

# THERMOANALYTICAL CHARACTERIZATION OF NANOMATERIALS

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Thermal Analysis methods find broad application for the characterization of nanomaterials during synthesis, part preparation and control of final product properties. Calorimetric methods, like DSC and High Pressure DSC are applied to study melting of nanosized materials, their temperature-induced reactions and the stability ranges. Carbon nanotube materials, ceramic and metal powders were analyzed by simultaneous Thermogravimetry and DSC (TG-DSC) to show the reactivity and thermal stability and the amount and decomposition ranges of the coatings. Electro-ceramic materials show a strong dependence of the mechanical and electrical properties upon the sintering process. Barium titanate ceramic powders were grinded in the NETZSCH disk agitator ball mill to nanosized powders. Specially prepared sample tablets were measured in the dilatometer up to the end of the sintering process. The tablets pressed from nanosized powders show a much earlier completion of the densification in the sintering step compared to materials with grain size in the micrometer range.

The aim of our studies was to demonstrate that the sensitivity of modern thermoanalytical methods is well suited for general applications on materials with a reduced particle size into the sub-micrometer range and that the results provide important parameters for the thermal characterization of organic and inorganic nanomaterials.

KEYWORDS: DSC, TG-DSC, melting, dilatometer, sintering, CNT, Barium titanate

## 1. Introduction

Nanotechnology is likely to have a profound impact on our economy and society in the early 21st century; it is widely felt that nanotechnology may lead to the next industrial revolution. Science and engineering research in nanotechnology promises breakthroughs in areas such as materials and manufacturing, electronics, medicine, energy and the environment, biotechnology, and information technology. The thermal characterization of nanomaterials during their processing steps and the applications was an issue from the beginning, especially for the inorganic materials. Thermoanalytical and thermophysical testing methods are successfully applied for the determination of phase transitions, thermally induced chemical reactions and decompositions, gas adsorption and desorption studies, and thermal transport properties.

## 2. Experimental and results

### 2.1. Thermal stability of carbon nanotubes

Simultaneous TG-DSC is an effective tool to study the thermal behavior of powders under the influence of different atmospheres. Carbon nanotube samples show significant difference in their thermal stability under oxidative atmosphere, depending on their preparation conditions (Figure 1). The two samples tested reveal the same oxidizable carbon content of 92.67 %, which burns out in the temperature range 400 to 750 °C, but the volatile content before start of oxidation is 10 times higher in the modified sample, and the residue at 1000 °C (ash) is 3 times less in the modified CNT sample. The oxidation range of this CNT samples is much lower compared with known ranges for bulk graphite and diamond samples. Though carbon atoms are involved in aromatic rings like for graphite, the C=C bond angles are no longer planar in the CNTs and the C-C bond length is actually elongated by the curvature imposed. In case single wall CNTs are ideally perfect, their chemical reactivity should therefore be highly favored at the tube tips, where there is the location of pentagonal rings.

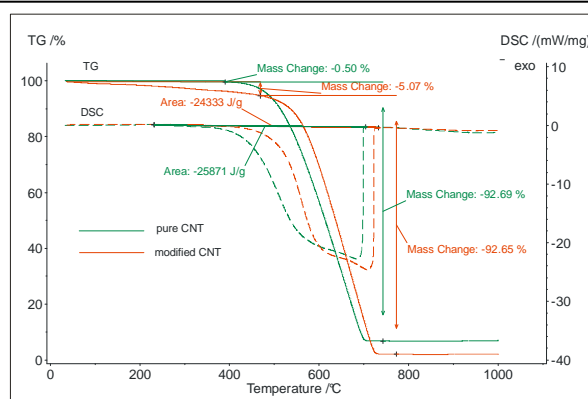


Fig. 1. Comparison of oxidation and thermal stability of two CNT samples with weight loss (TG) and energetic effects (DSC)

### 2.2. Melting behavior of nanomaterials

The melting of a dispersed nano sized metal in a metallic matrix can be determined precisely also at very small quantity level (Figure 2). Differential Scanning Calorimetry (DSC) can demonstrate the change of melting temperatures depending on grain sizes.

