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Report

High temperature calorimetry — a main topic of the "13. Ulm-Freiberger Kalorimetrietage"

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The organizing committee of the "13. Ulm-Freiberger Kalorimetrietage" (Freiberg/Sa., 17–19 March, 1999) selected the field of "high temperature calorimetry" to be one of the main topics of the conference. 15 contributions related to this field of research were given (oral and poster presentations, respectively). To discuss the current developments and problems of high temperature calorimetry concerning the different methods, calibration and standardisation, a workshop of two hours length was organized. The aim of the workshop was to bring together chemists, physicists, materials and earth scientists using similar methods of high temperature calorimetry and to discuss within this forum common methodical questions.

Thermodynamic data resulting from high temperature calorimetry are of increasing importance in materials science. This type of information on solid and liquid alloys as well as on ceramics and glasses provide the basis to understand the energetics of alloy- and compound-formation. Such data are indispensable for a knowledge-based development of materials technically applied at temperatures higher than 1000 K. Additionally, the methods of high temperature calorimetry are widely used by earth scientists and metallurgists to investigate the energetics of mineral phases and silicate melts. From these data information on petrological processes in earths mantle and crust and on slag thermodynamics are derived.

According to the large variety of materials under investigation and due to the different types of thermodynamic data required, various methods and calorimeters were developed in the past for the use at temperatures higher than 1000 K [1]. Supported by improved accuracy in measuring and data control, the sensitivity and reliability of all types of high temperature calorimetry has been significantly improved during the last decade. Moreover, commercial suppliers offer more and more equipment suitable for high temperature measurements. During the conference, examples for almost all different types of measurements using high temperature calorimetry were presented and are briefly reviewed here. The authors and titles of the contributions are given in parentheses.

High temperature *mixing calorimetry* directly provides data of integral and partial enthalpies of mixing of liquid alloys as a function of temperature and composition. With highly developed isoperibolic mixing calorimeters, alloys properties can be measured up to temperatures of 1900 K [2] (F. Sommer: Hochtemperaturkalorimetrie zur Bestimmung der Bildungsenthalpie von Legierungen; H. Flandorfer, E. Hayer: Partielle und Integrale Enthalpien in Geschmolzenen Al–Cu–Ag Legierungen). Enthalpies of mixing of liquid phases characterized by high vapor pressures or reactive components (e.g. alkali metals) can be derived in specific cases from relative enthal-

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pies measured with *drop calorimetry*. This method is used for the measurement of the relative enthalpies of various types of substances and was illustrated by workshop contributions on the characterisation of the phase transition of beryllium (H. Kleykamp: Thermische Eigenschaften von Beryllium) and on the enthalpy of ordering of a pyroxen phase (L. Cemic: Kalorimetrische Bestimmung der Ordnungsenthalpie in Mg–Fe-Ortho-Pyroxen).

As pointed out by F. Sommer and A. Navrotsky suitable solvents are necessary for successful measuring of enthalpies of formation of metallic alloys, oxides and nitrides by *(Drop) Solution Calorimetry* [2,3] (F. Sommer: Hochtemperaturkalorimetrie zur Bestimmung der Bildungsenthalpie von Legierungen; A. Navrotsky: High Temperature Reaction Calorimetric Studies of Nitrides and Oxinitrides). Frequently used solvents for measuring of metallic compounds are liquid aluminium or alloys (e.g. Cr–Ni alloys) or lead- and alkali-borate liquids for oxides and nitrides. The support of sample dissolution can be achieved by optimized solvent compositions and by providing the stirring of the melt by bubbling a gas (e.g. oxygen) through it. Using such highly sophisticated methods, the enthalpies of compounds with volatile components (e.g. carbonates, zeolithes) as well as of nitrides (Si_3N_4-based ceramics) and oxinitrides (SiAlON ceramics) and (refractory) oxides can be measured. This provides information on the energetics of compounds of technical relevance. Such phases are constituents of technical ceramics, high temperature oxide superconductors, piezo- and ferroelectrical ceramics and ceramics with high dielectrical constant. A workshop contribution giving an example on the measuring of a high-pressure phase by drop solution calorimetry illustrated the manifold scientific potentials of the method (K.-D. Grevel, A. Navrotsky: High Temperature Oxide Melt Solution Calorimetry of MgMgAl-Pumpellyite). Due to the high sensitivity of modern (solution) calorimeters and the extended availability of defined samples of high purity and homogeneity today it is possible to investigate systematically and with high reproducability stable and metastable phases, solid solutions, order/disorder phenomena, defect formation and redox reactions. In combination with the results of other types of sample analyses, scientific questions on crystal chemistry, the structure of glass phases and liquids (e.g. formation of associates) can be treated from different points of view. The use of ultrasensitive calorimeters allows the reduction of the required sample mass to 1–5 mg. This opens new fields of investigations such as the energetic characterisation of thin films and high-pressure phases which are difficult to prepare [3].

Thermodynamic measurements of alloys melting at very high temperatures or characterized by aggresive chemical behavior are possible by *levitation calorimetry*. Temperatures up to 4000 K can be reached by this method and sample contaminations with crucible materials can be avoided. Combining this method with a drop calorimeter allows the determination of relative enthalpies. Moreover, by using *levitation mixing calorimetry* exothermal enthalpies of mixing of systems with high melting temperatures can be measured. (M. Frohberg: 30 Jahre Schwebe-Schmelzkalorimetrie; Eine Bilanz). A recent and most successful further development of this method was presented by R. Wunderlich who introduced the auditorium into the topic of *Contactless Modulation Calorimetry*. This method was applied to derive data on the specific heat of glass-forming Zr-based alloys in the states of the stable and undercooled melt at temperatures between 1400 and 1900 K. Such experiments were carried under microgravity conditions in the Spacelab (R. Wunderlich: Anwendungen der Kontaktlosen Modulationskalorimetrie zur Thermischen Analyse Reaktiver und Unterkühlter Metallschmelzen).

