

ON THE HETEROGENEITY OF AOD SLAGS IN DIFFERENT STAGES OF BLOWING

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Depending on composition and temperature, pyrometallurgical slags are not always completely molten, but can contain significant amounts of solid phases. These solid phases may be slag forming agents (e.g. lime or doloma) or other added materials that are not yet molten and dissolved into the molten slag phase.

Additionally, slag heterogeneity may also be a result of composition and conditions in which some solid phases are thermodynamically stable with the molten phase. The purpose of this study was to study slag heterogeneity in the Argon-Oxygen-Decarburisation (AOD) process while producing austenitic stainless steels. Thermodynamic calculations were used to compute the amounts and compositions of molten and solid phases using slag compositions typical for different stages of the AOD process as initial values. In addition to slag composition, the effect of temperature was also studied.

KEYWORDS: AOD PROCESS – SLAG – THERMODYNAMIC MODELLING – SOLID PHASES – STAINLESS STEELMAKING

INTRODUCTION

Argon-Oxygen-Decarburisation (AOD) process is used for refining stainless steels. Replacement of oxygen with nitrogen and argon during the latter stages of the AOD process enables decarburisation without excessive chromium losses. Chromium, which is oxidised during the oxygen blowing of the decarburisation stage, is reduced during the reduction stage with either silicon alloys or aluminium. The final stage of the AOD process is desulphurisation. In contemporary single-slag practice, desulphurisation is conducted as a part of the reduction stage. Different stages of the AOD process are illustrated in Table 1.

Tab. 1 – Stages of the AOD process.

Stage	Purpose	Approximate duration	Gas	Other remarks
A	Decarburisation	20-40 min	O ₂ (top, tuyères), N ₂ (tuyères)	Top blowing only in the beginning.
B	Reduction of oxides	5-8 min	N ₂ / Ar (tuyères)	Nitrogen replaced by argon in stages.
C	Desulphurisation	5 min	Ar (tuyères)	May be combined with the reduction stage

As seen from Table 1, different stages have different goals. Hence, the conditions and the slag compositions in the AOD process also vary from one stage to another. Slag composition is defined by oxidising components (iron, manganese, chromium, silicon, etc.), slag forming agents (CaO, MgO) and dissolved refractory materials (mainly MgO and CaO) [1]. Due to both thermodynamic (*i.e.* system with a composition and temperature under the liquidus temperature) and kinetic (*i.e.* solid particles not yet dissolved into the slag phase) restrictions, solid phases may exist within the molten slag phase making slag a heterogeneous mixture of various phases.

The purpose of this study is to illustrate the changes in the slag phase composition during the different stages

of the AOD process. Using this information, it is possible to optimise slag composition from the view point of its phase composition.

METHODS

The amounts and compositions of different phases during the different stages of the AOD process were calculated using a commercial thermochemical software FactSage version 7.2 and its FactPS and FToxid databases. Equilibria was calculated for the slag compositions presented in Table 2.

Tab. 2 – Slag compositions [wt-%] considered in this study.

Stage	CaO	SiO ₂	MgO	Fe ₂ O ₃	Cr ₂ O ₃	Al ₂ O ₃	TiO ₂	MnO	CaF ₂
1	48.0	28.0	8.0	1.0	2.0	8.0	3.0	2.0	0.0
1	48.0	28.0	7.0	1.0	3.0	8.0	3.0	2.0	0.0
1	48.0	28.0	6.0	1.0	4.0	8.0	3.0	2.0	0.0
1	48.0	28.0	5.0	1.0	5.0	8.0	3.0	2.0	0.0
1	48.0	28.0	4.0	1.0	6.0	8.0	3.0	2.0	0.0
1	48.0	28.0	9.0	1.0	4.0	5.0	3.0	2.0	0.0
1	48.0	28.0	8.0	1.0	4.0	6.0	3.0	2.0	0.0
1	48.0	28.0	7.0	1.0	4.0	7.0	3.0	2.0	0.0
1	48.0	28.0	6.0	1.0	4.0	8.0	3.0	2.0	0.0
1	48.0	28.0	5.0	1.0	4.0	9.0	3.0	2.0	0.0
1	48.0	28.0	4.0	1.0	4.0	10.0	3.0	2.0	0.0
2	52.0	8.0	5.0	8.0	20.0	1.0	0.5	5.5	0.0
2	45.5	7.0	4.5	10.0	25.0	1.0	0.5	6.5	0.0
2	39.0	6.0	4.0	12.0	30.0	1.0	0.5	7.5	0.0
2	32.5	5.0	3.5	14.0	35.0	1.0	0.5	8.5	0.0
2	26.0	4.0	3.0	16.0	40.0	1.0	0.5	9.5	0.0
3 (Si)	54.0	27.0	8.0	1.0	1.0	2.0	0.0	0.0	7.0
3 (Al)	58.0	5.0	8.0	1.0	1.0	27.0	0.0	0.0	0.0

The compositions shown in Table 2 represent the slags in the beginning of the process (marked “Stage 1” in Table 2; 0 minutes from the beginning), after the decarburisation stage (marked “Stage 2” in Table 2; 29 minutes from the beginning) and after the reduction stage (marked “Stage 3” in Table 2; 36 minutes from the beginning). For each stage an average composition was defined based on the values available in the literature [1,2]. Analysed slag compositions from the two AOD vessels at the Outokumpu Stainless Tornio steel plant in Finland were also used as a reference. These average compositions represent typical conditions in the AOD process and are written in **bold** in Table 2.

