

UNDERSTANDING THE CaO-SiO₂-‘CrO_x’ SLAG SYSTEM¹

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Abstract

The quaternary Cr-O-Si-Ca system is an important system in metallurgy, particularly for its role in slags used for the production of stainless steels. This work is devoted to explore and explain some peculiarities of this system e.g. its dependence with the system pressure and the oddities of its variable composition.

Key words: Cr-O-Ca-Si; Thermodynamics; Slags; Phase diagrams.

ENTENDENDO O SISTEMA DE ESCÓRIAS CaO-SiO₂-‘CrO_x’

Resumo

O sistema quaternário Cr-O-Si-Ca é um sistema importante na metalurgia, especialmente por seu papel em escórias utilizadas na produção de aços inoxidáveis. Este trabalho é dedicado a explorar e explicar algumas das suas peculiaridades como, por exemplo, aquelas relacionadas com a dependência do sistema em relação à pressão e as singularidades da variável composição.

Palavras-chave: Cr-O-Ca-Si; Termodinâmica; Escórias; Diagramas de fases.

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1 INTRODUCTION

To the engineer or to the student interested in expanding his/her knowledge, a basic understanding of phase diagrams is of great significance. The lack of familiarity with the fundamentals of thermodynamics and misleading diagram appearances, however, can lead to uncertainties and contribute to impair his/her quest.

Some common peculiarities which lead to misunderstanding of the information given in technical or scientific reports will be addressed here. The present work, however, will be restricted to the oxides and slags containing metal chromium. These systems are of particular importance, since they are present in slags, especially those used in the production of stainless steels.

Equilibrium states of the following systems will be seen: Cr-O, Cr-O-Ca and Cr-O-Ca-Si – in order to create a logical path and promote understanding.

2 METHODOLOGY

To show the features of the Cr-O-Si-Ca system, some simulations were effected with the software *FactSage* (v.5.5).

The following databases were utilized:

- *FToxid solution database* (FToxid53Soln.sda); it contains the molten slag phase (SLAGA). This solution bears the fully optimized CaO-SiO₂-CrO-Cr₂O₃-Al₂O₃ system.
- *FToxid compound database* (FToxid53Base.cdb); it contains 247 stoichiometric solid and liquid oxide compounds consistent with the FToxid solution database.
- *FACT53* (FS53Base.cdb): contains data for over 4500 compounds (pure substances).

3 RESULTS

3.1 Cr-O

The thermodynamic equilibrium between *one* metal and its oxides – at a given temperature – is just a question of oxygen (more properly, *system*) pressure. Therefore, once system pressure and temperature are given, the complete set of information about the equilibrium state can be foreseen – including the participating phases. Stable phases are, however, usually displayed in phase diagrams as a function of yet another variable: the system *composition*.

While the 'real' composition covers from Cr to O,⁽¹⁾ the composition span which forms the usual base for phase diagrams of this system is frequently chosen as ranging from 'CrO' to Cr₂O₃ (Figure 1). While Cr₃O₄ (same as CrO·Cr₂O₃) has 50% mole fraction Cr₂O₃, (Figure 1) in the Cr-O composition axis, it would be at X_O = 0.57.

The preference for CrO-Cr₂O₃ has two effects: in addition to the false suggestion that 'CrO' should be recognized as a *substance* or *phase* (being in fact simply the Cr:O molar proportion of 1:1), there is the unusual coexistence of two phases (e.g. metallic Cr and 'liquid') when this 'end-member' molar proportion is reached.

Both diagrams pose additional doubts to the engineer/student by (commonly) showing *pressure* as an extra variable – depicted as isobaric lines.

