# High-temperature calorimetry as a basis for thermodynamic optimization using the CalPhaD approach

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The investigation of phase diagrams using the CalPhaD (Calculation of Phase Diagrams) approach is one of the central research interests at the Institute of Materials Science. This method can be applied to develop new metallic or oxide alloys with promising or improved materials properties. The CalPhaD method can help to reduce the number of experiments that are necessary for a conventional alloy development, because it identifies contradictions among different sets of experimental and theoretical data, and indicates the most crucial experiments that are needed to study the respective system. This approach takes into account all available experimental information simultaneously to derive a Gibbs energy function for each phase of the system, which will be used then to calculate phase diagrams. The usage of only experimental phase equilibrium data could give values of the thermodynamic quantities outside the uncertainty limits of the calorimetric data and can result in poor extrapolations to higher order systems. Thus, the modelling of the phase diagrams should be based on both, the measurement of thermodynamic properties and phase equilibrium data, in order to derive a consistent database. In this contribution, the application of different calorimetric and thermoanalytical methods as a basis for the modelling of metallic and oxide system using CalPhaD is illustrated.

Titanium aluminides are promising materials for high-temperature applications because of their low density, high-temperature strength, and creep and oxidation resistance. Additions of ternary alloying elements such as chromium can be used to improve the low temperature ductility and the oxidation resistance. Therefore, the ternary Al–Ti–Cr system was studied experimentally using complementary investigation methods. The heat capacities of the intermetallic phases $\gamma$-TiAl and $\tau$ were measured by the application of the classical three-step method and the procedure of small temperature steps in the heat flux DSC devices Pegasus 404C and Phoenix 204 (NETZSCH-Gerätebau GmbH, Germany). Due to the oxygen affinity of these titanium aluminides, the temperature range of the heat capacity measurements was limited to 600 °C (Fig. 1). Additionally, enthalpy increment measurements were performed using the AlexSys solution calorimeter (SETARAM, France) in transposed drop calorimetry mode. The phase transition temperatures in the ternary system were measured upon heating in the above-mentioned heat-flux DSC devices. The results of these experiments are the basis for the modelling of this ternary system.

Ceramic materials based on yttria, zirconia and alumina are of interest for many applications. Exemplarily, $Y_2O_3$-stabilized zirconia co-doped by rare earth elements are of interest for application as oxygen sensors, solid states electrolytes and thermal barrier coatings. Alumina-based rare earth oxide systems (also with $ZrO_2$ additives) are promising materials for applications using directionally solidified eutectics. Moreover, the phases stable in these systems are relevant for many applications due to their outstanding optical, dielectric and thermal properties. Materials based on the $ZrO_2$–$TiO_2$ system are of interest due to their

applications in electrical and optical devices such as capacitors, piezoelectric sensors, ultrasonic motors, and microwave dielectric resonators. In order to develop consistent thermodynamic databases for these ceramic systems, the phase relations were studied and thermal quantities such as heat capacities and formation enthalpies were investigated experimentally. The high temperature heat capacity of ceramic compounds were measured using the classical three-step method between 235 and 1373 K using power-compensated (Perkin Elmer, DSC 8000) and heat-flux (NETZSCH, Pegasus 404C) DSC devices. The data on heat capacities in mentioned temperature ranges were fitted using the Maier-Kelley equation to provide $C_P(T)$ in the temperature range between 298 and 1400 K. The heat capacities were measured for $Eu_2Zr_2O_7$, $Yb_3Al_5O_{12}$, $EuAlO_3$, $Eu_4Al_2O_9$ and $ZrTiO_4$ compounds (Fig. 1). The formation enthalpy of the $ZrTiO_4$ was determined using the AlexSys 800 calorimeter (SETARAM) and the 'drop solution' method. The temperatures of the invariant reactions taking place in the systems $ZrO_2$–$Eu_2O_3$, $Yb_2O_3$–$Al_2O_3$, $Eu_2O_3$–$Al_2O_3$ and $ZrO_2$–$TiO_2$ were determined using a differential thermal analysis device (SETARAM, Evolution 2400, DTA-TG). Based on experimental and literature data thermodynamic descriptions were developed for further use in higher order systems.

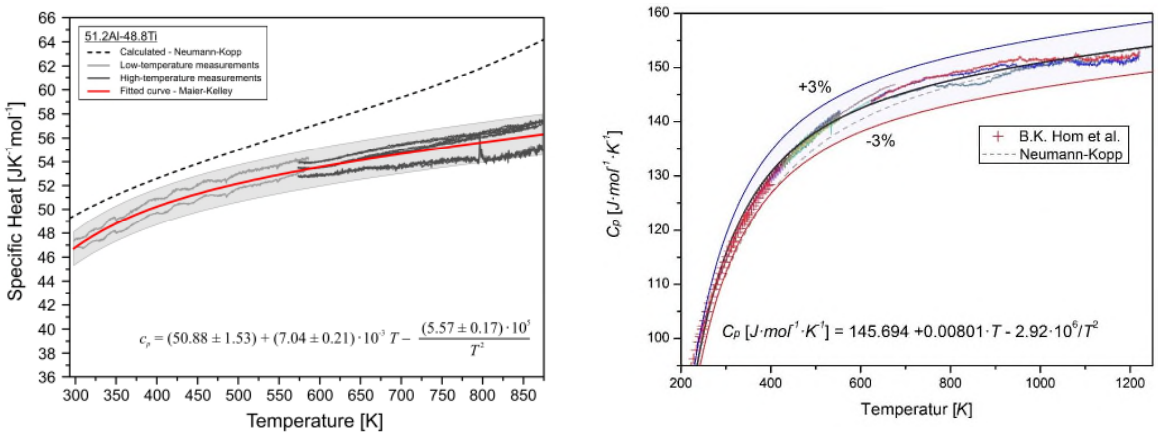


Fig. 1: Heat capacity measurements of the intermetallic γ-TiAl phase (left) [1], and the ceramic compound $ZrTiO_4$ (right) [2].

**References**


[1] M.J. Kriegel et al., Specific heat capacity measurements of intermetallic phases in the ternary Al–Ti–Cr system, J. Ph. Equilib. Diff. 35 (2014) 658-665

[2] I. Saenko et al., Experimental investigation of phase relations and thermodynamic properties in the $ZrO_2$–$TiO_2$ system, J. Am. Ceram Soc. 101 (2018) 386-399