

On-line slag composition analysis for electric arc furnaces

State of the Art (SoA)

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Introduction

Electric steelmaking has fast gained ground in developed countries due to reduced CO₂ emissions compared to blast furnace steelmaking and better production flexibility. Due to increased scrap usage, the quality of the scrap is getting worse and worse. This is reflected in the increase of non-metallic material in the scrap. Fluctuations in EAF scrap charge composition causes significant fluctuations in the EAF slag composition, since the non-metallic material in the scrap accumulates in the slag.

Fluctuation of scrap composition causes many challenges in EAF steelmaking. In stainless steelmaking one of the most important goals in EAF is to keep the chromium content of the slag low, since it causes costs due to increased alloying additions and problems in recycling of slag. In carbon steelmaking it is important to ensure foaming slag conditions, which increases energy efficiency of the EAF. Due to the slag composition fluctuations, the slag foaming is sometimes hindered when the slag composition drifts to the composition area with low foamability. Additionally due to changes in scrap melting, the timing of the carbon injection is hard to define accurately without information of scrap melting and slag formation. In ladle furnace the use of current practice of taking samples and analysing them in laboratory is problematic because of costs and long delay. The samples do not always get analysed in time before the ladle is already sent to the casting machine.

There are currently very few methods available for analysing slag composition and formation in the EAF and LF. One of the most popular methods to gain information of slag composition is taking slag samples and analysing them in laboratory. The problem with this approach is the only pointwise measurement as well as the long delay between the taking of the sample and getting the result. To tackle problems related to transient process conditions like slag foaming or chromium slagging, real-time and continuous information of slag composition and scrap melting is required. However, currently available online measurement systems in EAF furnaces are indirect in nature; they describe the level of foaming [3, 26, 27] or gas generation [2, 23, 24, 25], but cannot provide direct information of slag composition.

The OSCANEAF research project

This non-satisfying situation led to the formulation of the OSCANEAF research project funded by the Research Fund for Coal and Steel (RFCS). The OSCANEAF acronym stands for “On-line slag composition analysis for electric arc furnaces”. The basic idea of this project is to develop and test a device for the continuous online measurement of slag composition and formation based on arc emission spectroscopy. This project is aimed at providing important information on the slag composition in LF and EAF and scrap melting in the EAF in real-time to increase the general availability of process data and to optimize the operating practices of alloy additions in stainless steelmaking and slag foaming in carbon steel production, leading to a more resource and energy efficient process. The knowledge of the current slag composition and its changes over the course of a heat allow for a controlled instead of pre-calculated and therefore more resource efficient addition of slag formers and slag reducing agents. It can also allow for a better control of oxygen use for decarburization/ desiliconisation and reduce the amounts of slag that have to be handled. Another important issue will be the durability of the parts of the

measurement device to be installed on the furnace. Planning and construction of the system hardware will already be focused on low maintenance requirements to ensure the technical and economic feasibility of the system and its broad applicability in EAF steel industry.

Previous research at European and worldwide level

The first report describes a RFCS project which aimed to develop a tool for online composition analysis. The references 2 to 7 describe RFCS projects aimed at increasing electric arc furnace (EAF) performance. References from 8 to 10 describe the fundamental laboratory studies on analysing slag composition from electric arc furnace emission spectrum. References 11 to 13 are the only reported arc emission spectrum measurements on the industrial electric arc furnaces. References 15 and 16 describe a measurement of pilot scale arc emission spectrum. Reference 17 sums up the previous research (before 2009) on the electric arc furnace physics. References 18 and 19 describe how the optical emission spectrum is used in online process control in other fields of metallurgy besides steelmaking. In references 20 to 21 the use of optical emission spectroscopy is studied as a tool for controlling converter processes. References 22 to 25 describe the current EAF control philosophies relying on off-gas, visual and acoustic measurements. References 26 to 33 discuss the effect of slag composition on various process phenomena. Reference 34 is an online database for atomic emission lines. Reference 35 discusses the possible uses of EAF slag. Reference 36 describes the applications of laser-induced breakdown spectroscopy in monitoring of steel making processes.

