Modelling of the Refining Processes in the Production of Ferrochrome and Stainless Steel

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1. Introduction

In stainless steel production - as in almost any kind of industrial activity - it is important to know what kind of influence different factors such as process variables and conditions have on the process outcome. In order to productionally, economically and ecologically optimize the refining processes used in the production of stainless steels, one has to know these connections between the process outcomes and the process variables. In an effort to obtain this knowledge, process modelling and simulation - as well as experimental procedures and analyses - can be used as valuable tools (Heikkinen et al., 2010a).

Process modelling and optimization requires information concerning the physical and chemical phenomena inside the process. However, even a deep understanding of these phenomena alone is not sufficient without the knowledge concerning the connections between the phenomena and the applications because of which the process modelling is carried out in the first place. The process engineer needs to seek the answers for questions such as: What are the applications and process outcomes (processes, product quantities, product qualities and properties, raw materials, emissions, residues and other environmental effects, refractory materials, etc.) that need to be modelled? What are the essential phenomena (chemical, thermal, mechanical, physical) influencing these applications? What variables need to be considered? What are the relations between these variables and process outcomes? How these relations should be modelled? (Heikkinen et al., 2010a)

The purpose of this chapter is to seek answers to these questions in the context of ferrochrome and stainless steel production using models and modelling as a connection between the phenomena and the applications. The role of the modelling - as well as other methods of research and development - as a connective link between the applications and phenomena is illustrated in Figure 1. It should be noted that due to sake of clarity Figure 1 does not contain all the applications, methods nor phenomena that could be related to the production of ferrochrome and stainless steels. Its purpose is to be merely an example of how the link between the applications and phenomena is created via modelling, analyses and experiments.

Although one aim for this chapter has been to present the current state of the modelling concerning the refining processes in the production of ferrochrome and stainless steel, the main goal is not to give a comprehensive outlook on all the models that are being used in the modelling of the stainless steel production processes, but to illustrate the methods,



Fig. 1. Role of R&D methods as a connective link between the applications and the phenomena.

variables and dependences that are required to know in the optimization of these processes. In this sense some very useful process models may have been omitted here if it is considered that the questions mentioned above have already been answered by using other models as examples. All the examples presented in this chapter have been published before either by the authors and their colleagues or by other scientists in scientific papers. Although most of the examples presented in this chapter are related to the processes used in the Outokumpu Chrome and Outokumpu Stainless Tornio works, the results can be considered as general due to phenomenon-based nature of the models.

2. Stainless steel and ferrochrome

The amount of stainless steel that is annually produced worldwide has increased from approximately 19 million metric tons in 2001 to approximately 31 million metric tons in 2010 (International Stainless Steel Forum [ISSF], 2011a). Although this is not much when compared to the total annual production of crude steel (being approximately 1414 million metric tons in 2010; World Steel Association, 2011), there are certain areas of application in which the stainless steels have an essential role due to their resistance against corrosion (e.g. in construction, transport, process equipment and catering appliances). Corrosion resistance

is achieved by using chromium as an alloying element. In oxidizing conditions a thin yet dense layer is formed on the surface of the metal if the chromium content of the metal is over approximately 12 w-% (e.g. Wranglén, 1985). This layer passivates the metal and prevents corrosion in several corrosive media.

In addition to chromium - whose content may vary from 12 w-% to nearly 30 w-% - stainless steels also contain other alloying elements that are used to adjust the structure as well as physical and chemical properties of the final product. The most commonly used grades of stainless steels are austenitic steels in which nickel is a third major component in addition to iron and chromium. Other major stainless steel categories are ferritic stainless steels (no nickel), martensitic stainless steels (less chromium in comparison to e.g. austenitic grades) and duplex steels (more chromium, some nickel). Additionally, some other elements are used in certain grades to enhance certain critical properties (e.g. molybdenum to enhance the corrosion resistance against acids) or to stabilize a certain structure (e.g. manganese to replace nickel as austenite stabilizer). Typical contents of main elements for different stainless steel grades are presented in Table 1.

Grades	Cr	Ni	С	Si	Mn	Others	AISI
Austenitic	16-20	> 8	< 0.1	<1	< 2	Mo,Nb, Ti	e.g. 304, 216 217
Ferritic	11.5-17	-	< 0.1	<1	< 1	Al,Ti	e.g. 405
Martensitic	11.5-17	- / < 2.5	0.1-0.4	<1	< 1	,	e.g. 403, 410,414
Duplex	> 22	4-6				Мо	
Cr-Mn Austenitic	16-18	1-8	< 0.1	<1	5-10		

Table 1. Typical compositions (in w-%) of the different kind of stainless steel grades (collected from various sources).

Since all stainless steels contain chromium, it is necessary either to alloy chromium or to use chromium-containing raw materials (e.g. ferrochrome and stainless steel scrap) in the production of stainless steels. From the economic point of view, the latter option is more suitable than the former. Concerning these raw materials mentioned above, ferrochrome is usually produced from chromite ores and concentrates, in which both of the stainless steel's main components - i.e. iron and chromium - are present. Since the occurence - and hence also the availability - of these raw materials is globally rather limited (Riekkola-Vanhanen, 1999), the use of internal and/or recycled merchant stainless steel scrap as a raw material is essential in the production of stainless steels. For instance, in 2010 over 5 million metric tons of stainless steel scrap were exported worldwide (ISSF, 2011b) and it is estimated that the average content of recycled material in new stainless steel is over 60 % (ISSF, 2011c). The end-of-life recycling rate of stainless steels is approximately 70 % (Reck et al., 2010).

Typical compositions of ferrochrome as well as chromite ore and concentrates are presented in Table 2. The compositions of the stainless steel scrap correspond with the compositions presented already in Table 1.