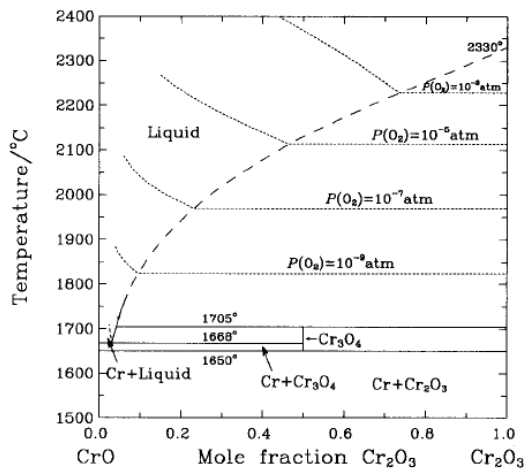


Figure 1: CrO-Cr₂O₃ phase diagram.⁽²⁾

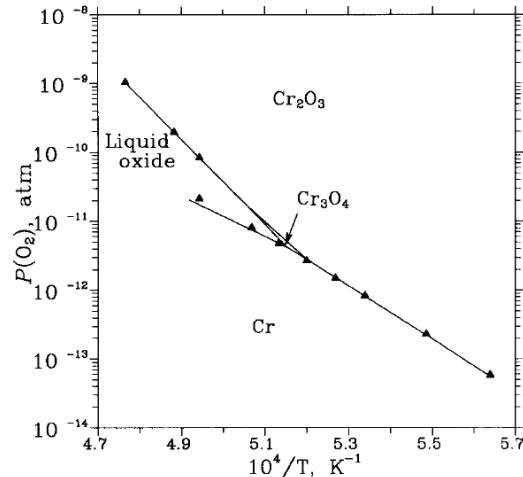


Figure 2: Cr-O phase diagram.⁽⁹²⁾

To completely overcome all uncertainties, the phase diagram given by Toker, Darken e Muan,⁽²⁾ (Figure 2) should be observed. For low pressures (or moderate to strong reducing conditions) and at near and above steelmaking temperatures, Cr₂O₃, Cr₃O₄ and 'liquid' are the currently accepted oxide phases for this system. As can be easily seen, along any (phase equilibrium) line, temperature *and* pressure change concomitantly. Any time a vertical (isothermal) line crosses a phase equilibrium line there is a correspondent two phase equilibrium *field* in the former phase diagram. Crossing such a line means going from 100% of the first to 100% of the second phase in the equilibrium state (Figure 1) – this is the reason why, during this transformation, pressure shows a *constant* value. Elsewhere, only *one* condensed phase is stable. For instance, at the temperature of 1600°C and $p_{O_2} = 1 \times 10^{-10}$ [atm], it is not possible to find metallic chromium taking part of the equilibrium state, since for equilibrium chromium / Cr₂O₃ the pressure is much lower, near 1×10^{-12} [atm]. This fact, however, is clearly seen only on phase diagrams of the type shown in Figure 2.

3.2 Cr-O-Ca

When calcium is added to the former system, two more composition axes must be taken into account: Cr-Ca and Ca-O. For phase diagrams, the metals Ca and Cr are regular 'end-members'. Often, as shown in some fundamental works by Degerov e Pelton,⁽³⁾ oxygen is incorporated into the system at a *constant pressure* basis. Thus, composition can only be set at the Cr-Ca side. The simplest way of doing this is by using the *metallic* mole ratio:

$$\text{Cr} / (\text{Cr} + \text{Ca}) .$$

This is a direct result of the fact that oxygen is being added as if coming from an 'endless source' (actually, the oxygen pressure sets the *oxygen chemical potential* for the entire system at the equilibrium state). As a consequence, the aforementioned diagrams are *not* true binary phase diagrams, but rather sections at constant pressure over the Ca-Cr-O composition *triangle*. Over that base, they follow lines which are not straight, but show instead some knees and can be, for the unaware engineer/student, in some degree, confusing.

Since the oxygen pressure for the Ca / CaO equilibrium is exceedingly low, the presence of metallic Ca is very unlikely. Therefore, when the ratio is set equal to zero, the phases present at equilibrium state will probably be solid or liquid CaO.

Even so, on the other side of the scale, metallic chromium (Cr / Cr₂O₃ equilibrium) is a possible phase (provided the system pressure is low enough (Figure 2)).