Introduction to optical emission spectroscopy

Optical emission spectroscopy is a method in which different wavelengths of the optical emission are studied. Previously optical emission spectroscopy has been a popular method in analytic sample analysis, which rely on generating the optical emission for example with plasma (ICP OES), spark (spark OES) or laser (LIBS). Optical emission spectroscopy can also be used as a passive tool for online process control in processes, which inherently generate the optical emissions. A few examples of these applications are control of laser welding [19] and surface treatment [18] processes with optical emission spectroscopy.

Optical emission spectrum measurements in metallurgical industry

In steelmaking optical emission measurements have mainly focused on various converters. It has been successfully used in measuring manganese content of the steel from the converters hot-spot [20, 21], as well as converter off-gas temperature [22]. Very few measurements of electric arc furnace emission spectrum have been reported, although its advantages in providing first-hand information on plasma characteristics have been highlighted [17]. The first industrial measurements were conducted by Block [13], who measured the arc emission spectrum from an industrial DC arc furnace. Veillette & Simard [16] conducted measurements on pilot scale ilmenite smelting furnace. The feasibility of measuring industrial AC electric arc furnace emission spectrum was demonstrated by Aula et al. [11]. Just recently, the feasibility of analysing Cr_2O_3 content of the slag from pilot scale EAF has been reported [15].

All the studies previously conducted on the industrial electric arc furnace arc emission spectrum have been qualitative in nature. The arc emission data is typically obtained only from short span of time. All the information of the slag composition changes during EAF processing have been obtained from samples taken during heats.

Composition analysis from electric arc furnace emission spectrum

The passive nature of arc emission spectrum measurement offers some very beneficial features compared to active measurement methods, but it also requires more careful analysis of arc emission spectrum. Active optical emission spectrum measurements rely on active excitation of the tested material, as well as the atmosphere between the sensor and the material causing as low distortion to the signal as possible. In the passive arc emission spectrum measurement the excitation energy varies with the arc power, which can fluctuate highly because of changes in steel and slag level. Earlier studies on industrial arc emission spectra also suggest that the far ultraviolet (UV) portion of the spectrum is highly absorbed by the dusts and fumes inside the furnace [11]. In combination these effects make it harder to use standard atomic emission lines, which work well in clean and well controlled conditions. To find suitable atomic emission lines for each component, detailed analysis of arc emission spectrum is required. Because the excitation conditions vary, the ionic emission lines are unsuitable for composition analysis.

In the earlier studies of arc emission spectrum, it was found that mostly lines of Cr I, Mn I, Mg I, Ca I are observed from industrial AC EAF [11]. The appearance of atomic emission lines of slag components in arc plasma is essential in composition analysis, since this shows that the arc plasma is mostly affected by the slag instead of steel. The reason for the atomic emission lines originating from the slag components is that the observed arc emission spectra is emitted by the outer edges of the arc plasma, which is near the slag. This is because the arc in industrial EAFs is optically thick, which means that the optical emission from the core of the plasma is absorbed and emitted by the outer edges of the plasma.

While chromium and iron have multitude of possible atomic emission lines for analysis, other components have far less suitable lines. Calcium, manganese and magnesium have less atomic emission lines, but still they have an order of ten suitable atomic emission lines observed from the industrial emission spectra. Fluorine has resonance lines in optical wavelengths, but their intensity can be low due to high first ionization energy of fluorine. The appearance of fluorine lines depend on the atmosphere the arc is generated in. Measurement of F I lines is likely to require spectrometer with very low noise, i.e. CCD with cooling to -50°C . The two remaining major slag components, aluminium and silicon have much less atomic emission lines. Aluminium has the most intense ground state atomic emission lines at wavelengths 308.2, 309.3, 394.4 and 396.2 nm [34]. The most promising of these lines are the lines 394.4 nm and 396.2 nm, since atomic emission lines of these wavelengths have been observed from industrial emission spectra. The far UV-lines are not suitable for analysis since the wavelengths much lower than 400 nm have been found to be significantly absorbed by EAF atmosphere [11]. According to the earlier studies [11], the most difficult component to analyse is SiO_2 . SiO_2 has high dissociation temperature, which causes the amount of atomic silicon vapour to be low in the outer edge of plasma where the arc emission originates. This requires the analysis of arc

emission spectra to focus especially to the wavelength regions near strongest Si I ground state transitions. The other possibility is to analyse the emission spectrum for excitation structures of SiO or SiO₂.

