Experimental study on the influence of the Ti/Al ratio and different addition practices on the inclusion landscape in ULC steels

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Abstract: The continuous casting of Ti-alloyed ULC steels is often afflicted to alumina clogging. Different mechanisms and influencing parameters affecting this phenomenon are described in literature. Among them, one essential aspect is the Ti/Al ratio mainly controlling the size of alumina particles. Secondly, the time between Al and Ti addition is seen to be decisive for the final inclusion landscape.

Within the present study, experiments on laboratory scale are carried out simulating the influence of different Ti/Al ratios as well as of various deoxidation and Ti-addition practices on size, chemical composition and morphology of non-metallic inclusions in ULC steels. Special attention is paid on multiphase inclusions. All experiments were carried out in a Tammann Furnace enabling very well controllable conditions. Next to the time between the Al and Ti addition also the duration time after Ti alloying was varied. Automated SEM/EDS analyses were used for inclusion characterization. The results are then compared to industrial observations. Furthermore, investigations using a high-temperature laser scanning confocal microscope allow the in-situ observation of the formation and modification of oxide inclusions through Ti-addition. Finally, based on the performed experiments the main aspects possibly influencing the clogging tendency of these steels are summarized and discussed.

Key words: Clogging, Microscopic Steel Cleanness, Ti-stabilized ULC grades, multiphase inclusions, Laser Scanning Confocal Microscope

1 Introduction

Alumina clogging is often observed in the production of Ti-alloyed ULC steels. Numerous studies have already been carried out dealing with this topic and literature proposes different factors which can be responsible for this phenomenon.

One of the most often discussed aspects in this context is the formation of Al-Ti-O inclusions – or at least the formation of an Al-Ti-O-layer covering the Al_2O_3-inclusions. Ruby-Meyer et al.[1] showed that Ti exists in the form of a binary TiO_x-Al_2O_3 phase in the inclusions observed in Ti-bearing Al-killed low carbon steels. These inclusions are seen to be wetted more easily by the liquid steel compared to the pure Al_2O_3[2]. As a result, the agglomeration and separation of TiO_x-Al_2O_3 inclusions at the steel/slag interface is inhibited what finally leads to a larger number of fine particles in the tundish. A similar layer formation around pure Al_2O_3 was also reported by Basu et al.[3].

Secondly the Ti/Al ratio is seen to substantially influence the final inclusion morphology which could finally cause more intense SEN clogging[4,5]. However, the real mechanism behind this is still unclear.

The present work focuses on these Al-Ti-O inclusions and their formation and modification due to different alloying and deoxidation practices. Laboratory experiments in a Tammann Furnace as well as an in-situ observation using a HT-LSCM are performed. Next to the influence of the Ti/Al ratio, the impact of time between Al and Ti addition as well as the duration time after Ti addition are discussed. Moreover, the influence of the total oxygen content on the observed inclusion landscape is described.

2 Experimental Procedure

In order to study the formation and modification behavior of inclusions through different deoxidation practices in Ti-alloyed ULC steels on laboratory scale experiments in a Tammann Furnace as well as in-situ observations using a HT-Laser Scanning Confocal Microscope were carried out. All experiments were done with the same raw material (composition given in Table 1).

Table 1 Chemical composition of the raw material used for all experiments.

	wt.-% C	wt.-% Si	wt.-% Mn	wt.-% Al	wt.-% Ti
ULC steel	0.0020	0.0010	0.0740	0.020	0.0040

2.1 Laboratory experiments in a Tammann Furnace

The Tammann Furnace is a high-temperature resistance furnace, which can be heated up to 2000 °C. Due to the carbon heating tubes inside the furnace and their reaction with the residual oxygen, the experiments are performed under slightly reducing atmosphere. For more details to the furnace itself as well as the experimental set-up it is referred to a previous publication [6].

All laboratory experiments were carried out under Ar-atmosphere (Argon 5.0), using a sample weight of 500 g commercial ULC steel. The samples were heated up to 1600 °C and hold at this temperature for a predefined time depending on the alloying and deoxidation practice. Two different test series were done:

- In the first series, the total oxygen content of the ULC steel was increased consciously using Fe-powder to appr. 300 ppm before the addition of Al and/or Ti. These conditions are similar to the oxygen activity after RH-treatment of ULC steels.
- In the second series, Al and/or Ti were added to the raw material without a previous increase of the total oxygen content.