	Cr	Fe	С	Si	0	Others
Ferrochrome	53-55	33 / 37	7	3-5	-	
Chromite ores and	25 21	12 10		16	32 37	Al 4-15
concentrates	25-51	12-19	-	1-0	52-57	Mg 7-13

Table 2. Typical compositions (in w-%) of ferrochrome as well as chromite ores and concentrates (collected from various sources).

3. Production of ferrochrome and stainless steel

As it was mentioned above, stainless steels are solutions of iron and chromium as well as other alloying elements that are used in order to obtain wanted chemical and mechanical properties for the final products. In the production of these highly alloyed steels it is important to utilize processes in which the yields of the valuable elements - such as chromium - are as high as possible. For the unit operations in which undesirable elements - such as carbon, silicon or sulphur - are to be removed, this obviously sets certain challenges that are not encountered in the production of low-alloyed steels. Taking decarburization as an example, it is necessary not only to decrease the amount of carbon to a required level, but to prevent excessive oxidation of chromium at the same time. This means that although there are certain similarities in the production routes of stainless and low-alloyed steels, some unit operations - such as decarburization mentioned above - are usually executed using different kind of process solutions in comparison to low-alloyed steelmaking.

One of the key issues in the production of stainless steels is in fact to solve how to execute this decarburization without the simultaneous oxidation of chromium; *i.e.* how to promote the oxidation reaction of carbon presented in Equation (1) and to prevent the oxidation reaction of chromium presented in Equation (2):

$$\underline{C}_{Fe} + \underline{O}_{Fe} = CO(g) \tag{1}$$

$$2 \underline{Cr}_{Fr} + 3 \underline{O}_{Fe} = (Cr_2O_3)_{Slag}$$
⁽²⁾

Equilibrium constants (K) for reactions (1) and (2) are presented in Equations (3) and (4), respectively:

$$K_{(1)} = \frac{p_{CO}}{a_C \cdot a_O} = e^{\frac{\Delta G_{(1)}^0}{R \cdot T}}$$
(3)

$$K_{(2)} = \frac{a_{Cr_2O_3}}{a_{Cr}^2 \cdot a_0^3} = e^{-\frac{\Delta G_{(2)}^0}{R \cdot T}}$$
(4)

in which p_i represents the partial pressure of component i, a_i representes the activity of component i, $\Delta G^0_{(x)}$ is standard Gibbs free energy for reaction (x) [in J·mol⁻¹ or cal·mol⁻¹], R is the gas constant [in J·mol⁻¹·K⁻¹ or cal·mol⁻¹·K⁻¹] and T is temperature [in K].

It is seen from Equation (3) that in order to enhance the oxidation of carbon (at constant temperature) one has to either increase the activity (and amount) of oxygen or to decrease the partial pressure of carbon monoxide in the system. According to Equation (4) the

increase in the activity of oxygen enhances also the oxidation of chromium and hence the only option is to decrease the partial pressure of CO. In order to do this, it is possible either to dilute the gas by blowing inert gases such as nitrogen and/or argon into the system or to decrease the total pressure of the system. The former method is used in AOD converters (Argon Oxygen Decarburization), whereas the latter is utilized in VOD converters (Vacuum Oxygen Decarburization).

In order to properly execute the decarburization, either AOD or VOD converter is used in nearly all stainless steel production routes. The AOD converter is more commonly used as approximately three quarters of the stainless steel world production is manufactured using an AOD. (Choulet & Masterson, 1993; Jones, 2001) On the other hand, the charge sizes of the VOD converter are usually smaller than the ones of the AOD, and therefore it is often used in the steel works in which the annual production is smaller.

Evidently stainless steel production consists of several other unit operations in addition to AOD (or VOD). These other processes are chosen based on the steel grades that are being produced as well as the raw materials that are being used. In the scrap-based stainless steelmaking, electric arc furnace (EAF) is used to melt the scrap, after which the molten metal is further processed in AOD, VOD and/or various ladle treatments depending on the requirements set by the product. In other words the melting of the material and the metallurgical processing (*i.e.* mainly decarburization) are separated from one another into two independent processes. If ferrochrome is used as a raw material, it is also melted in the EAF, unless the production of ferrochrome plant to the stainless steel plant. As for ferrochrome, it is most commonly produced in submerged arc furnaces (SAF) using chromite ores and/or concentrates as raw materials. A so-called (ferro)chrome converter (CRK) can also be used as a pretreatment process between SAF and AOD, if ferrochrome is transfered to stainless steel plant in a molten state.

A schematic presentation of the AOD process is presented in Figure 2. Due to geometrical similarities between the AOD and CRK processes, Figure 2 also gives an impression of what a CRK process looks like.



Fig. 2. Schematic presentation of an AOD converter. It should be noted that the ferrochrome converter is geometrically very similar to AOD presented in this figure.

The AOD (or VOD) is followed by e.g. ladle treatments, continuous casting, slab grinding, hot and cold rolling as well as pickling and annealing. However, these processes are omitted in this study, since the focus is on the refining processes preceeding these operations.

An example of the stainless steel production route is illustrated in Figure 3 in which the process flow sheet of the Outokumpu Stainless and Outokumpu Chrome Tornio Works in Finland is presented. The reason for choosing Tornio Works as an example is not only the fact that most of the models presented in the following section are validated using data from Tornio, but also because as an only integrated stainless steel plant in Europe (Riekkola-Vanhanen, 1999) it features most of the unit operations that are relevant for stainless steelmaking. In fact, VOD is the only significant process of stainless steelmaking that is not included in the Tornio works process route.



Fig. 3. Schematic presentation of the stainless steel production at the Outokumpu Chrome and Outokumpu Stainless Tornio Works (materials are presented in white boxes and processes in grey boxes).