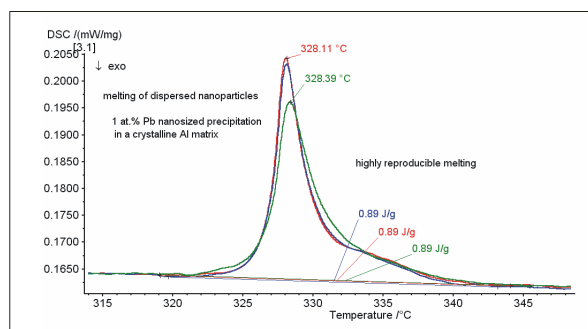


Fig. 2. Melting curves for 1 atom% nano dispersed lead in a crystalline Al matrix (17.42 mg in Al crucibles, pierced lid, N<sub>2</sub> atmosphere, 10 K/min)

In a systematic study of the influence of the particle size on the melting temperature of aluminum, a good agreement with the Gibbs-Thomson equation for spherical particles for the melting point depression with small crystals in the nanometer range was determined [1]:

$$\Delta T_m = T_m(b) - T_m(r) = \frac{2T_m(b)\sigma_{sl}}{\Delta H_f(b)\rho_s r}$$

Where  $T_m(b)$ ,  $\Delta H_f(b)$ , and  $\rho_s$  are the bulk melting temperature, the bulk latent heat of fusion, and the solid phase density, respectively.  $r$  represents the radius of a spherical particle, and  $T_m(r)$  is the melting point of a particle with radius  $r$ ;  $\sigma_{sl}$  is the solid-liquid interfacial energy. The Gibbs-Thomson equation predicts a linear relationship between the melting point depression and the inverse of the particle size. The authors in [1] studied the melting point of aluminum nanoparticles obtained from the onset temperature of DSC melting curves, and found with decreasing particle size, the decrease of the melting point showing a depression of about 10 °C, observed for aluminum nanoparticles between 40 nm and 8.6 nm. For samples prepared at different pathways with broad and narrow size-distributed particles, and partially oxidized aluminum particles the melting points were in good agreement with the Gibbs-Thomson equation. The melting enthalpy did not show the expected agreement with the derivation of the Gibbs-Thomson equation, which was also confirmed by our experiments for the melting of the nano-dispersed lead in figure 2.

2.3. Sintering of nanopowders

Three powder compacts (tablets) of barium titanate, grinded to different grain sizes down to the nanometer range, were measured in the dilatometer at a heating rate of 3 K/min (Fig. 3). The influence of the grain size on the sintering range of binder-free barium-titanate ceramics is shown clearly by a reduction of the sintering temperature by more than 80 °C, and the change of the sintering mechanism (see CTE curves). This indicates the higher sintering activity of nanomaterials, which could be utilized for optimizing process conditions to save time and energy.

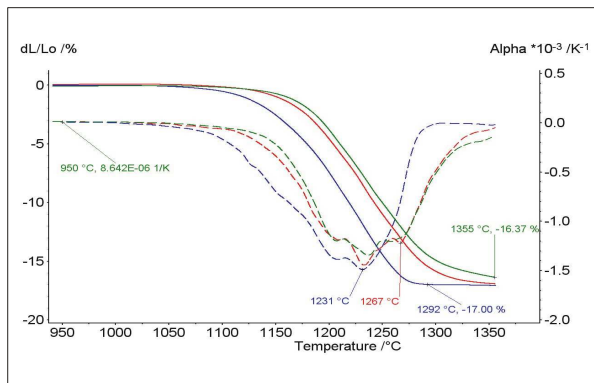


Fig. 3. Sintering ranges of barium titanate samples with different grain size

2.4. Thermal diffusivity and conductivity

Measurement of the thermal diffusivity by the Laser Flash technique is a fast and accurate method for the characterization of the thermal transport properties and of structural changes of ceramic materials, metals, polymers, and of liquids and melts. Figure 4 shows the temperature dependence of thermal diffusivity, specific heat and thermal conductivity of a thin

diamond layer produced by chemical vapor deposition. Clearly one can see the rapid change of diffusivity between room temperature and 400 °C in this thin diamond layer.