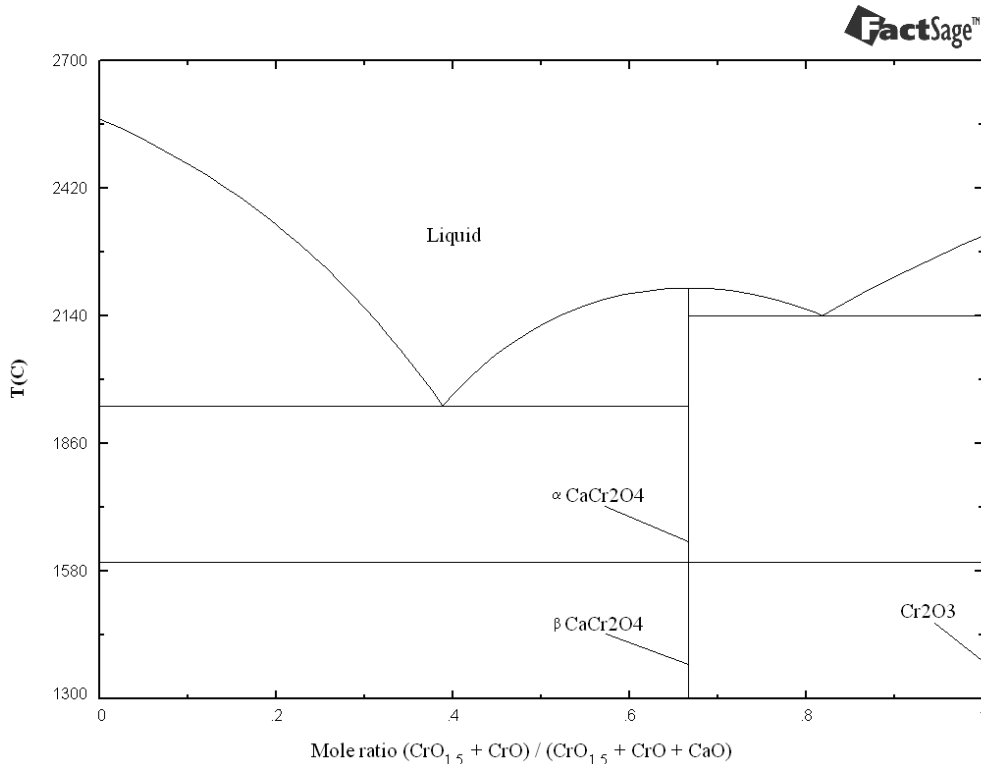


Figure 3. Cr-Ca-O phase diagram; $p_{O_2} = 1 \times 10^{-5}$ [atm]

Again, phase diagrams – at various constant oxygen partial pressures – e.g. given by the work already cited⁽³⁾ (Figure 3) show a horizontal axis which is rather confusing to the engineer/student of this subject *the oxide mole ratio*:

$$(CrO_{1.5} + CrO) / (CrO_{1.5} + CrO + CaO) .$$

Thus it is easily seen that the mole fraction of 'CrO_{1.5}' in CaCr₂O₄ (or CaO·2CrO_{1.5}) is 0.66 (see the 'position' of CaCr₂O₄ at the horizontal axis).

When the pressure drops, the 'X-phase' or (Ca_{0.4}Cr_{0.6})Cr₂O₄ appears, Figure 4. This substance can contribute to the understanding of the oxide mole ratio determination. Phase 'X' can be imagined as being made of: 2CaO·10CrO_{1.5}·3CrO. Its oxide mole ratio then has the value 0.87 – see Figure 4 for confirmation.

Another choice for representing this phase diagram would be:

$$Cr_2O_3 / (Cr_2O_3 + CaO) .$$

Phase diagram of Figure 3 was reconstructed using the new option, Figure 5. The phase CaCr₂O₄ (same as CaO·Cr₂O₃) has now 50% mole fraction Cr₂O₃, and is thus to be found in the middle of the horizontal axis.

For this case (valid also for Fig. 1), the *metallic* mole ratio is different; what is applicable is:

$$\frac{1}{2}Cr / (\frac{1}{2}Cr + Ca) .$$

As anyone can see, metallic mole ratio for CaCr₂O₄ remains 0.50 – or 50%.