The following section focuses on the refining processes of the ferrochrome and stainless steel production illustrated as dark grey boxes in Figure 3 (*i.e.* SAF, EAF, CRK and especially AOD), whereas the process steps illustrated as light grey boxes are omitted. From the modelling's point of view, the VOD converter, which is not included in Figure 3 and which is omitted in the next section, has many similarities with the AOD and therefore many things concerning the modelling of AOD can be applied to VOD, too, as long as the effect of reduced pressure can be taken into account.

4. Modelling of the refining processes

As seen already in Figure 1, the target of the modelling may be either processes (i.e. process modelling) or material properties and phenomena (i.e. phenomenon-based modelling). The phenomenon-based modelling may be further divided into analytical, numerical and physical modelling. Analytical models consist of pure equations describing the effect of certain variables on the modelled property in a way that is solvable analytically. In numerical models these interdependencies between the properties and certain variables are to be solved using numerical optimization and minimisation methods. Typical examples of numerical modelling are computational fluid dynamics (CFD) and computational thermodynamics (CTD). In addition to these computational models, some models are based on physical analogies between a real system and a physical model. An example of this kind of physical modelling is the modelling of metal and/or slag flows using small scale water models.

The purpose of this section is to present the essential features that need to be considered in the modelling of the SAF, EAF, CRK and AOD processes used in the production of ferrochromium and stainless steels (cf. Table 3). Although few more comprehensive models

Process	SAF	EAF	CRK	AOD	
Main purpose	Reduction of chromite	Melting of scrap	Silicon removal	Decarburization	
	Reduction of	Prevention of oxidation of chromium	Removal of silicon (and partly	Decarburization Control of	
Key issues to be modelled	chromite into ferrochrome	Energy consumption	carbon) from metal	nitrogen pickup	
	Energy consumption	Slag foaming	Prevention of oxidation of	oxidation of chromium	
		Removal of carbon	chromium	Sulphur removal	
Influencing factors	Reduction reactions	Heat transfer Electric potential	Oxidation and reduction reactions (metal, slag)		
	Electric potential Chemical and	Formation, stability and	Reaction surface and surface properties		
	mineralogical composition and	behaviour of electric arc	Convection		
	structure of raw materials	Viscosities	Viscosities		
Variables needed to be considered in the modelling Amounts, compositions and grain size distributions of raw materials		Amounts and compositions of raw materials FeSi and coke additions	Blowing practice (durations of different stages; proportions of oxygen, nitrogen and argon in different stages; lance height; top/bottom blowing)		
		Electric currents	Lime and scrap additions		

Table 3. Essential features in the modelling of the phenomena taking place in the production processes of ferrochrome and stainless steel.

are also presented in addition to phenomenon-based modelling, the goal is not to present any factory-specific process models, but to consider the phenomena - as well as the factors influencing these phenomena - that need to be understood in the control of these processes. The modelling as well as its results and validation concerning each individual process is presented in more detail in subsections 4.1 to 4.4.

4.1 Submerged arc furnace, SAF

The purpose of SAF is to produce ferrochrome by reducing chromite ores and concentrates. Whereas iron oxides can be reduced into iron with carbon in for example blast furnaces, the reduction of chromium with carbon requires temperatures too high to be implemented in blast furnace type ovens. SAF, which is the best available technology for high carbon ferrochrome production, uses electric current to increase temperature and to enhance the reduction reactions of the chromite. (Riekkola-Vanhanen, 1999) Concerning the modelling of this process, it is necessary to know what is the influence of the used electric current on the physical and chemical properties of the used materials (i.e. ores, concentrates, coke, silica) as well as on the physical and chemical phenomena taking place in the furnace (i.e. chemical reactions, heat transfer, flow patterns, electric conduction, and so on). With this information it is possible to estimate, how the amount and quality of the product as well as the energy consumption of the process are influenced if the electric current or the amounts, compositions and/or grain size distributions of the raw materials were being changed.

Although the reduction reactions of the chromite have been studied by e.g. Dawson & Edwards (1986), Niayesh & Dippenaar (1992), Xiao et al. (2004), Chakraborty et al. (2005) and Zhao & Hayes (2010), the influece of the electric current on the reduction reactions is usually omitted as anything else but a heat source (Rousu et al., 2010). Experiments conducted by Rousu et al. (2010) indicated the enhancing effect of electric current on the reduction reactions thus giving a little information concerning the dependancies between the current and the reactions. On the other hand, based on the analyses of the samples taken from the actual SAF process, Ollila et al. (2010) have concluded that the electrical properties of the materials change drastically as the reduction of the chromite proceeds. The same study also indicated the circulation phenomena of zinc, sulphur and the alkali that need to be considered in the modelling of the SAF process. (Ollila et al., 2010) However, the amount of information at the moment is not sufficient enough for proper modelling of the SAF phenomena and more experimental research is required before comprehensive models concerning the SAF could be presented. An extensive review on the research concerning the chemical reactions inside the SAF in the ferrochrome production is provided by Hayes (2004).

4.1.1 SAF in the production of other ferroalloys

At this point it is worth mentioning that the SAF process is used in the production of other ferroalloys, too. For example ferrosilicon and ferromanganese are being produced with SAF type processes. (e.g. Batra, 2003; Slizovskiy & Tangstad, 2010; Tang & Olsen, 2004) Concerning the modelling of these processes, it is necessary - as it is in the production of ferrochrome - to know the influence of the electric current on the physical and chemical properties and phenomena within the furnace. In the thermodynamic modelling of the ferroalloys production systems, the most important phases to be modelled are the liquid

slag and the metal alloy itself (Tang & Olsen, 2004). Despite the existing similarities, production of each ferroalloy has also its own characteristic features that needs to be taken into account in the modelling of these processes.