Differential scanning calorimeters (DSC) operating at temperatures higher than 1000 K are commercially available since a few years. Two different types of heat flux DSC are used: the *disk-type measuring system* and the *cylinder-type measuring system (Tian-Calvet-method)*, respectively [4]. Heat capacity data derived from application of these methods are crucial to calculate energetic balances during high temperature processes and to derive the heat conductibility from data on the thermal diffusivity. Additionally, quantitative information at temperatures higher than 1000 K with respect to enthalpy effects connected to solid phase transformations, liquid phase formation, glass transitions and crystallisation effects are nowadays directly accesible by DSC (T. Ludwig, H.J. Seifert, F. Aldinger: Die Wärmekapazität von Yttrium-Oxinitrid-Phasen; H. Kleykamp: Thermische Eigenschaften von Beryllium). Recently, an *adiabatic high temperature calorimeter* was developed for measuring the heat capacities of liquid and undercooled liquid alloys up to a temperature of 1500 K [5].

During the conference no examples on *direct reaction calorimetry* and on *combustion calorimetry* were presented but for reasons of completeness recently published results derived by this methods should be given here. Direct reaction calorimetry at a temperature of 1473 K was used to measure the enthalpies of formation of borides, silicides, germanites and aluminides of 3d-, 4d- and 5d-transition elements and of lanthanoid-carbides and -silicides. Most recently, the enthalpies of formation of 3d-transition metal gallides were measured at 1373 K. Mixtures of the pure elements were used as initial samples [6,7]. *Combustion calorimetry* in fluorine was used to derive the enthalpies of formation of α- and β-Si_3N_4 [8]. During the workshop, these data were discussed by A. Navrotsky in comparison with the same type of data resulting from DSC provided by her group. Possible reasons for deviations or correspondence of enthalpy of formation data derived by different methods were given. The consequences of incomplete combustion and dissolution of the materials, respectively, and the severe influence of different types of impurities (e.g. oxygen, metals) on the results were emphasized.

Calorimetric measurements at temperatures higher than 1300 K require a careful selection of the materials used for the crucibles and the construction of the calorimeters. Depending on the sample compositions and the applied atmosphere, possible candidates for high temperature measurements are crucibles made of Pt95Ir5 and Pt95Au5, respectively. At temperatures higher than 1600°C Ir, Re, graphite and some others can be used. The problems of materials selection were discussed during the workshop (D. Klimm, S. Ganschow, R. Uecker, P. Reiche: Thermoanalytische Untersuchungen bis 2000°C an Oxiden). A paper was given on the improved accuracy and reproducibilty of temperature measurements using Au/Pt- and Pt/Pd-thermocouples, respectively, compared to thermocouples of type S and type N, respectively (F. Edler, E. Tegeler: Neuartige Thermoelemente im Hochtemperaturbereich). The Pt/Pd-thermocouples can be used up to temperatures of 1500°C and may substitute to some extent type S thermocouples in the future.

The features of new, commercially available, calorimeters were presented and first data and experiences from using the equipment were documented (E. Hayer, F. Flandorfer: Erste Erfahrungen mit dem Multi-Hochtemperaturkalorimeter von Setaram; J. Blumm, J.B. Henderson, G. Bräuer: Das neue Hochtemperaturkalorimeter DSC404 Pegasus für Messungen von Enthalpie und Spezifischer Wärme zwischen -120°C und 1650°C; T. Rampke, J. Blumm, E. Post, G. Bräuer: STA449 C Jupiter — Simultane Messung von Kalorischen Effekten zwischen -120°C und 1650°C). The workshop discussion resulted in a call on companies to allow the users always direct access to the originally measured, non-transformed, calorimetric data. Such data access is crucial to reliably evaluate the results and avoid the use of the equipment as a "black box".

The thermodynamic data resulting from all types of high temperature calorimetry are an important basis for CALPHAD-type calculations (CALculation of PHAse Diagrams). These calculations provide thermodynamically optimized binary and ternary phase diagrams and the correlated thermodynamic functions. The data are used for extrapolations to simulate phase reactions in high component systems and technical processes not directly accesible by experiments. Several contributions on the research field of thermodynamic optimisation illustrated the way of taking into account thermodynamic data derived by high temperature calorimetry (H.J. Seifert, F. Aldinger: Kalorimetrie und Thermodynamische Rechnungen in Alumosilikatsystemen; J. Acker, K. Bohmhammel: Experimentelle Bestimmung und Optimierung von Thermodynamischen Daten im System Ni–Si; F. Römermann, Y. Feutelais, S.G. Fries, R. Blachnik: Thermodynamische Optimierung des Systems Thallium-Selen).

In spite of the manifold progress made during the last decade, the workshop has shown that high temperature calorimetry is not a routine method yet. Many requirements remain for the further development of the calorimeters. Additionally, questions concerning the standardisation of temperature- and enthalpy-calibration are not solved satisfactorally and define methodical topics and tasks of the future. The workshop has shown that achievement of efficient progress in the field of high temperature calorimetry requires a close interdisciplinary collaboration of the different research groups using the method. A very promising step in this direction was made during this conference.

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