

LADLE MELT TREATMENT OF HIGH SULFUR STAINLESS STEELS

^{1,2}Jaka BURJA

¹IMT - Institute of Metals and Technology, Ljubljana, Slovenia, EU, jaka.burja@imt.si

²Department of Materials and Metallurgy, Faculty of Natural Sciences and Engineering, University of Ljubljana, Ljubljana, Slovenia, EU

<https://doi.org/10.37904/metal.2023.4627>

Abstract

The influence of sulfur on both slag and melt is very important in steelmaking. This is especially true for high-sulfur machining steels. Machinability is achieved by alloying high sulfur contents, above 300 ppm. These are steels that form small chips and shavings during mechanical processing by cutting, which is more appropriate and favorable for both the workpiece and the processing tool and machine. However, the secondary steelmaking slag is typically designed for desulfurization. This means that the sulfur content rapidly falls after sulfur additions. This is especially true for high machinability stainless steel grades where S contents can exceed 1000 ppm. This causes the sulfur wire yield to vary greatly in each charge, making the process unreliable. Some aspects of understanding the interaction between the steel melt and slag and the effect on casting are presented in this work. Based on industrial charges, we analyzed the yield of sulfur additions and the influencing factors on the efficiency of the sulfur addition. The lower slag basicity was linked to lower sulfur distribution ratios, and lower sulfur distribution ratios were linked to higher sulfur yields. Melt and slag samples were analyzed. Slag entrapment during ingot casting was linked to the high sulfur contents.

Keywords: Desulfurization, sulfur, stainless steel, steelmaking

1. INTRODUCTION

Clean steels have a controlled concentration, distribution, size, shape, and composition of non-metallic inclusions. The control over non-metallic inclusions enable good formability and further processing of the steel as well as limiting the initiation sites for failure of steel components [1]. From the perspective of non-metallic inclusions, the ladle (secondary) treatment of the steel melt is crucial. During the secondary or ladle treatment, the melt is cleaned of impurities, gases are removed, and appropriate chemical composition, as well as temperature are achieved. To ensure low concentration of non-metallic inclusions, effective deoxidation and desulfurization of the steel melt are required during ladle treatment [2,3]. Desulfurization of the melt is important for reducing the harmful effects of sulfur. High concentrations of sulfur worsens the corrosion resistance and causes problems during welding, and in extreme cases can even lead to hot shortness. This is why the sulfur content in steels is usually limited to concentrations below 0.03 wt% (300 ppm).

The ladle (secondary) slag used in steelmaking normally consists of calcium oxide (CaO), alumina (Al₂O₃), magnesium oxide (MgO) and silica (SiO₂), and, as well as smaller amounts of other oxides such as iron oxide (FeO) and manganese oxide (MnO). To achieve low levels of oxygen SiO₂ must be below 10% and FeO + MnO less than 0.5% [4]. The reaction for removing sulfur from aluminum-killed steels using a high basicity slag can be described using equation 1 [5].



Square brackets [] indicate the phase in the molten metal, while round brackets () indicate the phase in the slag. Metallurgical reactions are of heterogeneous nature, where reactions occur between different phases.

Examples include solid-liquid reactions, slag-metal reactions, and gas-metal reactions. Let us consider reaction 2, which occurs between the melt and the slag [5,6]:



Since the slag has an ionic structure, it is assumed that S and O are present as ions S^{2-} (in CaS) and O^{2-} (in CaO). Reaction 3 occurs as a coupled electrochemical reaction at the interface between the slag and the metal [6]:



Reactions 3 and 4 take place at different locations at the phase boundary between the steel and the slag. The transfer of electrons from one site to another takes place through the molten metal, which is an electrical conductor. These transitions are schematically shown in **Figure 1** [6].

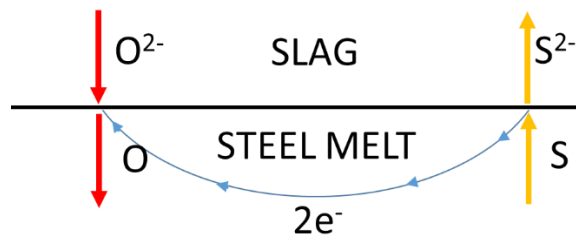


Figure 1 Electromechanical mechanisms of reactions at the slag/metal interface [6]

The entire process consists of several kinetic steps:

1. Transfer of sulfur from the majority metallic phase to the slag/metal interface.
2. Transfer of O^{2-} from the slag to the interface.
3. Chemical reaction at the interface.
4. Transfer of oxygen from the interface to the melt.
5. Transfer of S^{2-} from the interface to the slag.