In addition to these average systems, the influence of few chosen variables was studied by changing the chemical composition and the temperature of the system. For the systems representing the slags in the beginning of the AOD process, the contents of Cr₂O₃ and Al₂O₃ were used as variables. Based on the slag compositions analysed from samples obtained from Outokumpu Stainless Oy, it was assumed that the content of MgO decreased as the content of either Cr₂O₃ and Al₂O₃ was increased. Temperature was varied between 1500°C and 1600°C. For the systems representing the situation in the end of the decarburisation stage, the contents of Fe₂O₃, Cr₂O₃ and MnO were used as variables. The contents of these three components were increased together in order to simulate the conditions with varying oxidation (*i.e.* high contents of these components indicating more oxidised slag). Temperature in these calculations was varied between 1700°C and 1800°C. Finally, two different compositions representing the slags in the end of the reduction stage was

studied: one composition for reduction with silicon alloys and another for reduction with aluminium. Temperature was varied between 1600°C and 1700°C. The used composition variables are written in *italics* in Table 2.

RESULTS

The results of the calculations are shown in Figures 1-4. Variations in the fraction of the liquid phase as a function of blowing time are illustrated in Figure 1. Typical values in Figure 1 represent the liquid fraction for the slag compositions and temperatures considered as most representative for each stage; *i.e.* compositions written in bold in Table 2 and temperatures of 1550°C, 1750°C and 1650°C for beginning, end of the decarburisation stage and end of the reduction stage, respectively. Minimum and maximum values represent the lowest and the highest values for the liquid fraction within the composition and temperature ranges used in the calculations.

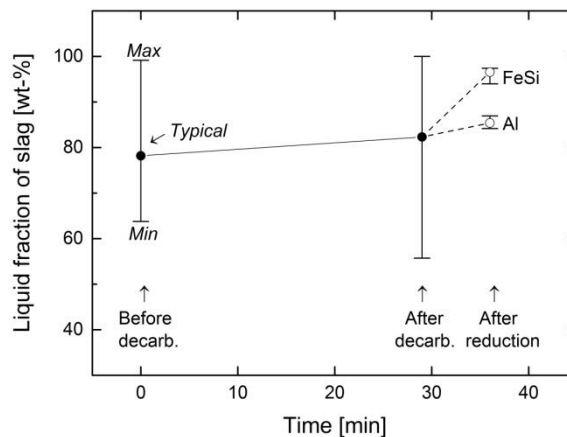


Fig.1 – Fraction of the liquid phase during the different stages of the AOD process.

Figure 2 illustrates the effect of varying Cr_2O_3 and Al_2O_3 contents on the liquid fraction in temperatures of 1500°C, 1550°C and 1600°C at the beginning of the decarburisation stage. It is seen that the liquid fraction is increased with increasing temperature and decreasing Cr_2O_3 content, whereas Al_2O_3 content does not have a significant effect on the liquid fraction. Solid phases stable in these systems are dicalcium silicate (Ca_2SiO_4) and spinel solid solution containing magnesium, chromium and aluminium.