The production of ferrosilicon consists of quartzite reduction using charcoal, pitch coke, petroleum coke, coke breeze or anthracite as reducing agents. The iron is provided to the system with the addition of steel chips, iron ores or mill scales. The obvious difference to the ferrochrome production is the higher stability of SiO₂ in comparison to Cr_2O_3 or FeCr₂O₄. This means that more energy is required for the reduction of SiO₂. In addition to this, one has to consider the possible formations of SiC and gaseous SiO. Thermodynamic calculations concerning the reduction of quartzite with carbon indicate that the formation of SiC may become a problem when the silicon content of the metal exceeds 22 w-%. On the other hand, the formation of SiO-gas my decrease the silicon yield in higher temperatures. (Batra, 2003)

In the modelling of the ferromanganese production, one also has to consider the influences of potassium and zinc compounds that are always present in the raw materials. The concentrations of these elements may increase in the furnace due to circulation phenomenon and hence lead to problems such as coke particle disintegration, formation of hard bank materials and irregular flows in the furnace. (Slizovskiy & Tangstad, 2010)

Concerning the modelling of the chemical and physical properties of the slags in the ferroalloys production, a comprehensive reviews on the topic has been provided by Lehmann et al. (2004) and Jahanshahi et al. (2004).

4.2 Electric arc furnace, EAF

The main purpose of EAF is to melt scrap with electricity and hence make it possible to perform melting and decarburization in two separate unit operations (i.e. EAF and AOD), although it is possible to perform decarburization also in the EAF. Since melting is in question, one of the most important things to be considered is obviously the heat transfer between the electric arc and the metal. Other key elements in the control of the EAF process are to prevent the oxidation of chromium (if/when chromium-alloyed scrap is being used), to stabilize the arc and to minimise specific energy consumption as well as to create a foamy slag that protects the refractory materials from the electric arc, lowers energy consumption, stabilizes the arc and insulates the metal from the atmosphere. (Alexis et al. 2000; Arh & Tehovnik, 2007; Kerr & Fruehan, 2000) The process variables that can be used to control these phenomena are the amounts and compositions of the raw materials, FeSi and coke additions, use of slag formers and the use of electricity at different stages of the process.

Heat transfer between the arc and the metal with different currents and arc lengths has been studied with computational fluid dynamics (CFD) in which the arc is treated as a fluid with temperature-dependent properties. The model in which various mechanisms of heat transfer (i.e. radiation, convection, condensation and energy tranported by electrons) were taken into account indicated that although the contribution of electrons on the heat transfer is significant at the center of the system, the radiation and convection seem to be more dominant in general. The longer the arc, the more dominant is the role of radiation in the system. (Alexis et al. 2000) In addition to CFD, physical modelling has also been used in the

investigation of the injection treatments in the EAF. The effect of lance height, lance angle and gas flow on the cavity that is formed at the melt surface when blowing oxygen into EAF is one of the applications for which the physical water models has been used in the context of EAFs. (Whitney 2003)

The oxidation of chromium in the EAF process has been studied with thermodynamic calculations, according to which the oxidation of chromium may be decreased with aluminium and silicon additions, since these two elements have a higher affinity for oxygen than chromium. On the other hand, the oxidized chromium may be reduced from the slag back to metal by using ferrosilicon, carbon, calcium carbide or aluminium. (Arh & Tehovnik, 2007; Park et al., 2004) When modelling the oxidation reactions, one always has to consider the competing oxidation reactions of carbon, chromium and silicon as well as in some cases aluminium and titanium.

Studies concerning the reduction of Cr_2O_3 as well as other oxides (MnO, FeO and SiO₂) from the EAF slags by using either carbon or aluminium as reductant indicate that the reduction is controlled by diffusional mass transfer in the slag phase. The mass transfer coefficient describing the diffusion rate of a certain oxide in the slag was found to be largest for MnO and clearly smallest for SiO₂. The coefficients describing the mass transfers of Cr_2O_3 and FeO are close to one another and slightly smaller than the one for MnO, although considerably higher than the one for SiO₂. However, the overall reduction degrees of these oxides decresed in the order of MnO (90 %), Cr_2O_3 (70 %), SiO₂ (59 %) and FeO (40 %). (Park et al., 2004)

EAF slag's ability to generate foam from injected or generated gas can be quantified with the foam index, Σ , for which the mathematical definition as well as the correlation with the slag properties is given in equation (5) (Ito & Fruehan, 1989; Kerr & Fruehan, 2000, 2002, 2004; Zhang & Fruehan, 1995):

$$\Sigma = \frac{H_f}{V_g^s} = \frac{H_f}{\frac{Q}{A}} = \frac{H_f \cdot A}{Q} = 115 \cdot \frac{\mu^{1.2}}{\gamma^{0.2} \cdot \rho \cdot D^{0.9}}$$
(5)

in which H_f indicates the foam height [in m] and V_g^s is the superficial gas velocity [in m·s⁻¹] defined as a ratio between the gas flow rate, Q [in Nm³·s⁻¹], and the cross sectional area of the vessel or crucible, A [in m²]. In the latter part of the equation (5), μ represents slag's bulk viscosity [in Po], γ slag's surface tension [in N·m⁻¹], ρ slag's density [in kg·m⁻³] and D the bubble diameter [in m]. (Ito & Fruehan, 1989; Kerr & Fruehan, 2000, 2002, 2004; Zhang & Fruehan. 1995).

