/solid reactions. The transfer of gas from the STA measuring head to the detector of the MS should be representative and be fast to reduce the delay time. Calibration of the MS and its connection is often done by measuring gasses of known composition or by measuring the gas composition during decomposition of (pure) substances in the STA apparatus, e.g. by measuring the concentration of CO_2 during decomposition of $CaCO_3$ at a well defined gas flow rate.

In order to characterize an unknown gas phase a full MS-spectrum, usually 1 - 100 amu, is recorded at intervals during the process in the STA-equipment, then in a second experiment a selection of significant peaks, e.g. 12 amu, are continuously monitored and compared to the STA data, to which they often show a minor delay. Peaks are compared to reference spectra for identification.

3.1 Production of β'-sialon by carbothermal reduction of natural aluminosilicates is a low cost route to advanced technical ceramics. Smectite was mixed with organic molecules in a slurry, and the complex of clay and adsorbed molecules were then heat treated to polymerize and pyrolyse the organic components which will then act as the reducing agent in the succeeding carbothermal reduction (Nielsen & Engell 1989). Kaolin and carbon black was mixed in a slurry, spray dried and finally pelletized. These materials were studied by STA/MS during carbothermal reduction because it is believed that the reactions of the different raw materials are alike. The reduction of Kaolin is already well understood (Higgins & Hendry 1986) and the overall reaction (I) is divided into the different steps (II)-(IV):

$$3Al_4Si_4O_{10}(OH)_8 + 30C + 10N_2 \Leftrightarrow 4Si_3Al_3O_3N_5 + 30CO + 4H_2O \qquad (I)$$

At 1200°C the Kaolin has broken down into a mixture of mullite and silica

$$3\ Al_4Si_4O_{10}(OH)_8 \Leftrightarrow 2\ Al_6Si_2O_{13} + 8\ SiO_2 + 4\ H_2O \qquad (II)$$

immediately followed by conversion of the free silica into silicon carbide.

$$8\ SiO_2 + 24\ C \Leftrightarrow 8\ SiO + 16\ C + 8\ CO \Leftrightarrow 8\ SiC + 16\ CO \qquad (III)$$

These reactions are independent of the kind of inert atmosphere but the next step(s) involves formation of nitrided phases and is further regarded as rate limiting.

$$2\ Al_6Si_2O_{13} + 8\ SiC + 6\ C + 10\ N_2 \Leftrightarrow 4\ Si_3Al_3O_3N_5 + 14\ CO \qquad (IV)$$

From experimental work on kaolin it is known that a steady supply of nitrogen and continuous removal of CO are essential and that the concentration of CO in the reaction gas is significant to the degree of conversion. It will therefore be of interest to find a volatile specimen just as significant for the reaction of the smectite-organic-complex. The final conversion into β'-sialon will also be sensitive to catalytic impurities that form liquids which can act as crystallizing medium.

The experimental results indicate a similarity between the reaction of the two materials as shown in figure 10 and 11. Firstly, the reaction of the smectite-complex basically follows the route of kaolin except that the thermal degradation of smectite depending on its composition leads to a mixture of slightly different composition at 1200°C. Secondly, the concentration of CO in the reaction gas is significant to the degree of reaction for both materials. Each set of curves are related to the DTG-signal from STA analysis and very close relationships are observed. The two materials differ in the way the carbon sources react. The smectite complex releases an atmosphere of hydrocarbons, carbon-oxides and water, and will not deplete the nitrogen gas of molecular oxygen as does the kaolin/carbon black mixture. The phases present after reduction show that the kaolin/carbon black mixture is converted into 95% β'-sialon$_{(z=3,0)}$, 2,5% of both X-sialon and alfa-Al_2O_3 and that the smectite organic complex is converted into (only) 56% β'-sialon$_{(z=0,9)}$, 34% Fe_xSi, 6% AlN and other phases.

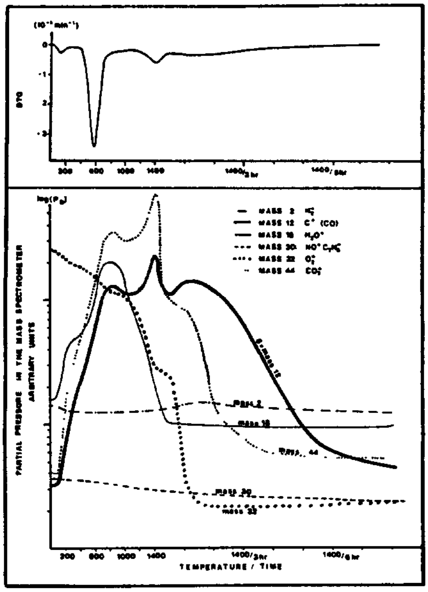

Figure 10: Carbothermal reduction of kaolin and carbon black in a nitrogen atmosphere characterized by TG/MS.