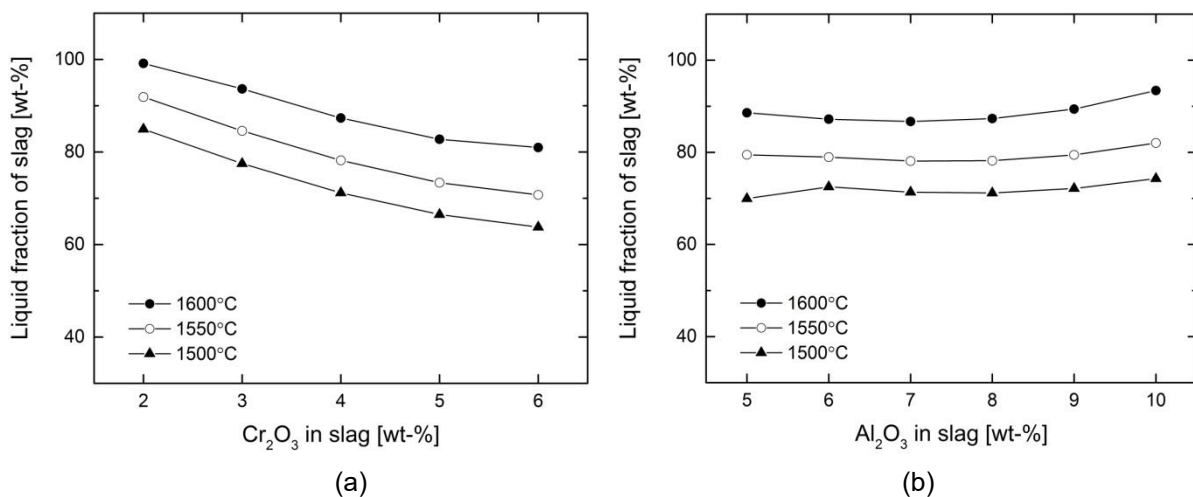


Fig.2 – Fraction of liquid phase in the beginning as a function of (a) Cr_2O_3 content and (b) Al_2O_3 content.

Figure 3 illustrates the effect of varying Fe_2O_3 , Cr_2O_3 and MnO contents on the liquid fraction in temperatures

of 1700°C, 1750°C and 1800°C at the end of the decarburisation stage. Five cases presented in Figure 3 represent varying oxidation states of the slag with case 1 being the least oxidised and case 5 the most oxidised situation. The pursued – and the most common – situation is in the region of cases 2 and 3, where the fraction of the liquid phase is largest. It is also seen that temperature has a large effect on the liquid fraction – especially in the region where the slag is less oxidised (*i.e.* cases from 1 to 3). Solid phases stable in these systems are CaCr_2O_4 and Ca-rich monoxide solid solution in less oxidising conditions and CaCr_2O_4 and spinel solid solution containing magnesium, chromium and iron in more oxidising conditions.

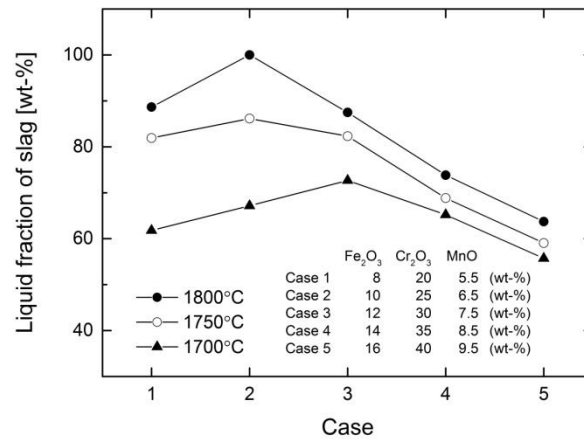


Fig.3 – Fraction of liquid phase at the end of the decarburisation stage in five cases representing varying oxidation states of the slag. Case 1 is the least oxidised whereas case 5 is the most oxidised case.

According to the analyses of the samples from Outokumpu Stainless Oy, the variations in the slag compositions at the end of the reduction stage are relatively small. Obviously the slag compositions are very different depending on the reducing agent that are being used (either silicon alloys or aluminium), but otherwise the compositional variations are much smaller in comparison to previous stages. Therefore the liquid fraction on this stage was only studied for two compositions presented in Table 2. Figure 4 illustrates the effect of temperature (from 1600°C to 1700°C) on the liquid fraction of the slag system for ferrosilicon and aluminium reductions.. It can be seen that in the case of FeSi reduction the liquid fraction is nearly 100% owing to the addition of CaF_2 , which is an effective flux, but makes the slag aggressive towards refractory lining [3]. The solid phase stable in these systems is Ca-rich monoxide solid solution.

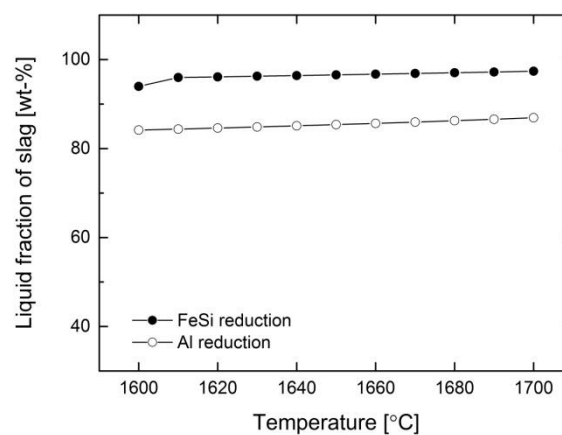


Fig.4 – Fraction of liquid phase at the end of the reduction stage as a function of temperature for aluminium and ferrosilicon reductions.

