

Database development for the HotVeGas project

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Complex oxide systems containing phosphorus along with silica, alumina, alkali-earth and alkali oxides are important in many scientific and industrial fields. Thermodynamic properties of such systems for which the measurements are experimentally difficult can be described and predicted by thermodynamic modelling on the basis of reliable experimental data and appropriate Gibbs energy models for various phases. In the framework of the HotVeGas project the oxide database containing SiO₂, Al₂O₃, alkali, earth-alkali, CrO_x, FeO_x, MnO_x with addition of sulphates of alkali and earth-alkali oxides and metal sulphides has been created. The corresponding systems have been thermodynamically assessed using all available experimental data on phase diagram and thermodynamic properties. Self-consistent datasets have been obtained covering experimental information on all binary, ternary, and quaternary subsystems.

The Gibbs energy of the liquid phase has been modelled using a non-ideal associate solution approach according to the successful method of Spear and Besmann [1]. The Gibbs energy of the stoichiometric compounds have been presented in form of a simple G(T) function. The solid solutions have been described using the sublattice approach, and the corresponding solid solution parameters have been found to obtain the adequate representation of the available experimental data.

The present aim is the expansion of the database by addition of CO₂ as the next component for the modelling of a complete coal ash (slag) system. The experimental data on the mixed systems containing CO₂ are scarce and difficult for interpretation due to instability of some carbonates depending on the partial pressure of CO₂.

Firstly, the corresponding M₂O-CO₂ systems (M=Na, K) should be considered if the experimental data are available. Further, the most attention is paid to the phase equilibria between different carbonates. The DTA-measurements which have been carried out in our lab were used for the assessment. On the next step, the ternary systems containing the different carbonates, sulphates and sulphides are calculated.

The solubilities of alkali/earth-alkali sulphates/sulphides have been already included in the database. The mutual solubility based on the high temperature modification of the salts is extended by addition of alkali carbonates, because all components crystallise in the same hexagonal structure. The solid solutions based on the low temperature modifications of Na₂CO₃ and K₂CO₃ are described using the sublattice model as well. The current dataset allows for the adequate description of the phase equilibria. The pseudo-binary sections in the framework of all ternary systems are calculated as a first approximation. The ternary phase diagrams including sub-solidus equilibria are proposed. Generally, the thermodynamic assessment of the further systems with CO₂ is continued, and earth-alkali carbonates have to be taken into account.

Non-metallic inclusions such as the sulfides are essential phases during steel making and processing. Iron containing sulfide systems are important for understanding of desulfurization of molten steel and formation of sulfides during the solidification process. Moreover, the sulfides can also occur in slags and ashes from coal combustion and gasification.

The Ca-Cr-Fe-Mg-Mn-S system has been updated using all available experimental data on phase equilibria and thermodynamic properties.

The Iron sulfide phase commonly called Pyrrhotite and Chromium sulfide at high temperature exhibit the same crystal structure and Pearson symbol [2] and form a continuous solid solution. This solid solution phase can be described using two-sublattice formula (Cr, Fe, Mg, Mn, Va) S, which allows both modelling the wide existence field of this phase in the binary Fe-S and Cr-S subsystems and the solubility of such elements as Mg and Mn in the higher order systems.

According to [2,3] calcium, magnesium and manganese monosulfides have identical Pearson Symbol *cF8*, Space group *Fm3m* and Prototype NaCl, although all three end-member sulfides have different mineral names: CaS = Oldhamite, MgS = Niningerite and MnS = Alabandite. This fact permits to describe this phase MeS as one phase called Oldhamite in the present database.

The solubility of Fe in Oldhamite is strongly temperature dependent and varies considerably depending on the solvent system. The Gibbs energy of the phase Oldhamite was described using a two-sublattice model with the formula (Fe, Mg, Ca, Mn) S assuming that Fe atoms dissolve on the metal lattice.

Since the compounds FeCr_2S_4 and MnCr_2S_4 indicate a nearly stoichiometric composition and crystallize at room temperatures in the normal spinel structure with space group $Fd\bar{3}m$, where the chromium trivalent ions occupy octahedral sites, the Iron and Manganese divalent ions are placed on the tetrahedral sites, respectively, they are denoted as the Thiospinel phase. Thiospinel or Sulfur spinel phase is described using the three-sublattice model $(\text{Fe}, \text{Mn})_1\text{Cr}_2\text{S}_4$. The complete solubility between the corresponding thiospinels forms in the system FeCr_2S_4 - MnCr_2S_4 [4].

The Sulfide database updated contains the gas phase, a multi-component liquid phase, solid solutions Thiospinel, Pyrrhotite, Oldhamite, Digenite, and several solid stoichiometric compounds including the elements. The Gibbs energies of pure elements and some known sulfides are taken from the SGPS database, the missing compounds are modelled using compound energy formalism.

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