Thermophysical Characterization of Nanomaterials

Erwin Kaisersberger
NETZSCH-Gerätebau GmbH, Wittelsbacherstr. 42, 95100 Selb, Germany
www.netzsch-thermal-analysis.com

1. Introduction

The thermal characterization of nanomaterials during synthesis, part preparation and control of final product properties is made with varios thermoanalytical techniques. The quantitative determination of the thermophysical properties of carbon nanotube materials, mainly the thermal diffusivity and conductivity, the thermal expansion and the heat capacity reveals results, which are not in the expected range. Especially the thermal transport properties are measured far below the often predicted high range.

Calorimetric methods, like DSC and simultaneous Thermogravimetry and DSC (TG-DSC) are applied to study melting of nanosized metal powders or nanosized clusters in a metallic matrix, the temperature-induced reactions of nanosized materials and their stability ranges.

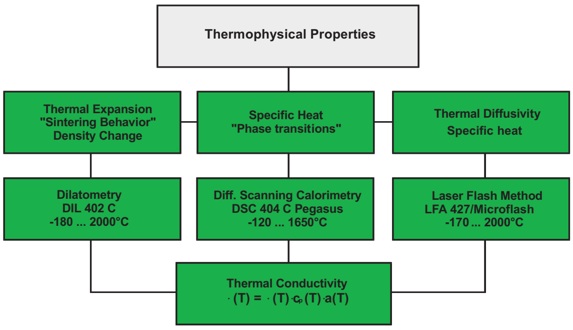


Figure 1: Thermoanalytical and thermophysical characterization methods for liquids, powders and bulk materials

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 conditions, depending on their preparation conditions (Fig. 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 diamond samples.

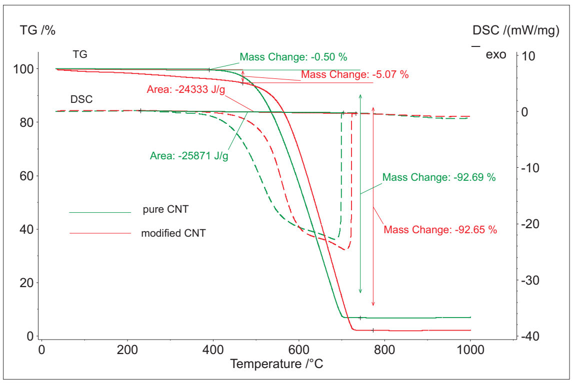


Figure 2: Comparison of oxidation and thermal stability of two CNT samples with weight loss (TG) and energetic effects (DSC)

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 (Fig. 2). DSC can demonstrate the change of melting temperatures depending on grain sizes according to the Gibbs-Thomson equation [1].

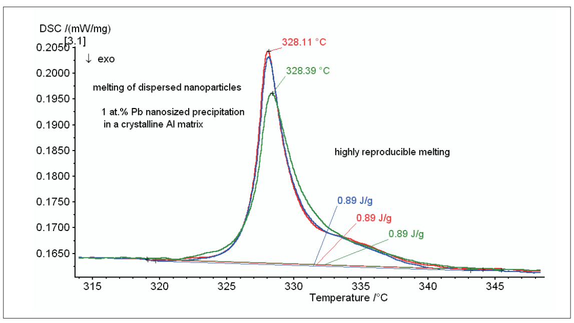


Figure 3: Melting curves for 1 atom% nanodispersed lead in a crystalline Al matrix (17.42 mg in Al crucibles, pierced lid, N2 atmosphere, 10 K/min)

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. 4). 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).

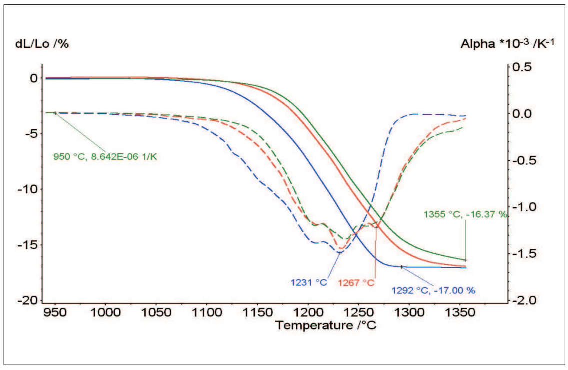


Figure 4: Sintering ranges of barium titanate samples with different grain size

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 5 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.

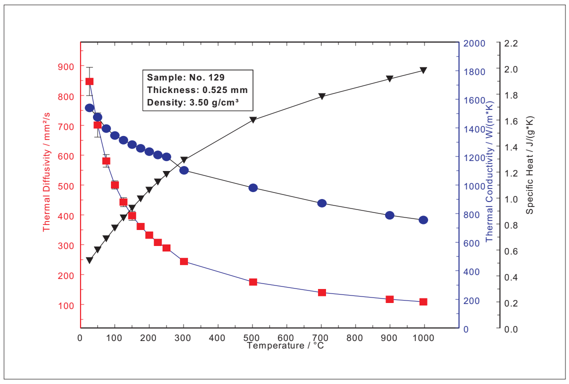
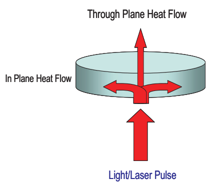


Figure 5: Thermal diffusivity, specific heat and thermal conductivity of a CVD diamond layer.

In experiments at polymer-composites, filled with carbon nanotubes, the expected improvement of thermal diffusivity and thermal conductivity at room temperature was measured with the LaserFlash technique. The results show the orientation effect of the CNTs in the polymer with 10 times higher in-plane thermal diffusivity (axial direction of the CNT) compared to the radial orientation.



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

Figure 6: Measuring principle and results for carbon nanotube filled polymer with orientation effect in the thermophysical properties

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, oxidation behavior, stability, sintering. Especially the determination of thermal transport properties allows an insight in orientation effects of CNT when used to improve the thermal conductivity of polymer composites. The binder burn-out and sintering of ceramic and powder metallurgical products can be optimized applying kinetic analysis based on thermoanalytical experiments [2, 3].

References

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[2] J. Blumm, Doctoral Thesis University of Wuerzburg, Report E 21-0103-2 (2003)
[3] A.C. Müller, J.R. Opfermann, E. Ivers-Tiffee, Thermochim. Acta 414 (2004) 11-17