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Thermodynamic description of the Fe–Mn–Ca–Mg–S system

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ABSTRACT

A thermodynamic description of the Fe–Mn–Ca–Mg–S system is presented. The compound energy formalism is used to describe all solution phases. This work includes assessments of all quaternary systems as well as the ternary systems Ca–Mg–S, Ca–Mn–S and Mg–Mn–S and the binary Ca–Mn system. The remaining ternary sulphur systems and lower-order systems were taken from previous assessments. The description of the solid phases reproduces the available experimental information well. However, due to lack of experimental data, approximations are used for the liquid in the Ca–Mg–S and Mg–Mn–S systems. The thermodynamic description presented in this work can be used to perform calculations related to sulphides in steels.

1. Introduction

Sulphur and sulphides play an important role in steels. In most cases sulphides are not desirable due to their negative influence on the mechanical properties, such as lowering of the impact toughness. Moreover, they are known to play a major role in pitting corrosion of stainless steels, where some sulphides are more detrimental than others [1]. Sulphides can however, also be beneficial as is the case with free cutting steels where they increase the machinability [2,3], some sulphides are particularly beneficial [3,4]. In either case it is important to understand the equilibrium of sulphur in iron-based alloys and the formation of sulphides. During the last century several papers have been published addressing the formation of sulphides in steels, see e.g. [5–9]. Today controlling the sulphur level in steels is more important than ever, not at least considering the tough situation on the steel market. Specialty steels with demands on low sulphur levels can be sold at higher prices than normal steel grades. However, vacuum degassing, where the sulphur content is reduced, is one of the most costly processes in the steelmaking process. Minimising the time in the vacuum degassing can thus be a way to increase the profit. Further on, the consumption of raw materials should be reduced both for financial and environmental reasons. To address this it is possible to make production trials or small scale experiments to develop new products and processes. This is however costly, which makes modelling an attractive alternative.

Computational thermodynamics, in particular the CALPHAD-method [10], is an important tool used to lower the development cost of new materials and processes. This becomes even more apparent in the advent of the Materials by Design approach which is pioneered at Northwestern University [11]. These ideas were later used by researchers at TU Delft, who utilised genetic algorithms for alloy design [12]. Recently, their methodology was extended to the steelmaking process [13]. That study investigated the vacuum degassing where desulphurisation often is the most important aspect. However, one limitation of that work was the fact that current lack thermodynamic descriptions of several sulphur-containing systems, not to mention systems containing both sulphur and oxygen. Nonetheless, sulphur is included in several large databases related to steel, including TCFE8 [14] and SLAG3 [15]. Additionally, the sulphide part of FTmisc [16] includes the Cu–Fe–Ni–Co–Cr–Mn–S system. Further on, a database concerned with sulphides and carbo-sulphides in stainless steel have been developed by Oikawa et al. [17]. However, their work does include neither calcium, which is of importance in many low and high alloy steel grades, nor magnesium, which is important due to MgO linings. As this work is a part of an effort to extend an oxide database, TCOX6 [18], with sulphur, the descriptions should be consistent with that database. Overall, the aim of this work is to use the CALPHAD-method to model the Fe–Mn–Ca–Mg–S system in a way consistent with that database. This system is believed to describe the most important sulphur-metal systems for low-alloy steels. More specifically, the compound energy formalism (CEF) [19,20] is used to model all solution phases, where the liquid is described using the ionic two-sublattice model [20–22].

In this study all the binary sulphur descriptions are taken from previous studies, Ca–S [23], Fe–S [8], Mg–S [23] and Mn–S [24].

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This also applies to all existing binary metal systems Ca–Mg [25], Fe–Ca [26], Fe–Mg [27], Fe–Mn [28] and Mg–Mn [27]. No assessment or experimental information of the Mn–Ca system was found and is thus assessed in this work. Existing descriptions of ternary sulphur systems are accepted, which include the Fe–Mn–S [24], Fe–Ca–S [23] and Fe–Mg–S systems [23]. No ternary or higher order descriptions of metallic systems were found.

2. Thermodynamic models

As is mentioned in the introduction all phases are modelled using the CEF [19,20]. This is in agreement with the earlier descriptions which are accepted in this work [8,23–28]. In this section the liquid, alabandite and pyrrhotite phases are described. For all systems besides the Ca–Mn system all parameters for the metallic phases are accepted from earlier studies [25–28] and thus descriptions regarding the modelling of these phases can be found elsewhere, see e.g. [28]. The pyrite phase is only present in the Fe–Mn–S system and information concerning this phase can thus be found in the description of that system [24].