Step 3 is a chemical reaction and is governed by the laws of chemical kinetics. The other steps are the laws of substance transfer. The kinetic steps described for reaction (2) occur in the listed order. If any of these steps are prevented, the overall reaction will not proceed. No processes occur in parallel, so we conclude that the slowest step in the series is the rate-determining step. Thus, the slowest step is the most important. The main goal of all kinetic studies is to determine which step is the slowest. Of course, other kinetic steps also affect the overall process to some extent. Sometimes, two or more steps can be of comparable magnitude.

The rate of metallurgical reactions between slag and metal is limited by the diffusion rate of the participating elements at the interface between the slag and metal. The success of steel desulfurization depends on temperature, sulfur and oxygen concentrations in steel, CaO content in slag, viscosity of slag, and the reaction surface between the melt and slag.

Sulfur distribution ratio between slag and melt (L_s) is an important factor in desulfurization. It is a measure of desulfurization. A high L_s indicates that a greater proportion of the sulfur is present in the slag [7,8].

$$L_s = \frac{(\%S)}{[\%S]} \quad (5)$$

The removal of sulfur also depends on the activity of oxygen in the liquid steel. Desulfurization of steel becomes more effective with lower activity of oxygen in the melt

The ability of the slag to absorb sulfur is dependent on the free CaO in the slag, thus on the slag basicity. In general, the higher the basicity of the slag, the greater the sulfide capacity of the slag. Basicity expressed as mass concentrations of oxides is [9]:

$$B_4 = \frac{(\%CaO) + (\%MgO)}{(\%SiO_2) + (\%Al_2O_3)} \quad (6)$$

Some steels have higher sulfur contents in the final chemical composition (above 0.035% S). This is due to the improved machinability caused by the formation of MnS non-metallic inclusions. MnS non-metallic inclusions enable easier breaking of chips, which contributes to better mechanical processing of such steels. MnS inclusions are not commonly found in the steel melt. However, they form during solidification, manganese and sulfur contents increase due to segregation between dendrites, leading to the formation of MnS. As a result, MnS is mainly precipitated in the interdendritic spaces at the end of solidification. Conversely, in steels with increased machinability (FMS-Free Machining Steels, FCS-Free Cutting Steels), where sulfur is intentionally added as an alloying element, the MnS inclusions are densely dispersed throughout the steel matrix. During the machining process, the cutting tool comes into contact with the MnS non-metallic inclusions, which help to break up the chips, which reduces the cutting forces required during machining. The improvement in machinability can be attributed to several factors. First, MnS inclusions tend to be softer than the surrounding steel matrix, which makes them more easily deformable and less likely to cause damage to the cutting tool. Second, the MnS inclusions are often elongated in shape, which means that they can help to guide the chips away from the cutting tool, reducing the risk of chip buildup and associated damage. Finally, the presence of MnS inclusions can also help to lubricate the cutting tool, reducing friction and further reducing the forces required for machining. [10]

Martensitic stainless steels are the smallest group of stainless steels. They possess high strength and due to the hardenability of the martensitic matrix, they have a higher carbon content compared to other stainless steel grades. In this paper the production of martensitic stainless steels with improved machinability (high sulfur) is discussed. Machinability of stainless steels is poor, so the additions of sulfur are even higher than in carbon steels [11,12].

2. EXPERIMENTAL

The production of martensitic stainless steels (0.1 wt% C, 1 wt% Mn, 13 wt% Cr, 0.1 wt% Mo) with high sulfur contents (0.09 – 0.15 wt% S) in a 50 t ladle was analyzed. The slag samples were taken at the end of the ladle treatment, before casting (around 10 minutes after sulfur addition), steel samples were taken before sulfur addition and along with slag samples.

The chemical analysis of steel and slag was carried out using inductively coupled plasma optical emission spectrometry (ICP-OES Agilent 720), and combustion method for carbon and sulfur analysis (ELTRA CS800).