Table 2 gives an overview on the performed experiments and the different alloying and deoxidation treatments.
The samples then solidified under accelerated cooling. Finally, the inclusion landscape in the samples was characterized using manual and automated SEM/EDS analyses. For the present investigation, a Scanning Electron Microscope manufactured by Fei (Quanta 200 MK2) was used in combination with an EDS system of Oxford Instruments (INCA). Details to the analyzing method and the procedure are given in [6].
The following influencing parameters on the final inclusion landscape in ULC steels were investigated within the two series:

- Addition time between Al and Ti (simultaneously, 2 min or 5 min)
- Holding time after Ti-addition (1, 3, 5 or 8 min)
- Ti/Al ratio in the steel (0.7, 1.2 or 1.8)
- Total oxygen content (appr. 300 ppm or appr. 30 ppm).

Table 2 Overview on performed experiments and the used test parameters.

	No.	Ti/Al ratio	Deoxidation practice	Holding time after Ti-addition
O_{tot}=appr. 300 ppm, N_{tot}=appr. 15 ppm	**S1-V1**	0.03	Al-deoxidation, 2 min holding time	no Ti-addition
	S1-V2	1.8	Al-deoxidation and Ti-addition at the same time	2 min
	S1-V3	1.8	Al-deoxidation, Ti-addition after 2 min	2 min
	S1-V4	1.8	Al-deoxidation, Ti-addition after 5 min	2 min
O_{tot}=appr. 20 ppm, N_{tot}=appr. 20 ppm	**S2-V0**	0	Al-deoxidation, 2 min holding time	No Ti-addition
	S2-V1	1.2	Al-deoxidation, Ti-addition after 2 min	1 min
	S2-V2	1.2	Al-deoxidation, Ti-addition after 2 min	3 min
	S2-V3	1.2	Al-deoxidation, Ti-addition after 2 min	5 min
	S2-V4	1.2	Al-deoxidation, Ti-addition after 2 min	8 min
	S2-V5	1.8	Al-deoxidation, Ti-addition after 2 min	1 min
	S2-V6	1.8	Al-deoxidation, Ti-addition after 2 min	8 min
	S2-V7	1.8	Al-deoxidation, Ti-addition after 5 min	1 min
	S2-V8	1.8	Al-deoxidation, Ti-addition after 5 min	8 min
	S2-V9	0.7	Al-deoxidation, Ti-addition after 2 min	1 min
	S2-V10	0.7	Al-deoxidation, Ti-addition after 2 min	8 min

2.2 In-situ observations with the HT-LSCM

The HT-LSCM was used to observe the formation and modification of inclusion in the ULC steel (see Table 1) with Ti-addition. The experimental setup at the Chair of Metallurgy consists of a Laser Scanning Confocal Microscope attached to a high temperature furnace. The LSCM is equipped with extra long distance objectives. In order to be out of the characteristic spectrum of samples with temperatures up to 1600°C, the wavelength of the laser is 405 nm. A detailed description of the method itself, the experimental setup and the different application possibilities can be found in [7].

For the present study appr. 2 g of the ULC steel were heated up in an Al_2O_3 crucible under Ar-atmosphere adding very small particles of FeTi in order to simulate Ti-addition. Then, at a constant temperature of appr. 1550 °C the formation and modification of inclusions was studied in-situ for several minutes. Finally, the sample was cooled down and the sample surface was analyzed in the SEM. Furthermore, the sample was subsequently prepared metallographically and the inclusions on the polished specimen were examined.

3 Results

3.1 Results of Series 1 of Tammann Furnace Experiments

Series 1 focused on the influence of the addition time between Al and Ti on the final inclusion landscape. Figure 1 summarizes the results of automated SEM/EDS analyses for S1-V1 to S1-V4. The chemical composition of all detected inclusions is represented in the quasi-ternary system Al-Ti-O. The inclusions are classified in four categories: Alumina inclusions (containing neither Ti nor N), Ti-oxides (containing neither Al nor N), AlTi-Oxides (containing no Nitrogen) and finally Alumina inclusions with TiN. It is worth noting that the alumina inclusion population includes also pre-existing alumina particles from the ULC steel and also reoxidation products. However, the use of a Ti-free ULC steel guarantees that only alumina inclusions preexist and prevents the introduction of other – and more difficult controllable – inclusions or trace elements. The symbol size indicates the amount of inclusions detected at a certain composition range.

