Effect of different process parameters on non-metallic inclusions during electro-slag remelting of a tempering steel

R Schneider1, S Schroft1,2, M Molnar1,2, G Klösch3 and C Schüller3

1 Univ. of Appl. Sciences Upper Austria, Stelzhamerstrasse 23, 4600 Wels, Austria
2 K1-Met GmbH, Stahlstrasse 14, 4020 Linz, Austria
3 voestalpine Stahl Donawitz GmbH, Kerpelystrasse 199, 8700 Leoben, Austria

stefan.schroft@fh-wels.at

Abstract. The remelting behavior of the tempering steel 50CrMo4, was investigated with several experimental melts on a lab-scale ESR-plant. The investigated parameters included a variation of the slag compositions and the use of a protective nitrogen atmosphere. Variations of the slag composition comprised slags with different contents of CaF2, CaO and Al2O3 as well as a variation of the SiO2-content. The remelted ingots were forged and analyzed regarding their chemical composition as well as their distribution and composition of the non-metallic inclusions (NMI) by automated SEM-EDX method. The chemical composition of the slag after remelting was analyzed as well. The results clearly show a relationship mainly of Si and Al in the steel with the process parameters. NMI changed in their total amount, type and size distribution. The protective atmosphere reduced the Si-losses during remelting. The majority of the NMI were of the Al2O3-& MnS-type. In general, remelting lead to an almost complete removal of sulfides, a reduction of oxisulfides and a shift towards more oxides. The total amount of NMI was most strongly reduced by the high CaF2-containing remelting slag.

1. Introduction

The electro-slag remelting process was and today is still used to minimize inhomogeneities like segregations or shrink holes and to improve the cleanliness level, in particular reducing the amount of larger non-metallic inclusions (NMI) [1-5]. Thereby the remelting slag has a direct effect on the cleanliness level as well as on the type of inclusions formed after remelting.[1,2,6-10] Furthermore, the slag composition and its basicity has a significant effect on silicon losses.[1,2,9,11]

With rising demand on steel quality, the effect of various remelting parameters on NMI has found renewed interest in recent years. The effect of a slag deoxidation treatment and of a protective atmosphere on a corrosion resistant die steel is described in [5], showing that both procedures can provide improvements when using electrodes with a high oxygen contents. Investigations on a similar additionally Ni-alloyed grade resulted in more, but finer NMI and in a corresponding increase of the oxygen content at higher melt rates.[12] This behavior was explained by differences in the precipitation and growth kinetics. Results from industrial trials on hot work tool steels and a martensitic Cr-Ni-steel in [13,14] demonstrate the strong refining capabilities of especially protective gas ESR. The effect of higher SiO2 contents in the remelting slag on the formation of NMI is documented in [15] for a hot work tool steel. Thereby larger mixed-type inclusions with higher SiO2 contents are formed, but, similar to results in [13], MA-spinels form the majority of the inclusions. This confirms also earlier results in [1,9].
Laboratory scale experiments on a die steels in [16] show advantages of low filling ratios, a protective gas (Ar) and a multi-component slag compared to a plain CaF$_2$-Al$_2$O$_3$-slag. Remelting a high-temperature steel, with slags containing up to 10 % MgO lead to a stronger reduction of larger NMI, but the number of small inclusions (< 4 µm) increased when the amount of magnesia was raised [10]. The different effects of slag compositions and a protective N$_2$-atmosphere on the remelting of a hot-work tool steel was comprehensively demonstrated in [17]. The main effect of protective gas was the elimination of the scaling behavior of the electrode and corresponding Si-losses. The strongest effect of the slag composition was found with a CaO-free almost plain CaF$_2$-Al$_2$O$_3$-slag.

With this work the effects of two different slag compositions and of a protective N$_2$-atmosphere were investigated with a tempering steel, focusing on changes in the chemical composition, especially Al and Si and on corresponding changes in content, size distribution and chemical composition of the NMI.

2. Experimental

All experiments were conducted on a laboratory scale ESR plant. A more detailed description on the plant configuration and typical operation modes can be found in [17,18].

The continuous cast and rolled tempering steel 50CrMo4 (Mat. No. 1.7228) was used. All electrodes had a diameter of 101 mm and a machined surface. Two different slags with the nominal compositions according to Table 1 were applied. The first slag (3C3A), was applied twice, once in direct contact with air, and once under protective gas (N$_2$). The other slag (2C2A) was slightly enriched with SiO$_2$ and had an increased CaF$_2$-content.