3. RESULTS AND DISCUSSION

The results of chemical analysis of the slag samples gave the oxide values in the range 45 – 50 wt% CaO, 5 – 12 wt% MgO, 25 – 30 wt% Al₂O₃, 10 – 20 wt% SiO₂. The steel melt had sulfur values between 0.09 and 0.15 wt%. The sulfur distribution ratio L_S in relation to slag basicity B_4 is presented in **Figure 2a**. The higher the slag basicity, the greater the L_S value. Since the L_S values for ladle slags are usually much higher, above 20, the system is clearly far from equilibrium [4,7]. In fact the desulfurization process is still active during casting. However, the mixing of the steel melt is limited during casting, so the kinetics are slow, as the transfer of sulfur from the metallic phase is limited. Most of the sulfur is lost up to the casting phase, where the melt is still mixed by argon blowing to ensure a homogeneous chemical composition throughout the melt. Generally, higher the L_S values mean that more sulfur was absorbed by the slag, so the sulfur yield thereby decreases, as shown in **Figure 2b** where sulfur yield is shown in relation to L_S .

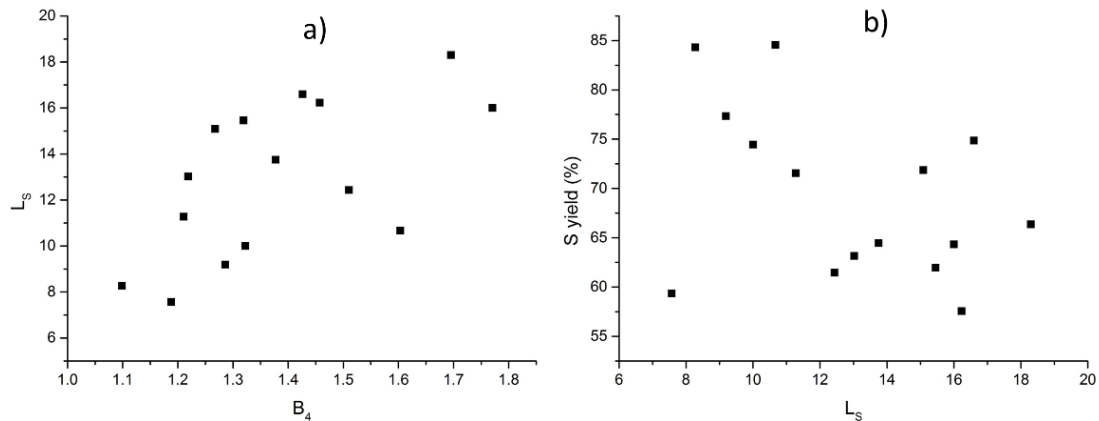


Figure 2 a) Sulfide distribution ratio (L_s) in relation to slag basicity B_4 and b) Sulfur yield in relation to Sulfide distribution ratio (L_s)

As seen from **Figure 2** lower basicity values are favorable, but then the issue of excessive refractory wear arises.

While the low yield of sulfur is problematic, the implications of desulfurization are even more so, if we consider the increase of oxygen. As explained beforehand each atom of sulfur that leaves the melt and enters the slag causes an atom of oxygen to leave the slag and enter the steel melt. When dealing with high values of sulfur (0.09 to 0.15) this means a couple of hundred of ppm O. The increase of oxygen can have a devastating effect on the amount of oxide inclusions. However, the topic of oxide non-metallic inclusions will not be discussed here. The nature of stainless steels, i.e. the high chromium content, means that there is an infinite amount of deoxidants present and that the oxygen activity will be limited, thus further promoting desulfurization.

Meanwhile, the slag/melt interphase is locally enriched with S during casting, causing CaS precipitation in the slag. The CaS rich slag physical properties change and it causes difficulties during casting, as it gets entrapped in the vortex that forms in the casting funnel. The entrapment of slag in the vortex during casting does not occur in continuous casting, but it can be an issue for ingot casting. In our case ingot casting was used. The melt is poured through the bottom of the ladle, the molten steel flows down through a vertical pipe and to one or more distribution channels that lead the melt further into the bottom of the vertical molds. The molds are filled from the bottom upwards. The surface of the molten steel in the molds is covered with a casting powder that protects the molten steel from re-oxidation and acts as thermal insulation [13]. As the casting proceeds, the boundary surface between the slag and the steel gradually deviates towards the bottom opening and takes on the shape of a funnel, which leads to the entrapment of the slag. The casting is stopped when the first traces of slag are detected in the ingot, and a significant amount (up to ten percent) of the molten steel can remain in the ladle [13]. If the entrapped slag reaches the molds it causes serious flaws in the ingot, also characterized as macro inclusions (**Figure 3**) [3]. In our case the pouring speed had to be lowered to prevent excessive funnel formation, thus lowering productivity.