While in S1-V1 only a large amount of alumina inclusions was found, the simultaneous addition of Al and Ti (S1-V2) also leads to the formation of a significant amount of AlTi-Oxides. The number of Ti-oxides is very limited and so is the number of alumina inclusions with surrounding TiN. A more detailed investigation of these AlTi-Oxides proved that in the case of S1-V2 mainly two populations of these type exist (see Figure 2a): Ti-rich inclusions with a low Al-content (TiOx and $TiOxAl_2O_3$) and Al-rich inclusions with low Ti-content (Al_2O_3 with $TiOxAl_2O_3$).

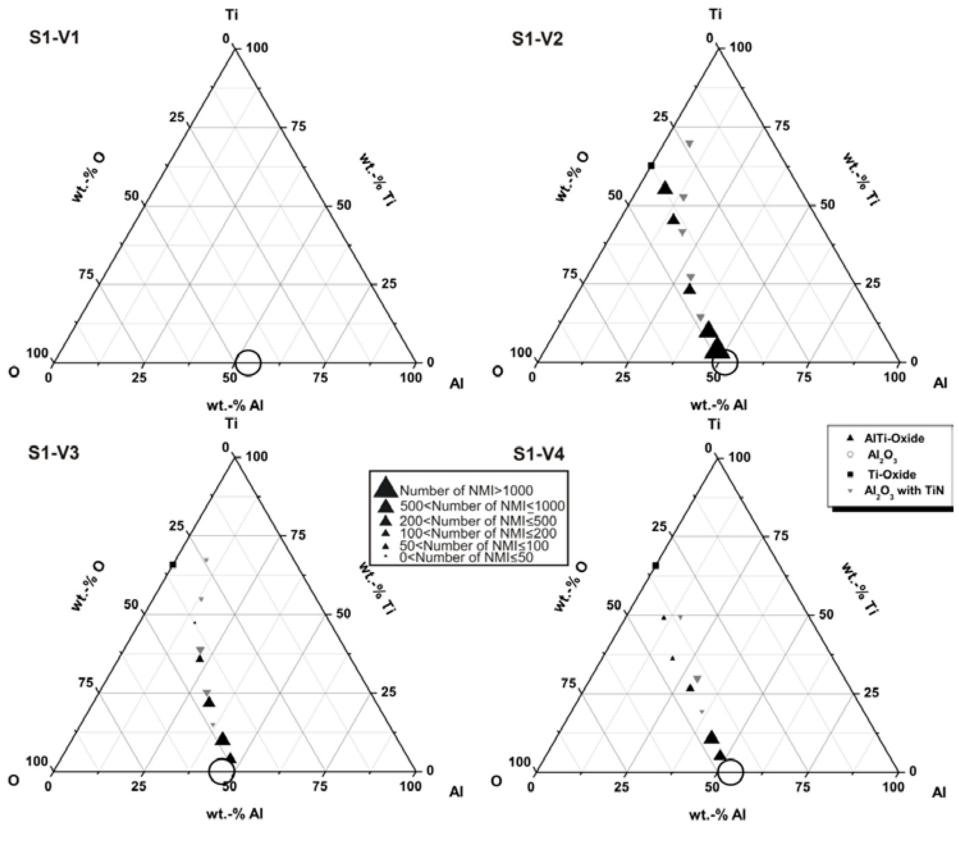

Fig.1 Inclusion composition within the quasi-ternary system Al-Ti-O for S1-V1 to S1-V4 simulating different deoxdation practices and times between the addition of Al and Ti.

Figure 2b illustrates the size distributions of Al_2O_3 in the four performed experiments. The mean ECD lies at appr. 3 µm for all cases. The mean ECD of the entire amount of AlTi-Oxides is higher and lies between 4 and 5 µm. But, as shown in Figure 2c, the Ti-content of AlTi-Oxides has a remarkable influence on their size: While the Al-rich inclusions show a comparable distribution to Al_2O_3, the higher the Ti-content the higher their mean ECD and the more irregularly the distribution itself.

S1-V3 (2 min between Al and Ti addition) results in a comparable inclusion landscape as S1-V2, but with one significant difference: The total number of the AlTi-Oxides is significantly lower and there exist only few Ti-rich AlTi-Oxides. This trend is continued with further increasing the waiting time between Al- and Ti-addition: In sample S1-V4, nearly all AlTi-Oxides are close to the composition of pure Al_2O_3.