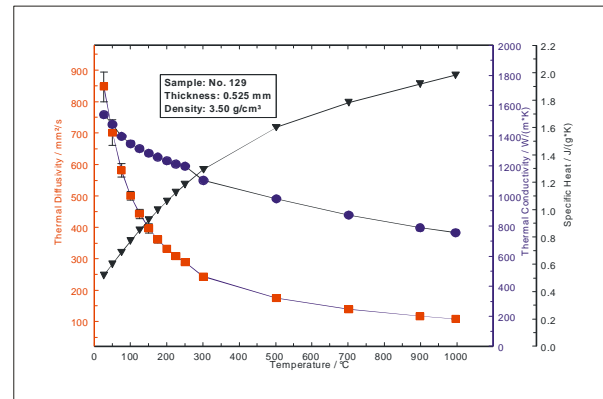


Fig. 4. Thermal diffusivity, specific heat and thermal conductivity of a CVD diamond layer.

In experiments with polymer-composites, filled with carbon nanotubes, the expected improvement of thermal diffusivity and thermal conductivity at room temperature was measured with the Laser Flash technique. The results (table 1) show the orientation effect of the CNTs in the polymer with 10 times higher in-plane thermal diffusivity (axial direction of the CNT, in-plane result) compared to thermal diffusivity of the composite with the CNT in radial orientation (through plane result). The measurement was made according to the schematics shown in figure 5.

Table 1. Polymer sheet filled with carbon nanotubes, effect of CNT orientation on thermal diffusivity and conductivity

Polymer composite with CNT	Density (g cm <sup>-3</sup> )	Specific heat (Jg <sup>-1</sup> K <sup>-1</sup> )	Thermal diffusivity (mm <sup>2</sup> s <sup>-1</sup> )	Thermal conductivity (Wm <sup>-1</sup> K <sup>-1</sup> )
Measuring direction				
Through-plane	1.191	1.212	0.172	0.248
In-plane	1.191	1.212	1.852	2.673

It is also reported for Polymer Matrix Composites that industrial epoxy loaded with 1wt% unpurified CVD-prepared CNTs showed an increase in thermal conductivity of 70% and 125% at 40K and at room temperature, respectively [4].

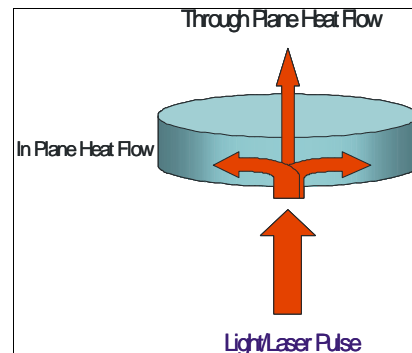


Fig. 5. Laser Flash measuring principle of in-plane and through-plane evaluations

2.5. Thermogravimetry with coupled gas analysis

With the coupling of thermogravimetry and gas analysis, decomposition and identification of volatile decomposition products are possible also for nanosized titanium dioxide powders with a functional polymer coating. The decomposition of the coatings on the ceramic powder and the identification of the type of polymer from the FTIR gas analysis are shown in figure 6. In case of the poly (methyl methacrylate) coating, the thermal decomposition starts already at 200 °C, whereas the polystyrene coating is stable up to 380 °C. The integral IR-absorption curve (Gram Schmidt plot) shows the start of the gas evolution from the decomposing sample with perfect temperature correlation with the TG curve due to the software integration of both methods. The identification of the gas components was done via a spectra search in a vapor phase library.

