THERMOCHEMISTRY OF VANADIUM CONTAINING SLAGS

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Introduction

For a good number of years GTT is now involved in the development of a high-component oxide database GTOx which is relevant for diverse fields of application as development and production of refractories, metallurgical slags, glass processing, coal combustion and gasification, and many others. Recently, vanadium has come into the focus of our work. It is used as alloying element in steel products for improving their tensile strength, fatigue performance and heat resistance. Besides, vanadium-titanium alloys are employed as new electrode materials in hydrogen storage batteries. Because of the high value of vanadium its recovery from metallurgical but also from other slags, *e.g.* from the gasification of PET coke, is of high importance. Thermodynamic calculations for oxide systems containing vanadium are a useful tool for the understanding of such recovery processes. vanadium oxides, mainly V_2O_5 and V_2O_3, have so far been integrated into the reduced core system CaO-MgO-Al_2O_3-FeO_x-Cr_2O_3-MnO-Mn_2O_3-NiO-SiO_2-TiO_2-Ti_2O_3 of the already existing database and is therefore now available in the thermodynamic modelling software packages FactSage, ChemApp, SimuSage and ChemSheet. This work resulted in the thermodynamic assessment of 16 binary and 12 ternary systems based on the presently available experimental data.

Thermodynamic models

The Gibbs energy of the liquid phase has been modelled using a non-ideal associate solution model. The compositions of the pure liquid oxide species as well as the associates have been chosen to have two moles of cations per associate thus keeping the successful method of Spear and Besmann[1]. For systems of the type MeO-V_2O_3 one associate species $MeO{\cdot}V_2O_3$ was included. Solid solutions are usually treated using the multi-sublattice approach. Vanadium was also introduced into the thermodynamic description of solid solution phases such as MeO, Spinel, Corundum, Ca_2SiO_4-α and Pseudobrookite using available experimental information. In the vanadium oxide containing systems particular attention was given to the phase Spinel which forms the wide completely miscible solid solution Fe_3O_4-FeV_2O_4-MgV_2O_4-MnV_2O_4. The cation V^{+3} was introduced on the second sublattice of the present description of the Spinel phase (see Table 1). In total, there are 16 vanadium

containing solution phases which allow to describe the experimentally determined wide solubility with respect to vanadium oxides and therefore also the equilibria involving solid, liquid and gas phases.

Table 1: Modelling of the complex vanadium oxide-containing solution phases

Phase	Description
Slag	Non-ideal associate species model
Spinel	$(Al^{+3},Fe^{+2},Fe^{+3},Mg^{+2},Mn^{+2},Ti^{+4})(Al^{+3},Fe^{+2},Fe^{+3},Mg^{+2},Mn^{+2},Mn^{+3},Va, Ti^{+3}, V^{+3})_2(O^{-2})_4$
PSbrookite-Ti_3O_5	$(Al, Mg, Fe, Mn, Ti, V)(Al,Ti, Fe)(Ti)(O)_5$
C2S-C3P	$(Ca^{+2},Cr^{+2},Mg^{+2},Mn^{+2})_3(\underline{Ca^{+2}}, \underline{Va})(\underline{P^{+5}},\underline{Si^{+4}}, V^{+5})_2(O^{-2})_8$
Corundum	$(\underline{Al^{+3}}, Cr^{+2}, \underline{Cr^{+3}}, \underline{Fe^{+3}}, \underline{Mn^{+3}}, \underline{Ti^{+3}}, \underline{Fe_{0.5}Ti_{0.5}}^{+3}, \underline{Mg_{0.5}Ti_{0.5}^{+3}}, Mn_{\underline{0.5}}\underline{Ti_{0.5}^{+3}}, \underline{V^{+3}}, V^{+4})_2(Cr^{+3},Va)(O^{-2})_3$
MeO	$(Al^{+3},\underline{Ca^{+2}},Cr^{+3},\underline{Fe^{+2}},Fe^{+3},\underline{Mg^{+2}},Mn^{+2},Mn^{+3},Ti^{+4},Ti^{+3},V^{+2},V^{+3},V, Zn^{+2},Va)(O^{-2})$
Garnet	$(Ca,Mg)_{0.5}(Ca)_{1.5}MgV_2O_8$

Assessed binary and ternary systems are collected in Table 2.

Table 2: Assessed binary and ternary systems

Binary systems	Ternary systems
V-O [2]	Al_2O_3-Fe_2O_3-V_2O_5
Al_2O_3-V_2O_5, Al_2O_3-V_2O_3	Al_2O_3-FeO-V_2O_3
CaO-V_2O_5	Al_2O_3-V_2O_5-SiO_2
Cr_2O_3-V_2O_5	CaO-NiO-V_2O_5
FeO-V_2O_3, Fe_2O_3-V_2O_5	CaO-SiO_2-V_2O_5
MgO-V_2O_5, MgO-V_2O_3	TiO_2-Ti_2O_3-V_2O_3
MnO-V_2O_5, Mn_2O_3-V_2O_5	FeO-Fe_2O_3-V_2O_3
NiO-V_2O_5	MgO-SiO_2-V_2O_5
TiO_2-V_2O_3 [3]	MgO-SiO_2-V_2O_3
Ti_2O_3-V_2O_3 [3]	CaO-SiO_2-$V_2O_3$0
SiO_2-V_2O_3,	FeO-SiO_2-V_2O_3
SiO_2-V_2O_5	CaO-MgO-V_2O_5

Binary systems with participation of V_2O_3 and V_2O_5

The V-O binary system contains five solid solution phases and 13 stoichiometric compounds. The thermodynamic assessments of the V-O system[2] and of the Ti-V-O system[3] were taken into account. The liquid phase was re-optimised in this work using the non-ideal associate solution model[1] with the associates V_2O_2, V_2O_3, V_2O_4 and V_2O_5 taken from the SGPS database[4]. Calculated phase diagram is given in Figure 1. Vanadium has several oxidation states. Depending on the partial pressure of oxygen the stable form of vanadium oxide changes. Consequently, the phase diagrams with the same oxide (*e.g.* MgO) change with oxygen partial pressure as shown in Figure 2.