It has been observed that as the Cr_2O_3 content of the slag is increased, the foam index stays constant for a while (up to approximately 8 %), after which there is a small increase in the values of the foam index in the Cr_2O_3 content range of approximately 8 to 13 %. If the Cr_2O_3 content is further increased, the excessive Cr_2O_3 begins to precipitate as a solid phase which increases the viscosity of the slag as seen from equation (6) and hence decreases the values of the foam index very rapidly. The critical Cr_2O_3 content over which the foam index decreases depends on temperature, slag composition and oxygen potential. (Arh & Tehovnik, 2007; Kerr & Fruehan, 2000, 2002, 2004)

$$\mu = \mu_0 \cdot \left(1 + 5.5 \cdot \xi\right) \tag{6}$$

in which μ is the bulk viscosity [in Po], μ_0 is the viscosity of the pure liquid [in Po] and ξ is the volume fraction of solid particles (Kerr & Fruehan, 2000, 2002). It has been concluded that the occurence of solid Cr₂O₃ particles in the slag is one of the reasons why slag foaming in stainless steelmaking is not as efficient as in the production of low-alloyed steels (Arh & Tehovnik, 2007; Kerr & Fruehan, 2000, 2002, 2004).

Another difference concerning the slag foaming between the productions of stainless and low-alloyed steels is the amount of FeO in the slag. In the stainless steelmaking the FeO content is usually considerably lower and hence the CO gas which is required for the slag foaming is not generated via the reaction between FeO and carbon, but via reactions of other oxides (e.g. CrO and Cr_2O_3) and carbon. Since the reaction rates for the reactions between chromium oxides and carbon are significantly lower than the one for reaction between FeO and carbon, it can be concluded that the CO formation is considerably slower when considering the production of stainless steels. (Arh & Tehovnik, 2007; Kerr & Fruehan, 2000, 2002, 2004)

The modelling of the electric arc itself and its influence on the chemical and physical phenomena occuring in the EAF is very complicated (cf. SAF). Even if the nature of the arc and its influence on e.g. chemical reactions were known, the modelling would be little more than educated estimations due to extremely high temperatures (which cannot be measured accurately) and the lack of material data and information in such high temperatures.

4.3 Ferrochrome converter, CRK

Ferrochrome converter is a link between the production of ferrochrome and stainless steel production. Its purpose is to enable the transfer of ferrochrome in a molten state from the ferrochrome plant to the stainless steel melting shop and to enable the utilisation of ferrochrome's chemical energy for scrap melting. During the CRK process oxygen is blown into the metal, due to which the silicon content of the metal is decreased from 4 to 5 w-% to less than 0.5 w-%. At the same time, the carbon content is decreased from approximately 7 w-% to approximately 3 w-%. Further decarburization would lead into excessive oxidation of chromium. Exothermic oxidation reactions of silicon and carbon release energy that is used to heat the metal and to melt scrap and slag formers. Although the purpose of CRK is different to more commonly used AOD converter, these two converters are geometrically very similar to each other with almost identical shape and both having sidewall tuyeres in addition to the top lance. (Fabritius & Kupari, 1999; Fabritius et al., 2001a, 2001b; Heikkinen et al., 2010b, 2011; Virtanen et al. 2004)

4.3.1 Thermodynamics

In the modelling of the CRK process it is essential to consider how the oxidation reactions of silicon, carbon and chromium (i.e. removal of silicon and carbon as well as prevention of chromium oxidation) are influenced by process variables such as metal and slag compositions as well as fluid flows and properties (e.g. viscosities). Knowledge concerning the interdependencies between the above mentioned oxidation reactions and process

variables enables the optimization of process parameters such as blowing practices and lime and scrap additions.

Thermodynamic computations validated with process samples from the Outokumpu Stainless Tornio steelworks have been used to estimate the chemical driving forces for the oxidation reactions of silicon, carbon and chromium (cf. equation (7) in which X represents Si, C and Cr) at the different stages of the process. (Heikkinen et al., 2010b, 2011)

$$\frac{2a}{b} \underline{X}_{Fe} + O_2(g) = \frac{2}{b} \begin{cases} (X_a O_b) \\ X_a O_b(g) \end{cases}$$
(7)

Thermodynamic equilibria of these oxidation reactions were compared with each other by using partial pressures of oxygen (p_{O2}) as parameters describing the equilibria. Smaller value of p_{O2} for a certain oxidation reaction indicate that less oxygen is needed for oxidation when compared to a reaction for which the value of p_{O2} is larger. The partial pressures were calculated using equations (8) and (8') the former being the equation for silicon and chromium (for which the oxidation products end up in slag) and the latter being the equation for carbon (for which the oxidation product is a gas). (Heikkinen et al., 2010b, 2011)

$$p_{O_{2}} = \frac{a_{X_{a}O_{b}}^{2/b}}{f_{X}^{2a/b} \cdot X_{X}^{2a/b}} \cdot e^{\left(\frac{\Delta G_{(7)}^{0}}{R \cdot T}\right)}$$
(8)

$$p_{O_2} = \frac{p_{X_aO_b}^{2/b}}{f_X^{2a/b} \cdot X_X^{2a/b}} \cdot e^{\left(\frac{\Delta G_{(7)}^0}{R \cdot T}\right)}$$
(8')

in which p_i represents the partial pressure of component i, a_i representes the activity of component i, f_i representes the activity coefficient of component i, X_i representes the mole fraction of component i, $\Delta G^0_{(x)}$ is standard Gibbs free energy for reaction (x) [in J·mol⁻¹ or cal·mol⁻¹], R is the gas constant [in J·mol⁻¹·K⁻¹ or cal·mol⁻¹·K⁻¹] and T is temperature [in K]. The compositions needed for the calculations were obtained from the analyses carried out for the process samples from Tornio works. Thermodynamic values needed for the calculations were calculated by using quadratic formalism by Ban-Ya (1993) and Xiao et al. (2002) for the slag phase and unified interaction parameter formalism by Pelton & Bale (1986) for the metal phase. Some values were also obtained from the databases of thermodynamic software such as FactSage and HSC Chemistry. (Heikkinen et al., 2010b, 2011)