2.1. Liquid

By using the ionic two-sublattice liquid model (i2sl) it is possible to model metallic liquid, liquid sulphides as well as liquid sulphur using the same model:

$(Ca^{+2},Fe^{+2},Mg^{+2},Mn^{+2})_P(S^{-2},Va^{-Q},S^0)_Q$

All binary sulphide systems have been assessed over the complete composition range [8,23,24]. More details about the liquid model can be found in [22]. For the implementation of this model in a sulphur system, Fe–Mn–S, more details can be found in [24].

2.2. Alabandite

The monosulphides of pure MnS, CaS and MgS all have the NaCl-structure [6,29]. MnS is the dominating sulphide found in most steels and its mineral name Alabandite is used here, as in [23,24]. The alabandite may be assumed to be stoichiometric with respect to sulphur and thus the phase can be modelled in the following way:

$(Mn,Ca,Mg,Fe)_1(S)_1$

MnS and MgS are completely miscible [30] while CaS forms miscibility gaps with both MnS [30] and MgS [30]. In addition, MnS [30–34] and MgS [30,35] can both dissolve high amounts of FeS while CaS has a very low solubility of FeS [30,36,37]. The reason for this is most likely that FeS and MgS have similar lattice parameter while CaS have a larger lattice parameter. A comprehensive investigation of the relationship between the lattice parameter and the interaction parameter for different sulphide and oxides mixtures can be found in [38]. MnS can have a small deviation from stoichiometry with respect to sulphur [39] and it is likely that this would be the case for [NaCl]-FeS as well. However, the non-stoichiometry is neglected since it is so small. CaS and MgS are more ionic, due to the lower electronegativity of calcium and magnesium, and for this reason they would most likely not show any deviation at all.

2.3. Pyrrhotite

The pyrrhotite phase, $Fe_{1-x}S$, is the stable Fe-monosulphide and has a NiAs structure [40]. The model used here is the same as in the Fe – Mn–S description [24]:

(Fe,Mn,Va)S

It can dissolve some manganese [30,32,33] but no reports concerning the solubility of calcium and magnesium have been found. Thus the pyrrhotite phase is modelled including only Fe and Mn as metallic species.

3. Thermodynamic calculations and experimental evaluation

As was described in the introduction several important subsystems have already been assessed in earlier studies. Of the ternary sulphide systems, the Fe–Mn–S [24], Fe–Ca–S [23] and Fe–Mg–S [23] systems have been assessed as part of this research project. Thus the Ca–Mg–S, Mn–Ca–S and Mn–Mg–S systems as well as the quaternary systems remain to be assessed. In addition, the Ca–Mn binary system remains to be assessed. In order to fit the experimental data some interaction parameters in these systems are optimised. To a large extent this work is based on a paper by Skinner and Luce [30], who have made an extensive experimental work regarding the sulphides within the Fe–Mn–Ca–Mg–S system. This is also the only paper which presents investigations the quaternary sub-systems. Even though it might be a limitation to base a thermodynamic assessment almost entirely on one paper it should be emphasised that their work agree well with other experimental reports within the Fe–Mn–S, Fe–Ca–S and Fe–Mg–S systems, which was shown in earlier publications [23,24], and the Mn–Ca–S system which is shown in this study.

3.1. Ca–Mg–S system

The only available information for the Ca–Mg–S system is the investigation of the miscibility gap by [30]. No experimental information regarding the liquid in the CaS–MgS system could be found. Considering this lack of experimental information the interaction parameter for the liquid is taken from the CaO–MgO system, assessed by [41]. The reason for this assumption is that O and S have similar electronegativity. The calculated pseudo-binary phase diagram using this assumption is shown in Fig. 1 together with experimental information from [30]. Besides the pseudo-binary no ternary information is found in this system. Although no reciprocal parameters is added it is assumed that the ternary can be interpolated from the binaries and the sulphide pseudo-binary relatively well, as would be the case for the Fe–Mn–S system.

3.2. Ca–Mn–S system

From a metallurgical perspective the Ca–Mn–S system is probably the most important ternary discussed in this study besides the already assessed Fe–Mn–S [24] and Fe–Ca–S systems [23]. This is because both CaS and MnS are common in steels. As no thermodynamic description of the Ca–Mn system has been found this metallic binary is described within this work. One experimental study reporting solubility data in this system have been found [42]. The Mn-solubility in Ca-rich liquid and Ca-solubility in Mn-rich solid metallic phases are reported in the temperature range 1173–1473 K. Due to the low solubility of Ca in Mn-rich solids it is neglected in α-Mn (CBCC) and β-Mn (CUB). However, BCC, FCC and HCP are considered as calcium is already included in other systems including them. Several phase transitions occurs in manganese in the temperature interval but given the limited information the same interaction parameter is set for all solid phases. The calculated Ca–Mn phase diagram is presented together with experimental data in Fig. 2.