DISCUSSION

The results shown in Figures 1 to 4 indicate that there are large variations in the amounts and compositions of the solid phases during the different stages of the AOD process. For typical slag compositions and average process temperatures, the fraction of the liquid phase increases slightly as the process proceeds from the decarburisation to the reduction stage. The liquid fraction at the end of the reduction stage is larger for the FeSi reduced slag in comparison to the slag reduced with aluminium.

In addition to this general trend of increasing liquid fraction, there may be large variations in the amounts of solid phases due to variations in either slag composition or temperature. Depending on these variables, the combined fraction of solid phases may vary between 0% and 40%. Even small variations in the Cr_2O_3 content in the beginning or in temperature at the end of the decarburisation stage may have a significant effect on the heterogeneity of the slag system.

Systematic comparisons between the calculated results and analysed process samples have not been made within this study. However, it is possible to make a few comments based on the observations from the actual process:

- Lime and doloma are added to the AOD process as a slag forming agents during the early decarburisation stage. Owing to their relatively slow dissolution rate, undissolved lime particles are frequently found from samples taken during the decarburisation stage [4,5]. Figure 5 shows an example of undissolved lime particle surrounded by a solid shell. However, the occurrence of these undissolved lime particles cannot be estimated based on the results presented in previous chapter because dissolution kinetics are not taken into account in thermodynamic equilibrium calculations.
- Liquid fraction at the end of the reduction stage is very high – especially for the FeSi reduction. In a real process, the temperature of the top surface of the slag is likely to be lower than that of the lower surface – which is in direct contact with molten metal – due to heat losses to converter atmosphere. Since the liquid fractions presented in Figure 4 are calculated for isothermal systems in temperatures corresponding the conditions in contact with the metal bath, it is likely that in practice the fraction of solid phases is larger (especially close to the top surface) than the one presented in this study.



Fig.5 – Undissolved lime particle in the solidified slag sample. Sample is taken during the decarburisation stage.

The occurrence of solid phases has diverse effects on the process. With other variables held constant, an increase in the solid fraction of the slag increases its effective viscosity and may increase the metal losses associated with metal droplets entrapped in slag. An example of metal droplets within slag is shown in Figure

6 [2]. Existence of metal droplets within AOD slags is also reported by Lindstrand *et al.* [5]. Results of computational fluid dynamics simulations suggest that a more viscous slag decreases the intensity of vessel oscillation [6]. Nevertheless, it needs to be kept in mind that a less viscous slag is can penetrate the refractory material more easily.

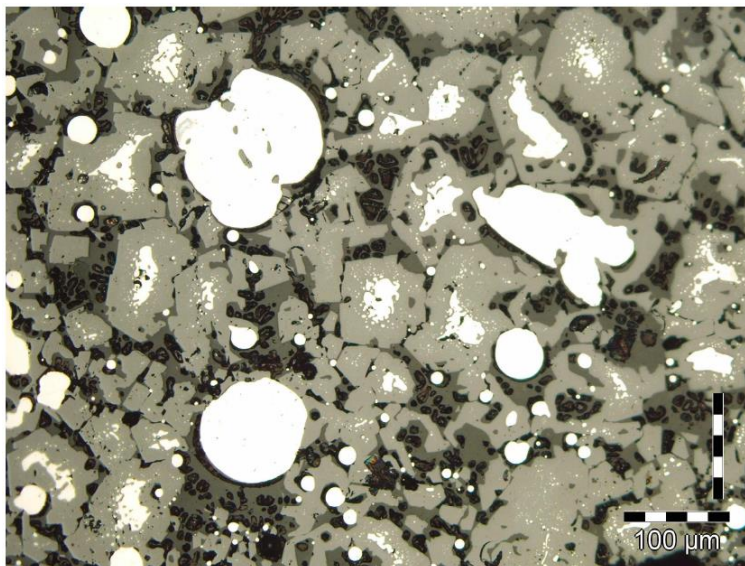


Fig.6 – Metal droplets inside solidified slag sample from the decarburisation stage. Figure taken from [2].

SUMMARY

The purpose of this study is to study the changes in the slag phase composition during the different stages of the AOD process. The amounts and compositions of different phases during the different stages of the AOD process were calculated using a commercial thermochemical software FactSage version 7.2 and its FactPS and FToxid databases. The calculated slag compositions represent the compositions before the decarburisation stage, after the decarburisation stage, and after the reduction stage. The results indicate that the liquid fraction of slag increases towards the end of the decarburization stage and achieves its peak value in the subsequent reduction stage. The increase in the liquid fraction is mostly due to increase in temperature during the decarburisation stage. In the decarburization stage, the effect of temperature on the liquid fraction was more pronounced when the slag contained a relatively low content of oxidized metallic. A high liquid fraction can be advantageous for reducing vessel oscillation and metal losses, but can lead to faster refractory wear. Finally, it was suggested that owing to temperature gradients, the slag phase composition is likely to vary from lower surface to top surface. The results can be used for improving the slag practice from the view of slag phase composition.

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