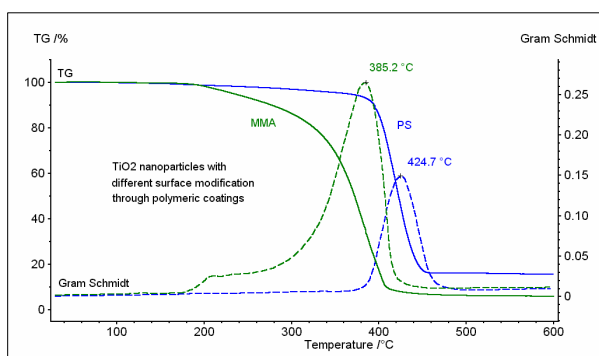


Fig. 6. Decomposition of coatings on nano sized TiO<sub>2</sub>

2.6. Mineral reactions

The chemical reaction behind the thermally induced transition of Goethite to Hematite is very simple:



The process is shown as a two-step transition in the thermogravimetric (TG) tests, as the water at begin of the reaction creates a diffusion barrier, hindering the further reaction. Aim of these tests is to demonstrate the influence of grain size on the course of this transition.

The thermal transformation, i.e. the dehydration, of goethite to hematite shows a complex dependence on the crystallite size and the experimental conditions [5, 6]. The two-step process for micrometer-sized crystals (figure 7) turns to a single step process for nanosized crystals (figures 8 and 9). The effect of reduction in grain size is also seen in the drastic reduction of the transition temperature from 325 °C (figure 7) to 247 °C (figure 8) (DTG peaks).

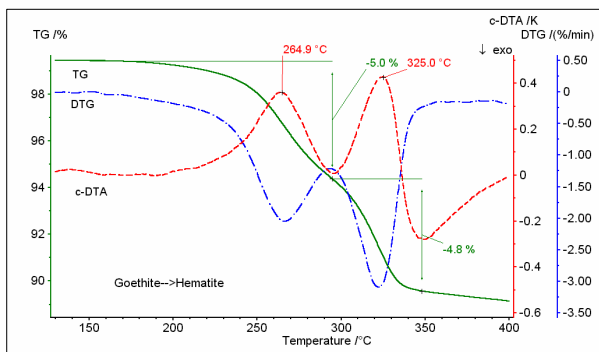


Fig. 7. Weight change and energetic effects for the transition of synthetic Goethite to Hematite in two steps

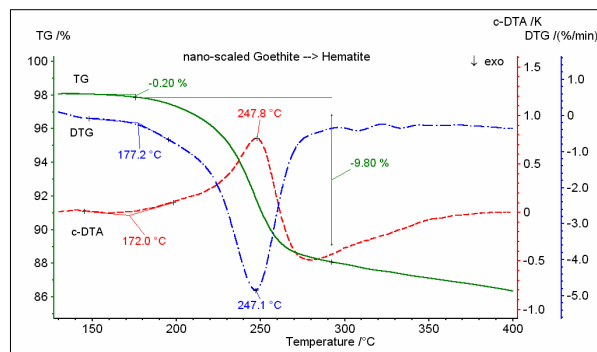


Fig. 8. Single step transition of nanosized Goethite to Hematite, measured by TG, DTG and c-DTA

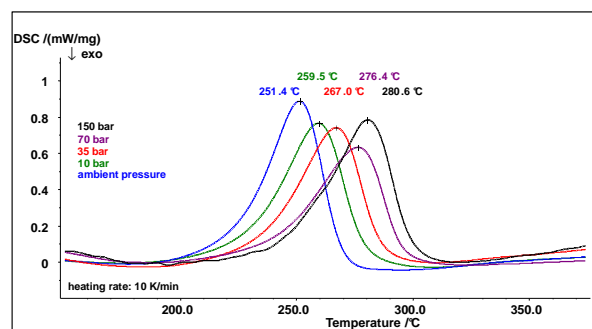


Fig. 9. Nanosized Goethite to Hematite transition under increased gas pressure

The dehydration mechanism of the Goethite does not change when the inert gas pressure around the sample is increased in high-pressure DSC experiments, but the process for the nanosized crystals is shifted to higher temperatures (figures 9 and 10). Apparently there will be a maximum of the process temperature reached near to the applied maximum pressure of 15 MPa of an inert gas. Further studies are planned to investigate the influence of humidity of the gas atmosphere on the mechanism and temperature of the thermal transition of goethite with different crystal size to hematite.