Advantages of using fibre optic measurement in EAF environment

The most advantageous aspect of fibre optic emission spectrum measurement is that it does not require lenses. Lenses are not required to focus the light since high temperature of the electric arc causes abundant emissions of light. The light emitted from the electric arc can be guided to optical fibre through a small hole in the measurement head, which is much easier to keep clean with gas purging than lenses [11]. The clogging of lenses by slag has been found to be the most serious issue in previous optical measurements on EAF [4].

Another important advantage is that optical emission spectrum measurement requires minimal equipment near the furnace. The optical fibre transports the light to remote spectrometer, which means that only optical fibre will have to withstand harsh environment of EAF. Optical fibres are easy to cool since they are small and special optical fibres can withstand temperatures above 600 °C.

Slag composition in stainless steelmaking

In stainless steelmaking the composition of the slag has been found to vary greatly in different process stages. One of the most extensive studies was conducted by Durinck et al. [29]. They found that during the oxygen blowing and before the possible FeSi additions and tapping the chromium content of the slag can vary between 2 and 20 %. The increased mixing during the tapping allows the reduction of chromium from slag to metal phase, thus the chromium content of the slag is lower in the samples taken after the tapping.

The problem in high variance of chromium content is that when the chromium content is high enough, the solubility limits of the liquid slag are exceeded and solid Cr₂O₃ containing spinel precipitates start to form. These precipitates cause a kinetic barrier in chromium reduction since the spinel particles have to first dissolve to slag, before the chromium oxides can be reduced [29]. If excessive amount of spinel particles form before the tapping, the chromium content of the slag remains high after tapping [28]. The formation of spinel particles is also affected by other factors, for example basicity of the slag, but their effect is not as clear as the total amount of Cr₂O₃ in the slag [28, 31].

The precise online control of slag composition allows many advantages to current process control philosophy. If the amount of chromium oxide in slag is known, the amount of required deoxidant materials (for example FeSi) can be optimized. The high chromium content of the slag indicates too low silicon and carbon levels in the steel, which act as reducing agents for Cr₂O₃. The better control of reducing material additions enables better control of chromium content in the final slag after the tapping, thus reducing the chromium alloying costs and also making the recycling of the slag easier. The chromium in the slag is lost as an alloying agent and equal amount has to be added to the melt later. The problems in slag recycling arise from increased chromium leaching values of the slag with higher Cr₂O₃-content. On the other hand better control of FeSi additions also reduces the variance of the silicon

content of the steel after the tapping. This is very beneficial in subsequent process steps (AOD/VOD), because too high silicon content of the steel causes excessive amount of SiO_2 to form during oxygen blowing, which has to be compensated with additions of lime, thus increasing the slag volume and material costs.

Slag composition and optimized slag foaming in carbon steelmaking

In carbon steelmaking the most important slag components are SiO_2 , CaO , FeO , Al_2O_3 and MgO . The relative amounts of these components define the properties of the slag. Slag chemistry affects many furnace performance indicators; it has an effect on electrical efficiency in the EAF, recovery of injection carbon and oxygen, as well as metallic yield [28].

Also, the amounts of some components in carbon steelmaking slags have implications of their own. MgO content of the slag needs to be precisely controlled since it acts as a flux for the slag. Refractories in EAFs usually consist of MgO-C bricks, which aggressively dissolve to the slag if the slag MgO level is too low. Since MgO acts as a flux, too high amount MgO will on the contrary increase the refractory wear because of excessive decrease of viscosity (contact angle).

The slag composition also has high effect on the slag foaming. Slag foaming is a very beneficial phenomenon, since it surrounds the electric arc and reduces the radiation losses to the furnace sides and roof. The foaming depends on both the foaming properties of the slag i.e. foaming index of the slag and the gas generation [32]. The current method to control foaming is to ensure high gas generation by oxygen blowing and combined oxygen-carbon blowing [27]. The problem in this method is that the time when to start oxygen blowing can be hard to define since scrap melting is not accurately measured. With precise information of the generation of early slag and its composition as well as scrap melting, it is possible to adjust the start of the oxygen blowing to minimize the time when the unshrouded electric arc is visible to the furnace refractories. Preliminary results on the timing of carbon injection indicate that one minute delay between scrap melting and the start of carbon injection causes energy efficiency loss of approximately 0.8 %.