The results of the modelling were used to estimate the oxidation order of silicon, carbon and chromium in different process conditions. The results indicated that with the high silicon contents in the early stages of the CRK process silicon is most likely to be oxidized before carbon and chromium. As the silicon content decreases below approximately 0.3-0.6 w-%, the oxidation of carbon becomes more favourable and the carbon content of the metal begins to decrease. If the oxygen blowing is continued even further, chromium begins to oxidise excessively if the carbon content is decreased below approximately 2.5 w-%. This means that the reduction of Cr_2O_3 from the slag is required in order to produce low carbon ferrochrome with the CRK process. (Heikkinen et al., 2010b, 2011)

4.3.2 Flow patterns

Obviously a comprehensive look on the phenomena taking place in the CRK cannot be given by a thermodynamic study alone and therefore it is also necessary to consider the influence of blowing parameters on the flowing patterns of the liquid metal. This is important not only due to flow pattern's influence on the reactions, but also due to optimization of sufficient mixing and minimisation of unwanted spitting and splashing. The influence of the lance height and amount of holes in the lance as well as the amounts of gas blown through the lance and through the tuyeres at the sidewall of the converter have been studied using physical water models built to correspond the actual CRK process in Tornio, which was also used to validate the results of the modelling. (Fabritius & Kupari, 1999; Fabritius et al., 2001a, 2001b; Virtanen et al. 2004)

The use of physical water models to investigate the flow patterns of a converter is based on an assumption according to which the lack of information concerning the extremely turbulent conditions inside the converter limit the numerical modelling of the process. Therefore it is considered to be more meaningful to construct physical models with dynamic similarities to real processes. This way it is not necessary to know mathematical expressions for all the interdependencies between the process parameters and variables as long as it is possible to ensure the dynamic similarities between the model and the real process. Confirmation of these similarities is defined by using dimensioless numbers such as Froude's, Reynold's, Weber's, Ohnesorge's and Morton's numbers which describe the ratios between different forces in the model and in the real process. The values of a certain dimensioless number defined for the model and for the real process should be set as close to equal as possible by choosing the model geometry in a way that corresponds with the real process. The Froude number, which describes the ratio between gravitational and inertial forces and which has an essential role in the physical modelling of the CRK process, is presented as an example of a dimensioless number in equation (9). (Fabritius & Kupari, 1999; Fabritius et al., 2001a, 2001b; Virtanen et al. 2004)

$$Fr = \frac{\rho_g}{\rho_1} \cdot \frac{U^2}{gD_c}$$
(9)

in which ρ_g and ρ_l are the densities of the gas and liquid phases [in kg·m⁻³], respectively, g is gravitational constant [in m·s⁻²], U is the velocity of the gas [in m·s⁻¹] and D_c is the diameter of the converter [in m] (Fabritius & Kupari, 1999).

As the name suggests, water is used in physical water models to illustrate the metal due to kinematic similarities between the liquid water at room temperature and liquid steel at approximately 1600 °C. On the other hand, its transparency helps to make observations inside the process.

The results of the physical modelling have indicated that the rates of the oxidation reactions of silicon and carbon may be increased due to enhanced mixing by increasing the total amount of gas blowing and by increasing the amount of inert gas that is blown through the sidewall tuyeres. These changes have also been noticed to increase the penetration of the tuyere gas jets and hence decrease the occurrence of the so-called back-attack phenomenon that is detrimental to the refractory materials close to the tuyeres. The positive influence of the changed blowing practice has also been verified with the process experiments. Another results from the flow pattern studies suggest that the removal of silicon can be improved by using a higher lance position at the first stage of the blowing, whereas the removal of carbon in the later stages is improved with a lower lance position. The oxidation of chromium was observed to decrease with the use of a top lance with wider nozzle angles. Furthermore, the physical models have been used to illustrate how the change from one-hole lance to threehole lance decreases unwanted spitting and splashing in the converter and hence enables the use of greater gas volumes - and increased productivity - without increasing the amount of metal losses due to splashing. (Fabritius & Kupari, 1999; Fabritius et al., 2001a, 2001b; Virtanen et al. 2004)

4.4 Argon Oxygen Decarburization converter, AOD

AOD is the process in which most of the world's stainless steel is being produced. Its purpose is to remove carbon - as well as silicon if CRK is not used - without excessive oxidation of chromium from the metal that consists of ferrochrome and molten scrap. Other important features concerning the AOD are nitrogen control and sulphur removal, latter of which is usually executed as a separate stage at the end of the processing. In order to control the process it is important to know how to influence oxidation reactions and how to control the nitrogen content with accessible process variables. The variables by which the AOD is usually being optimized are the blowing ratios between top and bottom blowing, lance positions and oxygen/nitrogen/argon -ratios in the gas during the different stages of the blowing as well as the durations of stages themselves. Furthermore, it is possible to control the process via additions of scrap, lime and alloying elements. Since the carbon is removed much more efficiently when compared to CRK, a reduction stage in which the oxidized chromium is reduced is needed after the decarburization at the end of the processing.

Due to similarities with the CRK process presented above, it is unnecessary to repeat certain things that are already covered in the previous section.

4.4.1 Thermodynamics

Thermodynamic considerations of the reaction equilibria in the AOD are more or less similar to the CRK considerations, since both of the considered systems consist of same phases (i.e. Fe-Cr-Si-C-based metals, silicate slags and gas) and the considered reactions are the same (i.e. oxidation reactions of silicon, carbon and chromium). Therefore it is safe to assume that if a certain thermodynamic model is suitable for the melts in the CRK, it is suitable for the considerations of the AOD, too. Higher metal concentrations of chromium, silicon and carbon in the CRK may restrict the application of some of the AOD models into the CRK systems, but the problem should not exist vice versa.