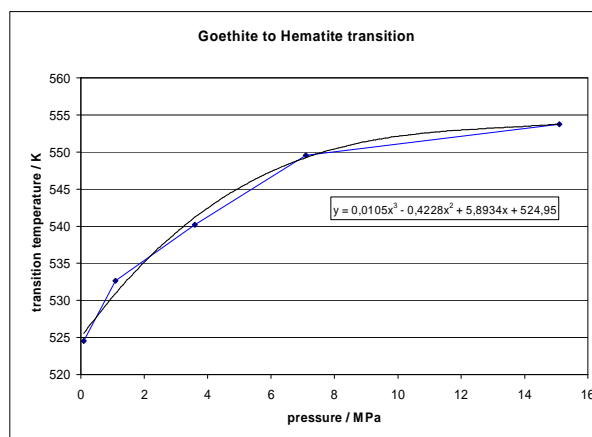


Fig. 10. Shift of the transition temperature Goethite to Hematite under inert gas pressure

### 2.7. Nanosized material for hydrogen storage

Alanates offer a promising capacity for hydrogen storage by chemical bonds. It could be shown that the grinding of Magnesium alanate down to the nanometer range reduced the temperature for the hydrogen release from 160 °C to 120 °C (DTG peak-temperature) [7]. In figure 11 we detect the hydrogen release from magnesium alanate (with a mean grain size of 30 nm) by thermogravimetry under vacuum as a sudden weight loss at 163 °C (superimposed by a small weight increase due to a repulsion effect from the high release rate of hydrogen into the surrounding vacuum). The coupled mass spectrometer identifies hydrogen ( $m/z=2$ ) as the released gas. Also in this application, the high pressure DSC is successfully applied to study the reversibility, pressure and temperature ranges of hydrogen uptake and release from alanates and similar chemical compounds.

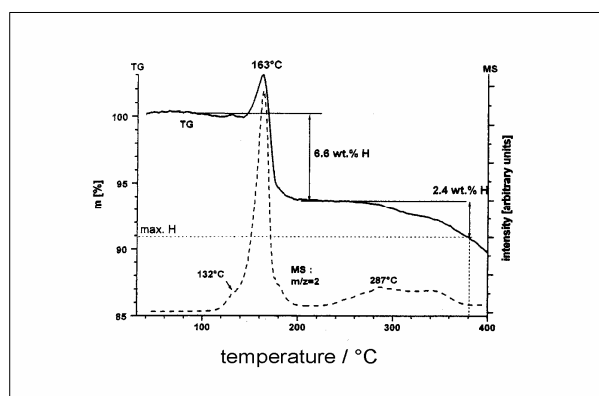


Fig. 11. Hydrogen release from nanosized magnesium alanate measured by TG-MS in vacuum

## 3. Conclusions

Thermal analysis techniques and the determination of thermophysical properties offer manifold information on materials containing nano-sized particles. The characterization of nanomaterials yields information on thermal properties, reactivity, oxidation behavior, thermal stability, and sintering. This could be shown for carbon nanotubes, nano dispersed lead, barium titanate and zirconia, goethite and magnesium alanate. Especially the determination of thermal transport properties allows an insight into orientation effects of carbon nanotubes when used to improve the thermal conductivity of polymer composites. The binder burnout and sintering of ceramic and powder metallurgical products can be optimized applying kinetic analysis based on thermoanalytical experiments [2, 3].

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