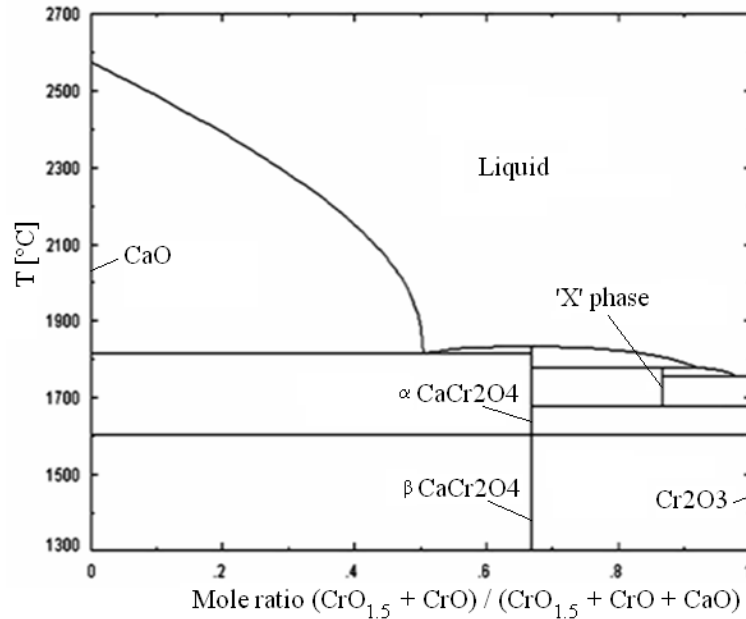


Figure 4. Cr-Ca-O phase diagram; $p_{O_2} = 1 \times 10^{-10}$ [atm]

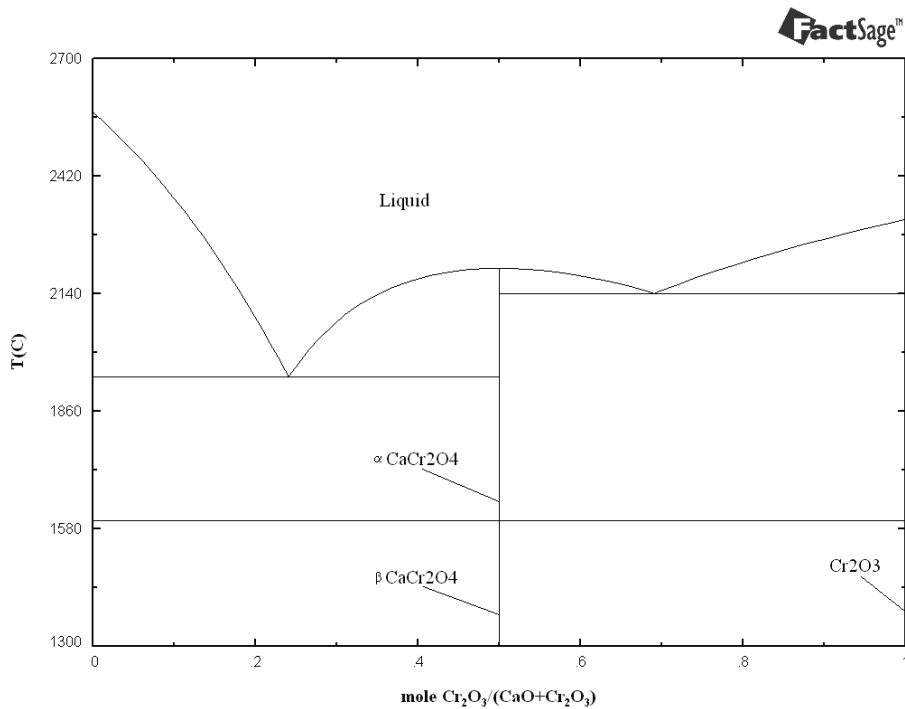


Figure 5. CaO-Cr₂O₃ phase diagram; $p_{O_2} = 1 \times 10^{-5}$ [atm]

Still, phase diagrams can be done which take into consideration oxygen partial pressure *versus* metallic mole ratio (see next system for details).

3.3 Cr-O-Ca-Si

For the Cr-O-Ca-Si system, six composition axes are possible and together they generate a *composition* tetrahedron volume.