Table 1. Chemical composition of the slags after remelting in wt.%.  

| Trial, Slag | CaF$_2$ | CaO | Al$_2$O$_3$ | SiO$_2$ | MgO |
|------------|--------|-----|-------------|--------|-----|
| 3C3A       | 32     | 30  | 33          | 2      | 3   |
| 3C3A+N$_2$ | 32     | 30  | 33          | 2      | 3   |
| 2C2A       | 54     | 18  | 21          | 5      | 2   |

All experiments were performed with a frequency of 4.5Hz. The parameters were selected to realize comparable melt rates, which required the adjustment of the melting current. The voltage is the result of the electrical conductivity of the slag as well as of an immersion depth of about 1 cm (see Table 2). No deoxidants were added to the slag during remelting.

Table 2. Process parameters of the remelting experiments.  

| Trial, Slag | Atmosphere | Slag [kg] | Current [kA] | Voltage [V] | Melt rate [kg/h] |
|------------|------------|-----------|--------------|-------------|------------------|
| 3C3A       | air        | 5         | 3.1          | 62 - 64     | 39               |
| 3C3A+N$_2$ | N$_2$      | 5         | 3.3          | 58 - 62     | 39               |
| 2C2A       | air        | 5         | 4.0          | 52 - 54     | 41               |

After remelting, the ingots were forged to a diameter of 40mm. Samples for chemical analysis and investigations on NMI were taken from the upper third of the forged ingot. Additionally, the slag was analyzed after remelting. The automated SEM-EDS NMI scans were acquired in standardized fields of approximately 150mm$^2$. All detected NMI with an oxygen content of ≥ 5 wt% and an S:O-ratio of < 0.15 were considered oxides. Inclusions with oxygen and sulfur contents of ≥2 wt% each and an S:O-ratio between 0.15 and 6.67 were categorized as oxisulfides (conglomerates of oxides and sulfides). NMI with a sulfur content of ≥2 wt% and an O:S-ratio of < 0.15 were taken as sulfides.

3. Results

3.1. Changes in the chemical composition during remelting

There were only minor changes of the alloying elements C, Mn, Cr and Mo. More significant changes could be observed at the deoxidants Si and Al as well as in the S-content, which was reduced almost independent from the process parameters from 105 ppm to 20-27 ppm at all remelting trials. The
correlation between the Si- and the Al-content is visualized in Figure 1. While remelting under a protective atmosphere showed a stoichiometric exchange reaction between Si, Al and its corresponding oxides, there is a clear loss of Si for open remelting conditions, and in the case of the slag 2C2A also a significant loss in Al.

![Figure 1. Silicon and aluminium contents prior and after remelting](image)

The Chemical composition of the top slags after remelting are summarized in Table 3. The observed increase in SiO$_2$ at the open remelting processes correlates well with the Si-losses in the steel. There is also a clear correlation of the protective gas on the FeO content in the slag.

| Trial, Slag | CaF$_2$ | CaO | Al$_2$O$_3$ | SiO$_2$ | MgO | FeO |
|-------------|---------|-----|-------------|---------|-----|-----|
| 3C3A        | 32.8    | 29.0| 31.4        | 2.9     | 3.9 | 0.13|
| 3C3A+N$_2$  | 32.2    | 30.3| 33.8        | 1.8     | 3.7 | 0.05|
| 2C2A        | 50.7    | 19.5| 20.4        | 7.6     | 1.7 | 0.09|

3.2. Non-metallic inclusions
The specific amount of NMI per mm$^2$ and the corresponding area-% of the three main types of NMI are shown in Figure 2. Two general trends can be observed. The first is a strong reduction of sulfides and a corresponding increase in oxides. The second is a general trend towards less NMI in total after remelting. Furthermore, it is evident that the best results could be achieved with the CaF$_2$-rich slag 2C2A.

![Figure 2. Content of non-metallic inclusion (NMI) left: amount/mm$^2$; right: area %](image)
There was a strong increase in oxides after remelting for all inclusion sizes. Oxisulfides showed a reduction in small inclusions and an increase of larger inclusions. This effect is more pronounced for the slag C2A2. The sulfides were strongly reduced at all sizes. Combining all three types in Figure 3, there is a clear reduction in almost all inclusions sizes during remelting. This effect is better visible for larger inclusions (> 5 µm), despite the number of these inclusions is anyway quite low. Large inclusions (> 15µm) were completely removed by ESR. Despite the logarithmic scale, small differences between the results are within the accuracy of the test method and only major differences are of significance.