Obviously the consideration of the oxidation reactions is not the only application for which thermodynamic modelling can be applied in the AOD, but other applications of less relevance such as solidification of the slag and its utilization to protect the refractory material (Heikkinen et al., 2004) are omitted here.

4.4.2 Reaction rates

Although thermodynamic modelling helps us to define the chemical equilibria for the reactions taking place in the AOD, it gives us no information concerning the rates and mechanisms of these reactions. Based on the results of the studies concerning the decarburization rates of Fe-Cr-melts with a top blown oxygen, it has been concluded that the decarburization phenomenon can be classified into two separate stages, during which the decarburization rates can be modelled by using equations (10) and (11), respectively (Kitamura et al., 1986):

$$-\frac{d[\%C]}{dt} = \alpha \tag{10}$$

$$-\frac{d\log[\%C]}{dt} = \beta \tag{11}$$

in which [%C] is the carbon content of the metal [in w-%], t equals time and α and β are condition-specific constants. At the beginning of the decarburization (cf. equation (10)) the carbon content of the metal is still high and during this first stage the decarburization rate is increased with increased oxygen supply and increased bath stirring intensity. At the same time, the oxidation of chromium is also increased with increased oxygen supply, but decreased with increased stirring intensity. Below the critical carbon content the decarburization is controlled by mass transfer of carbon and the equation (10) is no longer valid. During this second stage equation (11) is used to model the decarburization rates. At this stage both decarburization and oxidation of chromium are increased with increased oxygen supply and stirring intensity. (Kitamura et al., 1986)

4.4.3 Flow patterns

Due to geometrical similarities, the modelling of the flow patterns of the AOD process is also very similar to the one of the CRK. The things about dynamic similarities and dimensioless numbers mentioned in the context of the CRK are as relevant for the modelling of the AOD as they are for the CRK, but it is unnecessary to repeat those things here. Some of the results of physical modelling concerning the AOD and CRK flow patterns are also quite similar. For example, the positive influence of the increased gas volumes through the sidewall tuyeres on the penetration of gas jets and on the duration of the refractory materials close to tuyeres has also been observed with the AOD process (Fabritius et al., 2000, 2003).

Since AOD is much more widely used in comparison to CRK, it has also been modelled much more frequently in comparison to CRK, which makes it impossible to present all the investigations here. However, some examples of the results are presented in order to give an outlook on the conlusions that have been made based on the physical modelling of the AOD process:

• The minimum gas flow that is required to prevent the occurence of the back-attack phenomenon depends on the phenomena such as melt oscillation and tuyere blockage and it could be defined by modified Froude number (Fabritius et al., 2003).

- Depending on the ratio between bath height and diameter as well as on the intensity of the gas blowing through sidewall tuyeres the main circular flow in the AOD may change its direction (Fabritius et al., 2003).
- There are two different kind of wave motions after which the melt inside the AOD converter may oscillate. The oscillation depends on sidewall blowing and according to the water models the appearance of the oscillation is most likely during the end of the decarburisation stage or during the reduction stage if tuyeres with large diameters are being used. With smaller tuyeres the penetration of the gas jets is deeper and the oscillation occurs most likely during the decarburisation stage. The modelling results concerning the oscillation have been confirmed with vibration measurements from the real AOD process in Tornio. (Fabritius et al., 2003, 2005; Kato et al., 1985; Mure et al., 2004)

In the section concerning the modelling of the flow patterns in the CRK converter it was mentioned that physical modelling is often prefered over numerical due to high complexity of the flows inside the process. Computational fluid dynamics (CFD) have nevertheless been used to simulate the flows within the AOD in some cases and the results indicate relatively good accordance with the physical modelling and real process measurements. The key issues to be considered in the CFD modelling of the AOD are model geometry, grid distribution, behaviour of free surface, introduction and removal of materials into the system, modelling of turbulence and the interaction between different phases. Additionally, one has to consider whether it is necessary to take heat transfer and chemical reactions into account. It is usually easier and faster to consider isothermal and non-reactive systems, although in some cases this might lead into oversimplification of the model. (Gittler et al., 2000; Tang et al., 2004; Tilliander et al., 2004)

4.4.4 Nitrogen and interfacial phenomena

One of the differences between the AOD and CRK processes concerns the behaviour of nitrogen. Whereas the CRK process can be considered as a pretreatment unit for the stainless steel production, in which the control of nitrogen is not yet essential, it is important to control the amount of nitrogen of the metal during the AOD process in order to be able to produce stainless steel grades with strict composition limits. In the early stages of the AOD process the blowing gas consists of pure oxygen, but in order to decrease the oxidation of chromium - and to be able to reduce Cr_2O_3 during the reduction stage - the oxygen needs to replaced by nitrogen and argon. The use of cheaper nitrogen can be justified with economic reasons in the earlier stages, but due to nitrogen pick-up (of up to 1000 ppm) it is necessary to use more expensive argon during the last stage of decarburisation and the reduction stage. In order to control the nitrogen content of the metal, it is necessary to know what is the effect of process variables on the nitrogen pick-up (during the stages in which nitrogen is blown into the system) and nitrogen removal (during the stages in which argon is used). (Heikkinen et al., 2007; Kärnä et al., 2008; Riipi et al., 2009)