As already seen, for the Ca-O axis, CaO-phase is the single point of interest. Same concept can be applied to the Si-O axis; now SiO₂ (in fact: trydimite,

cristobalite, etc.) is the sole existing phase. Oxygen is treated by two different manners: (i) either as a gas phase under *fixed* pressure (same way as before) – or (ii) as a gas under a *variable* pressure – set on the system by the equilibrium Cr / oxides. Due to the chromium dependence on oxygen, Cr-O is, therefore, the last axis. When under the first condition – depending on the pressure magnitude –, both or each of Cr or Cr₂O₃ phases can take part in the equilibrium state, while, in the last situation, chromium will always be present.

Phase diagrams under *fixed* oxygen pressure (Figure 6) can be seen in some works and correspond to the first option.

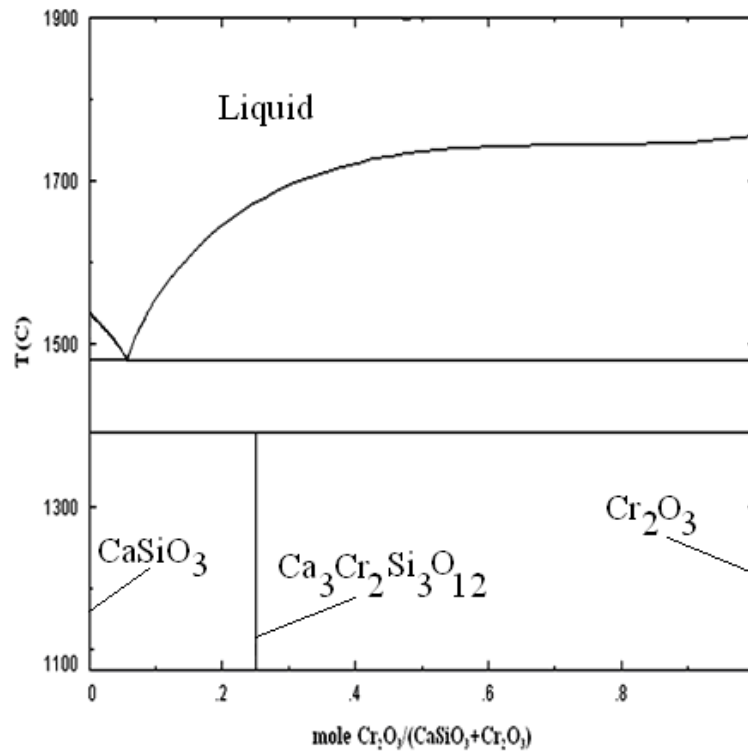


Figure 6. Phase diagram CaSiO₃-Cr₂O₃; $p_{O_2} = 1 \times 10^{-10}$ [atm]

And, as mentioned, phase diagrams which take into consideration oxygen partial pressure *versus* metallic or oxide mole ratio should be much more useful than those displaying temperature *versus* mole ratio – since furnace temperature is, to a certain extent, constant –, but they are not usual (Figure 7).

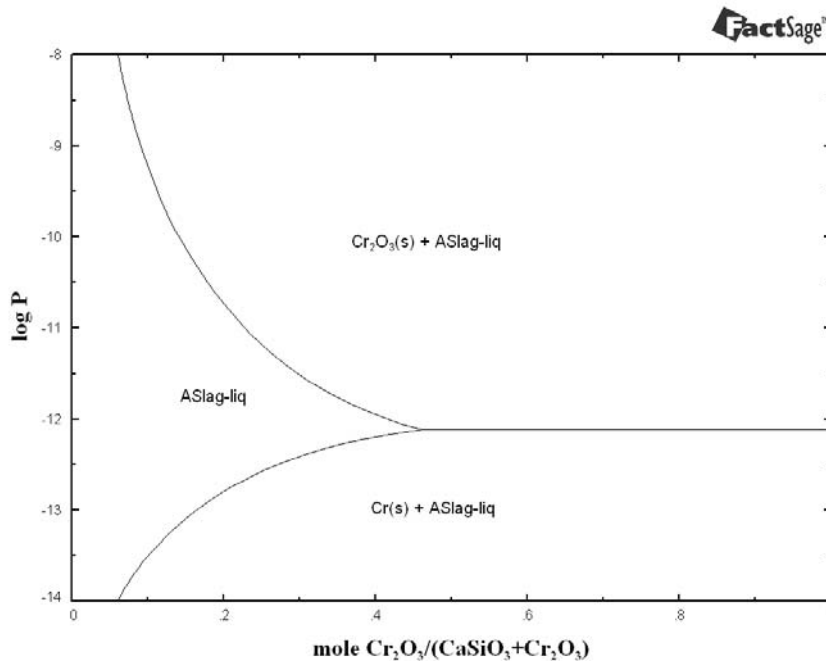


Figure 7. Phase diagram CaSiO₃-Cr₂O₃; T = 1600[°C]; pressures in [atm]