![Figure 3. Size distribution of non-metallic inclusion (NMI)](image)

![Figure 4. Size distribution of non-metallic inclusion (NMI) top-left: electrode; top-right: 3C3A; bottom-left: 3C3A-N2; bottom-right: 2C2A.](image)

The chemical composition of the NMI is visualized by means of the ternary system Al₂O₃-MgO-CaO in Figure 4. Most of the oxide inclusions, including the oxidic share of the oxisulfides, were allocated to the diagram. The compositions were projected to 100% by keeping their specific shares. White areas
represent compositions without NMI. Blue areas correspond to chemical compositions where only low concentrations of inclusions could be detected. On the other hand, red areas designate chemical compositions with a high share of the total inclusions. The chemical composition of the sulfides prior and after remelting was always in the range of pure MnS.

The NMI of the electrode show two different populations, one of pure CaO and the other in the range of high Al$_2$O$_3$-contents. After remelting the CaO-type inclusions have largely or completely disappeared. The detailed composition of the high-alumina-type inclusions changes slightly during remelting.

4. Discussion

According to [1,2,8-10,17,19] the loss of Si and the gain of Al in the steel can be partially explained by equation (1).

$$3[Si] + 2(Al_2O_3) \leftrightarrow 3(SiO_2) + 4[Al] \quad (1)$$

This equilibrium condition is the primary reason for the reduced Si- and the increased Al-contents after remelting under the protective atmosphere. This relationship is indicated as a dashed line in Figure 1. In case of the slag 2C2A the SiO$_2$-content and activity of the slag was increased while the Al$_2$O$_3$-content and activity was reduced, shifting the equilibrium to lower Al contents at almost similar Si-values. Both trials operated without protective atmosphere show a loss in total Al+Si and are therefore situated below the equilibrium line due to additional oxidation effects.

As described in [5,16,17] scaling at the electrode surface just above the slag from iron to iron oxide, which is the main reason for an oxygen uptake into the slag when remelting is performed in contact with air. Such uptake of FeO into the slag, results in an additional loss of Si (and/or Al). These oxidation reactions also contribute to the observed increase on SiO$_2$ and FeO in the slag for the open remelting conditions which can only be prevented by the use of a protective atmosphere. [8,17]

The strong desulfurization in all remelting trials is in agreement with earlier findings in e.g. [1,16,17,20]. A significant difference between open remelting and protective gas operation as described in [1,16,17] could not be observed. This indicates that the desulfurization reaction according to equation (2) did not lead to a saturation of the slag with sulfur and the regeneration of the slag in contact with oxygen from the atmosphere according to equation (3) is not yet dominating the result.

$$2[S] + 2(O^{2-}) \leftrightarrow 2[O] + 2(S^{2-}) \quad (2)$$

$$2(S^{2-}) + 3\{O_2\} \leftrightarrow 2\{SO_2\} + 2(O^{2-}) \quad (3)$$

The reason for this behavior might be found in the relatively small ingot size compared to the slag volume of this laboratory size experiments.

All remelting trials led to strong reductions in sulfides, partially also of oxisulfides and a significant increase in oxides. The reduction in sulfides (and oxisulfides) is directly related to the reduction of sulfur as described before. To some extent, and according to findings in [5,8,12,17], this effect can also be held responsible for the increase in oxides, as oxides often act as nucleus for the sulfide formation leading to mixed NMI. Therefore the determined threshold values for the S:O-ratio between oxides, oxisulfides and sulfides may lead to a general shift in the categorization from oxisulfides to oxides and from sulfides to oxisulfides when the S-content in such mixed NMI is reduced.

The chemical compositions of NMI, both prior and after remelting with and without protective atmosphere, differ from results of other steels as described in [9,13,14,16,17] where MA-spinel-type inclusions are dominating. A positive effect of higher CaF$_2$-contents on inclusion removal as described in [21] for a Ni-base Superalloy could be confirmed.