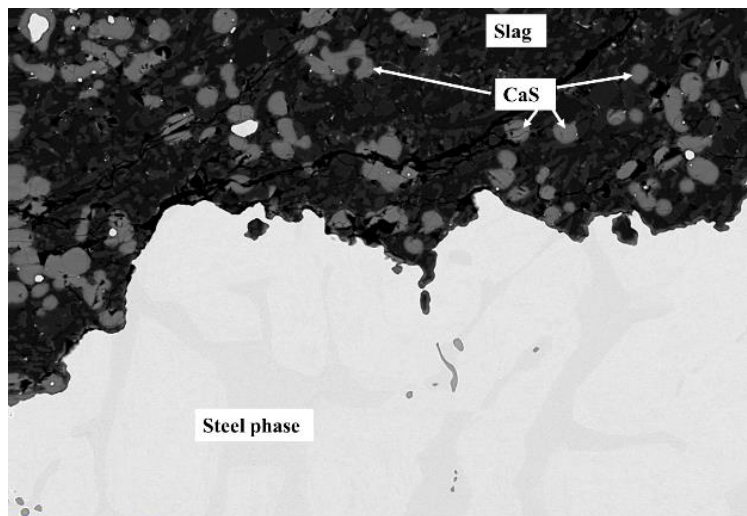


Figure 3 Microstructure of the macro inclusion – entrapped slag in the ingot

4. CONCLUSION

The production of high sulfur stainless steels is prone to low sulfur yields, which makes the process unreliable. The yield of the sulfur can be improved by lower slag basicity values, but other aspects of the steelmaking process must be considered.

The high sulfur content further proves problematic, due to the changes in the slag physical properties (CaS formation) that cause slag entrapment and macro inclusions in the ingot.

ACKNOWLEDGEMENTS

The author would like to thank Jelena Lazarević and Mitja Praznik from SIJ METAL RAVNE for the data collection.

REFERENCES

- [1] DA COSTA E SILVA, A. L. V. Non-metallic inclusions in steel origin and control. *Journal of materials Research and Technology*. 2018, vol. 7, no. 3, pp. 283-299.
- [2] ZHANG, L., THOMAS, B. G., WANG, X., CAI, K. Evaluation and Control of Steel Cleanliness – Review, In: *85th Steelmaking Conference Proceedings*. Warrendale: ISS-AIME, 2002, vol. 21.
- [3] ZHANG, L., THOMAS, B. G. State of the Art in the Control of Inclusions during Ingot Casting. *Metallurgical and Materials Transactions B*, 2006, vol. 37, no. 5, pp. 733-761.
- [4] PRETORIUS, E. B., CARLIDLE, R. C. Foamy Slag Fundamentals and their Practical Application to Electric Furnace Steelmaking. In: *EAF Conference*. York: Baker Refractories, 1998, vol. 24.
- [5] SEETHARAMAN, S. *Treaties on process metallurgy, Industrial processes, Part A, Volume 3*. Oxford: Elsevier, 2014.
- [6] GOSH, A. *Secondary Steelmaking: Principles and Applications*. Kapur: Indian Institute of Technology, 2001.
- [7] TURKDOGAN, E. T. *Fundamentals of Steelmaking*. London: The Institute of Materials, 1996.
- [8] SHAMSUDDIN, M. *Physical chemistry of metallurgical processes*. London: Minerals, Metals, Materials Society, 2016.
- [9] PRETORIUS, E. *Fundamentals of EAF and Ladle Slags and Ladle Refining Principles*, York: Baker Refractories, 2015.
- [10] ANMARK, N., KARASEV, A., JÖNSSON, P. G., The Effect of Different Non-Metallic Inclusions on the Machinability of Steel, *Materials*, 2015, 8, 751-783.
- [11] ZERTI, A., YALLESE, M., ZERTI, OUSSAMA, NOUIOUA, M., KHETTABI R., Prediction of machining performance using RSM and ANN models in hard turning of martensitic stainless steel AISI 420. *Journal of Mechanical and Engineering Science*. 2019, pp. 1-24.
- [12] KALADHAR, M., VENKATA SUBBIAH, K., SRINIVASA RAO, C. H. Machining of austenitic stainless steels – a review. *International Journal of Machining and Machinability of Materials*. 2012, vol. 12, no. 1/2, pp. 178-192.
- [13] MAZZAFERRO, G. M., PIVA, M., FERRO, S.P., BISSIO, P., IGLESIAS, M., CALVO, A., GOLDSCHMIT M. B. Experimental and numerical analysis of ladle teeming process. *Ironmaking&Steelmaking*. 2004, vol. 31, no. 6, pp. 503-508.