Change in process control practice

Online analysis of EAF slag composition offers a possibility to change the current EAF process practice to better suit the need of flexibility posed by changing charge material. The trend in electric steelmaking has long been to use more and more scrap in the EAF charge. The increased use of bought scrap not only reduces the environmental load through decreased need for virgin materials, but also reduces alloying costs since the scrap is usually cheaper than more pure alloying material. The challenge in using high amount of scrap in charge material is that the exact composition of the scrap is rarely known since there are no methods to analyse the whole scrap volume [33]. During the recent years the amount of dirt in the scrap has increased [33] making it even harder to use high amounts of bought scrap in the charge.

The current state of art process practices rely on information on the scrap composition gained from previous heats, online information from indirect measurements, for example off-gas analysis and fast sampling [33]. The changes in

process caused by the variance in scrap composition can only be observed after the tapping or very late in process. With changing charge material, the current inflexible process practice does not provide optimal results. With online information on slag composition and slag formation, it is possible to create more flexible process control practice, which reacts to the changes in scrap content. This mitigates the process variance problems caused by the changes in the scrap, thus allowing use of lower quality scrap and higher ratio of scrap to total charge.

The information obtained from online OES can be used in controlling additions of reducing agents to the furnace. By measuring the amount of CrO_x in the slag, it is possible to calculate or correlate the correct amount of carbon and silicon additions in order to keep CrO_x content of the slag in acceptable levels. On the other hand, the chromium content of the slag can be used in determination of the oxygen blowing end point. When carbon and silicon run out in the oxygen blowing, the chromium will start to oxidize and the CrO_x content of the slag starts to increase. Keeping chromium levels in the ladle slag low is important in both economic and environmental point of view, all the chromium going to slag is lost as an alloying agent and the high chromium content of the slag will increase the chromium leaching. The high chromium content of the slag also significantly increases the apparent viscosity of the slag, which means that the residence time of metal droplets in slag is high. This will increase the amount of metal droplets in the ladle slag, which will also contribute to the loss of metal and increase in leaching of metals.

Another use of having online information of slag CrO_x content is to allow separate treatment of slags with high CrO_x content. The slags with higher chromium content can be separated from the slags with lower content, which makes the potential recovery of chromium from the slag much easier in the future. Alternatively, the slag with high CrO_x can be processed in a different way to allow better recovery of metals.

In manufacturing of carbon steel grades, the main use of slag composition is to provide a tool for assessing the starting time of carbon injection as well as allow optimization of the process to reduce the amount of slag. By measuring the slag FeO content it is possible to optimize the process by minimizing the FeO formation. This will again reduce metal losses and also reduce the amount of produced slag. Less slag from EAF means less slag to be landfilled, as EAF slag is rarely recycled [35]. On the other hand, the appearance of arc emission spectrum signifies naked arc conditions, which should be covered by foaming slag promoted by the injection of carbon.

Yet, another use of slag composition system in process control is to provide an alternative for laboratory ladle slag analysis. Analysing slag samples from ladle takes time and requires laboratory facilities. By measuring ladle slag composition from ladle furnace arc emission, it is possible to reduce the delay and provide affordable *in situ* measurement method, which does not require manpower in sample preparation.

Other online slag analysis methods

Some other online slag analysis systems are also in development. The most promising one has been a sensor based on laser-induced breakdown spectroscopy (LIBS) [36]. The biggest challenges in this method are the inhomogeneity of the slag, which causes the surface analysis not to represent the whole slag composition and

the requirement for clean atmosphere between the measurement system and the melt [1]. In carbon steelmaking and in ladle furnace the inhomogeneity is not a problem. However, LIBS has not been tested in industrial EAFs and it is not probable that the harsh process conditions of EAFs will meet the requirements of LIBS.

Conclusions

Currently there is no method available to analyse online the slag composition in industrial electric arc furnaces on European or worldwide level. Better understanding of slag composition allows better control of the Cr_2O_3 content in stainless steelmaking, which reduces alloying and addition material costs. In carbon steelmaking the information of online slag composition makes it possible to optimise the slag composition in order to reduce metal losses, slag amount and refractory wear. Additional information on scrap melting and slag formation enables the better timing of carbon injection and increases energy efficiency.

This OSCANEAF project will develop a technique, which enables the online analysis of electric arc furnace slag composition in EAF steelmaking.

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