In this study the main content of inclusions is < 10µm and, similar to results in [17], can be regarded as newly formed during solidification. Therefore their composition is mainly based on equilibrium condition between aluminum and oxygen in the steel, which is similar to the high-Al$_2$O$_3$-type inclusions of the electrode but not a question of survival from the electrode. In contrast CaO-type inclusions were almost completely removed. Such small inclusions cannot be removed into the slag by floatation in the liquid melt pool and become trapped in the advancing solidification front [5,7,8].
5. Summary and Conclusions
Based on these results the following conclusions can be drawn.

Chemical reactions:
- The reactions between the melt (Al, Si) and the slag (Al₂O₃ and SiO₂) follow the corresponding equilibrium reaction.
- Except for remelting under protective atmosphere, all remelting trials showed a loss of Si+Al due to a FeO uptake into the slag by the scaling of the electrode.
- Open ESR leads to higher FeO- and SiO₂-contents in the slag.
- Sulfur was reduced at all remelting conditions.

Non-metallic inclusions:
- The total content of non-metallic inclusions was reduced by all remelting experiments.
- Higher CaF₂-containing slag lead to less NMI and therefore to a better level of cleanliness.
- While the content of oxides rose significantly, oxisulfides were partially reduced and sulfides strongly removed, this may be related to a shift of the S:O-ratio of mixed-NMI.
- Better cleanliness is based on the reduction of sulfides and on the elimination of larger NMI.
- Similar to one of the main populations in NMI-composition of the electrode, the highest content of NMI after remelting was of the high-Al₂O₃-type, with small concentrations of CaO and MgO.

Acknowledgments
The authors wish to thank voestalpine Stahl Donawitz GmbH for the financial, personnel and intellectual support. Likewise, the financial support of the Austrian Research Promotion Agency (FFG) for the “Competence Center for Excellent Technologies in Advanced Metallurgical and Environmental Process Development” (K1-Met) within the frame of the COMET-program is gratefully acknowledged.

References
[1] Holzgruber W and Plöckinger E 1968 Stahl Eisen 88 638
[2] Holzgruber W and Plöckinger E 1968 Berg- Hüttenmaenn. Monatsh. 113 83
[3] Plöckinger E 1973 J. Iron Steel Inst. 211 533
[4] Mitchell A 2005 J. Mater. Sci. Eng. A 10 413
[5] Shi C B, Chen X C, Guo H J, Zhu Z J and Ren H 2012 Steel Res. Int. 83 472-86
[6] Mills C K and Keene B J 1981 Int. Met. Rev. 1 21
[7] Mitchell A 1974 Ironmaking Steelmaking 1 172
[8] Mitchell A, Carmona F R and Wei C H 1982 Iron Steelmaker 9 37
[9] Allibert M, Wadier J F and Mitchell A 1978 Ironmaking Steelmaking 5 211
[10] Radwitz S, Scholz H, Friedrich B and Franz H 2015 Proc. Int. Symp. Liq. Met. Process. Cast. (Leoben) N71
[11] Miska H and Wahlster M 1973 Arch. Eisenhuttenwes. 44 81
[12] Korp J 2012 Berg- Hüttenmaenn. Monatsh. 157 174
[13] Reiter G, Schuetzenhoefer W, Tazreiter A, Martinez C, Wuerzinger P, Loecker C 2013 LMPC 2013, Proc. Int. Symp. Liq. Met. Process. Cast. (Austin) p 213
[14] Liu J H, Wang G X, Bao Y P, Yang Y, Yao W and Cui X N 2012 J. Iron Steel Res. Int. 19 1
[15] Schneider R, Schüller C, Würzinger P, Reiter G and Martinez C 2015 Berg- Hüttenmaenn. Monatsh. 160 117
[16] Dong Y W, Jiang Z H, Cao Y L, Yu A and Hou D 2014 Metall. Mater. Trans. B 45 1315-24
[17] Schneider R, Molnar M, Gelder S, Reiter G and Martinez C 2018 Steel Res. Int. 89
[18] Schneider R, Paar A, Zeller P, Reiter G, Schützenhöfer W and Würzinger P 2011 Berg- Hüttenmaenn. Monatsh. 156 112
[19] Mitchell A 1981 Can. Metall. Q. 20 101
[20] Miska H and Wahlster M 1973 Arch. Eisenhuttenwes. 44 19
[21] Manjili M H and Halali M 2017 Metall. Mater. Trans. B 49 61