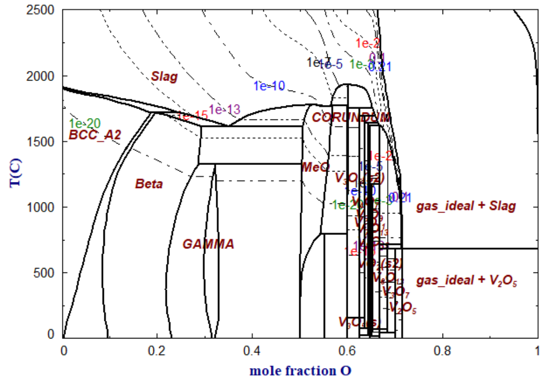

Figure 1: Calculated V-O binary system with isobars

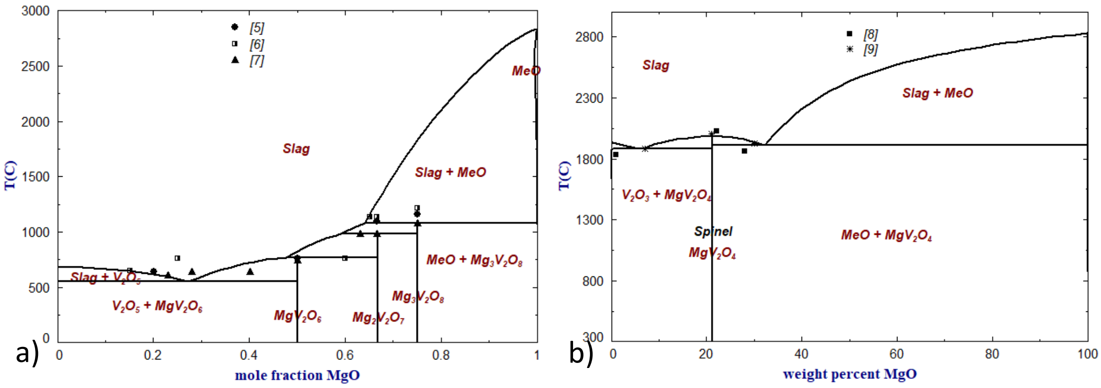

Figure 2: MgO-VO_x phase diagram in air (a) and under reducing conditions (b)

Ternary systems

Since experiments with vanadium are difficult to carry out and expensive, the existing database can be used to predict the behaviour of a slag. For example, using the experimental data[10,11] for the ternary phases $CaMgV_2O_7$ and Garnet and also the mutual solubility of CaO and MgO in appropriate vanadates it is possible to predict an isothermal section or a liquidus surface in the CaO-MgO-V_2O_5 system as shown in Figure 3.

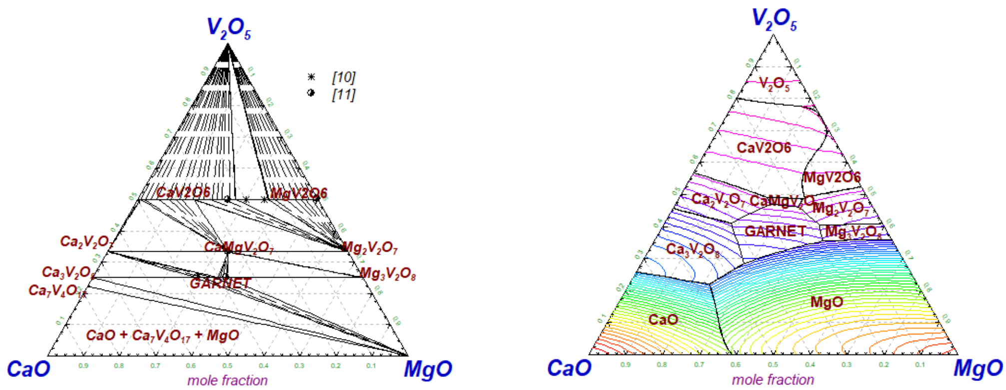

Figure 3: Isothermal section at 550°C and liquidus surface of CaO-MgO-V_2O_5

Conclusions

The self-consistent thermodynamic database for the system CaO-MgO-Al_2O_3-FeO_x-Cr_2O_3-MnO-Mn_2O_3-NiO-SiO_2-TiO_2-Ti_2O_3-V_2O_3-V_2O_5, integrated in GTOx, permits the calculation of phase diagrams and thermodynamic properties for any composition and temperature. Phase diagrams calculated using this database show generally good agreement with the experimental phase boundaries. All phase diagrams assessed are presented in a Slag Atlas provided by GTT-Technologies.[12] The GTOx database is successfully used in a very wide range of applications (coal combustion and gasification, metallurgy, fluxing, viscosity modelling).

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