Unlike the oxidation and reduction reactions which can be modelled using computational thermodynamics with tolerable accuracy, a thermodynamic model, that describes the effects of metal compositions and partial pressures of nitrogen in the gas bubbles on the nitrogen solubility of the stainless steel melts, is not sufficient for the modelling of nitrogen. Although it is important to recognize chromium's increasing effect and nickel's decreasing effect on

the nitrogen solubility, it is necessary also to model the mass and heat transfer in the gasmetal systems. Since the mechanisms of both nitrogen absorption (i.e. nitrogen pick-up) and desorption (i.e. nitrogen removal) can occur in either single-site or dual-site mechanism depending on the amount of surface active elements in the metal, it is necessary to model the influences of these surface active elements such as oxygen and sulphur on the interfacial properties, nitrogen absorption and desorption rates and furthermore on the nitrogen content of the metal. (Heikkinen et al., 2007; Järvinen et al., 2009; Kärnä et al., 2008; Riipi & Fabritius, 2007; Riipi et al., 2009)

Behaviour of nitrogen is not the only thing in which the interfacial phenomena have an important role. In a systems of three separate phases (metal, slag and gas; excluding the refractory materials) the interfacial properties - of which interfacial tensions are the most essential - always have an effect on all heterogeneous phenomena. In order to describe these effects, variables such as film coefficient, $\theta_{m\nu}$ and flotation coefficient, $\Delta_{m\nu}$ have been introduced. Based on the values of these coefficients, that are calculated using equations (12) and (13), it is possible to estimate, whether the gas bubbles and metal droplets exist separately inside the slag or whether the bubbles are surrounded by metal films or metal droplets attached to the bubbles. (Fabritius et al., 2010; Minto & Davenport, 1972)

$$\theta_{\rm m} = \sigma_{\rm slag-gas} - \sigma_{\rm metal-gas} - \sigma_{\rm metal-slag} \tag{12}$$

$$\Delta_{\rm m} = \sigma_{\rm slag-gas} - \sigma_{\rm metal-gas} + \sigma_{\rm metal-slag} \tag{13}$$

in which $\sigma_{\text{slag-gas}}$ and $\sigma_{\text{metal-gas}}$ are the surface tensions of slag and metal [in N·m⁻¹], respectively, whereas $\sigma_{\text{metal-slag}}$ is the interfacial tension between metal and slag [in N·m⁻¹] (Fabritius et al., 2010; Minto & Davenport, 1972).

As a conclusion one could state, that with sufficient knowledge concerning thermodynamics, reaction rate kinetics as well as surface and transport phenomena, it is possible to create submodels describing these phenomena and then include them in more comprehensive process models in which for example CFD is used. (Järvinen et al., 2009; Kärnä et al., 2008)

4.4.5 Process modelling

As opposed to phenomenon-based models, in which each phenomenon is considered separately, process models aim for more holistic approach by combining several submodels into bigger entities. Because the combination of several very detailed submodels creates slow and non-robust models that usually are not very useful, the accuracy of describing an individual phenomenon with a larger process model is usually not as high as it is in the phenomenon-based models. On the other hand the process models are usually more adaptable to real processes and in some cases they might even be part of the control and automation systems. A typical feature for many process models is, that in order to be able to model the relevant phenomena by using appropriate submodels, it is necessary to define certain parameters which are required for the modelling but are not measurable or otherwise known. These kind of parameters are often used to fit the model to better correspond with the real process. For instance, one might

need to know what is the bubble size (and bubble size distribution) in order to calculate the mass transfer between the molten metal and the gas phase. However, the bubble size distribution inside the converter is difficult to measure and therefore the modeller needs to be satisfied with estimated values. By trying different bubble sizes and bubble size distributions, it is possible to adjust the model in order to make it more equivalent with the reality (Järvinen et al., 2011).

Process models may be constructed in various ways based on their purpose and usually the phenomena that are considered to be most critical on the process optimization are modelled in greatest detail (e.g. chemical equilibrium, reaction kinetics, mass transfer, fluid flows, heat transfer, interfacial phenomena, and so on). This means that separate researchers may end up with very different kind of models based on the target of their modelling as well as on their own impressions. In addition to what is included in the process models and in which extent and accuracy, the models may also differ from one another based on the connections that link the submodels with each other. Process models for the AOD converter have been proposed by e.g. Fruehan (1976), Sjöberg (1994), Wei & Zhu (2002), Zhu et al. (2007), Wei et al. (2011) and Järvinen et al. (2011).

5. Conclusion

Phenomenon-based models illustrating both physical and chemical phenomena in the refining processes of ferrochrome and stainless steel have been presented with an attempt to use models as connecting links between the phenomena and the applications relevant for the production engineer. The results obtained by using these models are not only helping us to control and optimize the metal production processes, but also helping us to understand how various process parameters and variables are linked to the process outcomes via the phenomena for which the variables have an influence on.

As accurate modelling often requires time resources that are not available for engineers working daily with the processes in the steel plants, this usually has to be made by researchers working at the universities and research institutes. However, the results, no matter how accurately modelled, can only be as good as the assumptions behind them. Therefore it has been - and always will be - necessary to validate the results obtained from the models with the real process data. This means that reliable modelling is only rarely achieved without an open and long-term co-operation between the modellers and the production engineers.

Although most of the models presented in this chapter focus on individual phenemona rather than total processes, it has not prevented the use of these models as well as the results obtained from the models as parts for more comprehensive process models. In fact, many of the results concerning the CRK and AOD processes have been implemented in the control systems of these processes at the Outokumpu Stainless Tornio steelworks.

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Metallurgical Engineering is the science and technology of producing, processing and giving proper shape to metals and alloys and other Engineering Materials having desired properties through economically viable process. Metallurgical Engineering has played a crucial role in the development of human civilization beginning with bronze-age some 3000 years ago when tools and weapons were mostly produced from the metals and alloys. This science has matured over millennia and still plays crucial role by supplying materials having suitable properties. As the title, "Recent Researches in Metallurgical Engineering, From Extraction to Forming" implies, this text blends new theories with practices covering a broad field that deals with all sorts of metal-related areas including mineral processing, extractive metallurgy, heat treatment and casting.

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