Figures 6 and 7 are, actually, cross-sections at isobasicity (CaO / SiO₂ = 1, here) of the pseudo-ternary CaO-SiO₂-CrO_x. While the pseudo-ternary allows for the whole range of basicities, cited figures explore the effects of temperature and pressure. They all are part of the composition triangle CaSiO₃-Cr-O (Figure 8), which is actually a section of the composition tetrahedron Cr-O-Ca-Si.

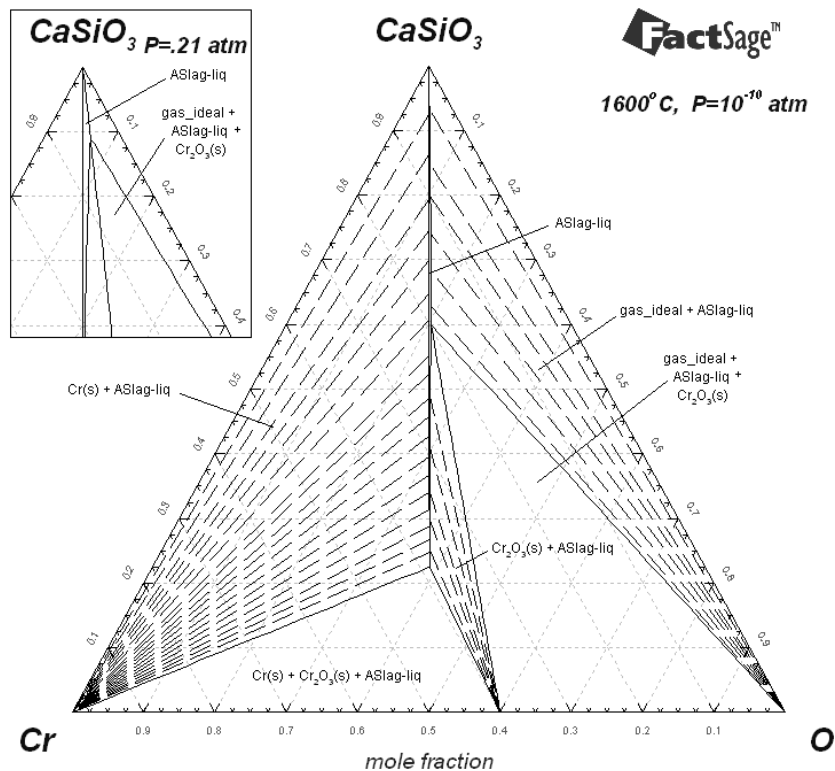


Figure 8. Phase diagram Cr-O-CaSiO₃ at two single pressures

Notice the different atomic mole ratios selected to plot these diagrams.

CaO-SiO₂-CrO_x – in the same way as the previously seen systems and unlike the ‘white’ oxides CaO-SiO₂-Al₂O₃ – forms a pseudo-ternary subsystem which is fully dependent on the oxygen pressure. To the researcher, therefore, remains the decision, again, of how to set the oxygen pressure for his/her investigation.

Morita *al.*,⁽⁴⁾ for example, studied the activity of chromium oxide for slags of this subsystem under constant pressure of 7.04×10^{-6} [Pa].

The other general option – chromium always present, or chromium activity (with reference on the metallic chromium) equal to 1 – was used,⁽⁵⁾ when determining activities of the same oxide in slags.

4 CONCLUSIONS

Some common peculiarities of chromium containing systems, which lead to misunderstanding of the information given in technical or scientific reports, were addressed here and discussed.

As long as the engineer/student continues gaining familiarity with the fundamentals of thermodynamics and identifies misleading diagram appearances (what otherwise would lead to uncertainties and contribute to the misunderstanding of information), production will run under a scientific/technological base and industry processes can have a superior performance.

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