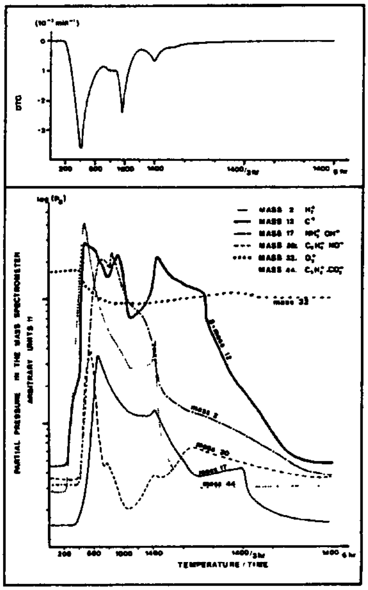

Figure 11: Carbothermal reduction of smectite-organic complex in a nitrogen atmosphere characterized by TG/MS.

3.3 Binder-burn-out of a green body (pre-sintered body of ceramic materials) is usually a very slow process so that the microstructure of the body is not altered by gradients of heat or shrinkage. The heating rate should either be constant and rather low or be controlled by the decomposition rate in such a way that the heating is stopped when this rate exceeds a preset limit. The reaction rate is monitored by the DTG-signal (derivative thermogravimetry) or by signal output from the mass spectrometer. Decomposition products of the binder are dependent on the burn-out process and shall preferably be small molecules that are easily removed from the body by diffusion and which will not condense inside the furnace.

4. CONCLUSION

Thermal analysis is useful and necessary in the research of ceramics as well as for many other materials, and with some experience it is possible to choose the set of experimental conditions which more accurately reveals the properties of the reactions studied even though the choice is often a compromise; on the other hand it is possible to study the material response to a well-defined change in the set of conditions. In comparing results from different sources extreme attention must be directed towards the experimental conditions. In many cases influence of the conditions could to some extent be avoided by using the degree of reaction of the sample, e.g. weight loss, instead of the furnace temperature as parameter to control the heating rate.

It has been argued that versatility is perhaps the most important quality of an analytical instrument since the demand for accuracy is generally met by manufactures. In quantitative methods of analysis it is important to correct measured data when necessary, but usually a kind of semi-quantitative analysis will give results adequate within the same range of experimental error.

Thermal analysis alone, whilst yielding valuable information, will often be insufficient to characterize a material or a reaction and needs to be combined with other analysis, e.g. characterization of crystalline phases by XRD or simultaneous characterization of gaseous components by MS.

ACKNOWLEDGMENTS

Permission to use the data of G. Stenstrop and F. De-Chun is greatly appreciated as is the financial support from The Danish Technical Research Council through contract no. 5.17.1.6.19 and through The Center of Advanced Technical Ceramics. G. Krarup is thanked for her skillful experimental work.

REFERENCES

Augis, J.A. & Bennet, J.E. (1978):"Calculation of the Avrami parameters for heterogeneous solid state reactions using a modification of the Kissinger method".
J. Therm. Anal, 13, p. 283

Bansal, N.P. & Doremus, R.H. (1984):"Determination of reaction kinetic parameters from variable temperature DSC or DTA".,
J. Therm. Anal., 29, p. 115

De-Chun, F. (1990): "Crystallization of gels and glasses"
Ph.D. Thesis, Institute for Mineral Industry, Technical University of Denmark, DK-2800 Lyngby.

Higgins, I. & Hendry, A. (1986):"Production of β'-sialon by Carbothermal Reduction of Kaolinite".
Br. Ceram. Trans. J., 85, p. 161

Holba, P. (1975):"On the applicability of isothermal kinetic equations for non-isothermal investigations of heterogeneous processes"
In "Thermal Analysis", Proc. 4th ICTA, vol I, p. 33
ed. I. Buzás, Heyden & son ltd., Spectrum House, London

Holba, P. (1987):"Processing of thermoanalytical curves and exact use of thermal analysis".
Thermochimica Acta, 110, p. 81

Marotta, A. & Buri, A. (1978):"Kinetics of devitrification and differential thermal analysis".
Thermochimica Acta, 25, p. 155

Nevriva, M., Holba, P., Sesták, J. (1975): "On correct calorimetric measurement by means of DTA"
In "Thermal Analysis", Proc. 4th ICTA, vol III, p. 981
ed. I. Buzás, Heyden & son ltd., Spectrum House, London

Nielsen, K. & Engell, J. (1989):"Sialon prepared from smectitic clay by carbothermal reduction"
In "New Materials and Processes", Proc. of the 5th Scand. Symp. on Mat. Sci., 22-25 May 1989, p. 457
ed. H. Lilholt, Danish Society of Materials Testing and Research, Ingeniørhuset, Copenhagen, Denmark.

Paulik, F., Paulik, J. (1986):"Thermoanalytical examination under quasi-isothermal - quasi-isobaric conditions."
Thermochimica Acta, 100, p. 23

Stenstrop, G., Engell, J., Hansen, C, Mortensen, S. (1989): "High-T_c Superconductors in the Ba-Y-Cu-O and Ca-Sr-Bi-Cu-O systems: Fabrication, Properties and Phase relations"
In "New Materials and Processes", Proc. of the 5th Scand. Symp. on Mat. Sci., 22-25 May 1989, p. 641
ed. H. Lilholt, Danish Society of Materials Testing and Research, Ingeniørhuset, Copenhagen, Denmark.

Yinnon, H. & Uhlmann, D.R. (1983): "Applications of thermoanalytical techniques to the study of crystallization kinetics in glass forming liquids, Part I"
J. of Non-Cryst. Solids, 54, p. 253