Utilizing high-temperature calorimetry for a thermodynamic assessment based on the CalPhaD approach

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The investigation of phase diagrams making use of the CalPhaD (Calculation of Phase Diagrams) approach is one of the central research interests in our group. This method can be applied to develop new metallic or oxide materials with promising or improved 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, however, can easily yield CalPhaD descriptions predicting thermodynamic quantities outside the uncertainty limits of 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.

Iron-based shape memory alloys (SMAs) have gained significant attention from researchers in recent years due to their numerous advantages over conventional NiTi-based alloys, especially in fields like damping in civil infrastructure and actuation for aerospace applications. These advantages include lower material costs, ease of manufacturing due to good cold workability, and the possibility of applying steel-based processing procedures. A thermodynamic description of the Al–Fe–Mn–Ni system was developed with a specific focus on the target composition of 43.5Fe-34Mn-15Al-7.5Ni (at.%). This description aimed to explore new compositional regions relevant for Fe-based SMAs and to adjust necessary heat-treatment procedures. To achieve this, complementary investigation methods were used to experimentally study the quaternary Fe–Mn–Al–Ni system. The heat capacities of intermetallic phases were measured using the classical three-step method in the Pegasus 404C heat flux DSC device (NETZSCH-Gerätebau GmbH, Germany) and the power-compensated DSC 8000 (Perkin Elmer, Inc., USA). Enthalpy increment measurements were also performed using the MHTC-96 calorimeter (SETARAM, France) in transposed drop calorimetry mode. Phase transition temperatures were determined through heating in the aforementioned heat-flux DSC devices, and the results were used as a basis for modeling this quaternary 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 (TBC). Simultaneous co-doping of ZrO_2 by Y_2O_3 and Ta_2O_5 (at the level of 9-11 mol. % of each) makes the tetragonal phase non-transformable to monoclinic phase up to 1500 °C. Moreover, this material presents interests as possible TBC due to an increase of stability and durability of coating. The orthorhombic compound $Ta_2Zr_6O_{17}$ presents interest for structural applications. 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 capacities of ceramic compounds were measured applying the classical three-step

method between 220 and 570 K using power-compensated (Perkin Elmer, DSC 8000) and between 330 to 1473 K using heat-flux (NETZSCH, Pegasus 404C) DSC devices. The data on heat capacities in the 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 $Eu_2Zr_2O_7$, $Yb_3Al_5O_{12}$, $EuAlO_3$, $Eu_4Al_2O_9$, $ZrTiO_4$ and $Ta_2Zr_6O_{17}$ (Fig. 1) compounds. 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, ZrO_2–TiO_2 and ZrO_2–Ta_2O_5 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.

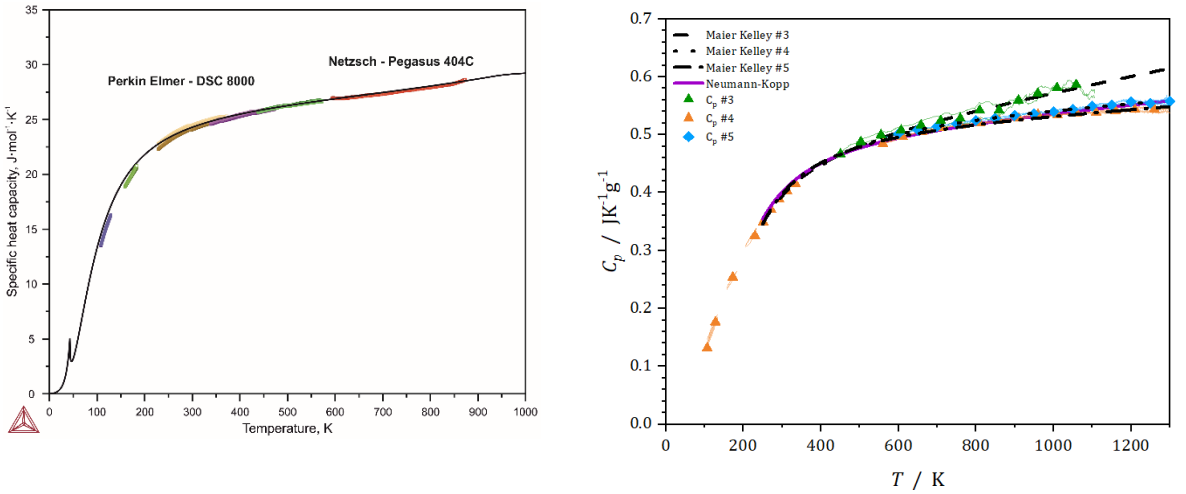

Fig. 1: Heat capacity measurements of the intermetallic Ni_3Al phase (left), and the ceramic compound $Ta_2Zr_6O_{17}$ (right) [1].

References

[1] M. Löffler et al., Phase equilibrium investigations and thermodynamic modelling of the ZrO_2–Ta_2O_5 system, J. Am. Ceram Soc. submitted