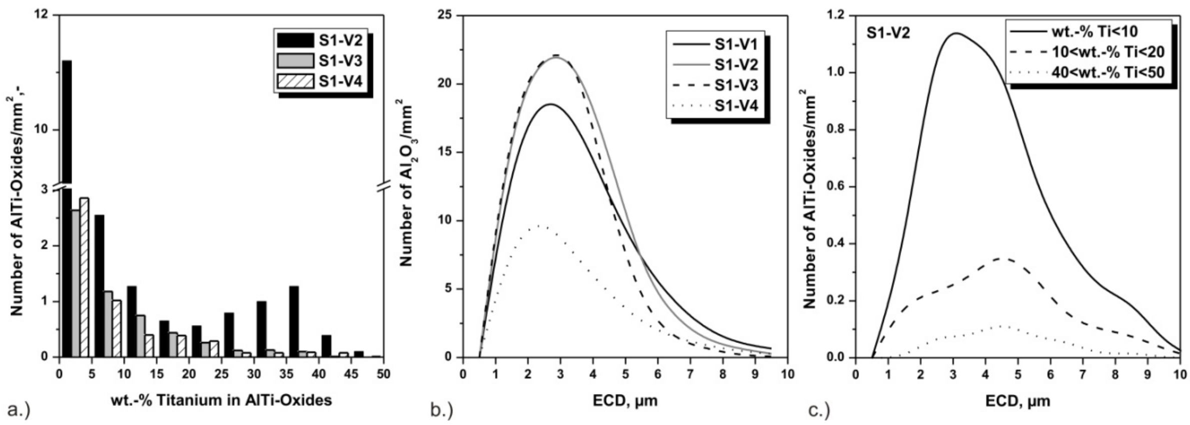

Fig. 2 Detailed analysis of AlTi-Oxides and comparison with pure Al_2O_3: a.) Ti-content of AlTi-Oxides; b.) Comparison of Al_2O_3 size distributions between S1-V1 and S1-V4 and c.) Comparison of size distribution of AlTi-Oxides with different Ti-content.

3.2 Results of Series 2 of Tammann Furnace Experiments

Series 2 offered totally different pre-conditions for Al- and Ti-addition due to the significantly lower total oxygen content which results in a very different overall inclusion landscape: While in series 1 the predominant inclusion types were pure Al_2O_3 and AlTi-Oxides, in the second series TiN and Al_2O_3 with TiN are the two most frequent inclusion types. This trend gets more obvious with increasing Ti/Al ratio in the steel. The influence of the Ti/Al ratio on the final inclusion landscape can be summarized as following:

- The total number of inclusions was found to increase with higher Ti/Al ratio as well as with longer holding time after Ti-addition. However, it has to be kept in mind that the predominant inclusion types in this series were nitrides. Thus, a possible related impact to clogging has to be considered very carefully.
- As shown in Figure 3 the mean ECD of Al_2O_3 decreases with increasing Ti/Al ratio in the steel (exemplarily displayed for 2 min between Al and Ti addition and a holding time after Ti-addition of 8 min).

Focusing on the morphology of multiphase inclusions Al_2O_3 with TiN in series 2, a strong influence of holding time after Ti-addition as well as of the time between Al- and Ti-addition was observed. The Al_2O_3 inclusion tends to act as heterogeneous nuclei for TiN. A longer holding time after Ti-addition enhances the complete surrounding of the Al_2O_3 with TiN. The time between Al- and Ti-addition affects the size ratio between the two inclusion phases. The longer the distance between the addition the larger the initially formed Al_2O_3 in relation to the surrounding TiN.

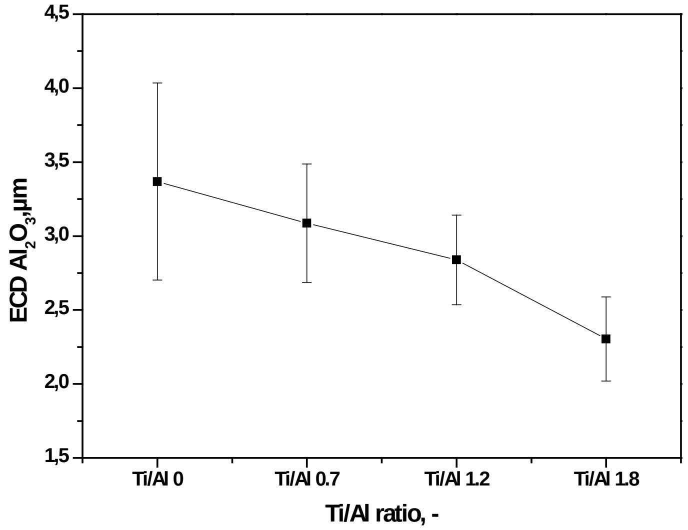

Fig. ECD of Al_2O_3-particles versus Ti/Al-ratio of the steel.

3.2 Results of in-situ observations with the HT-LSCM

This method enables the in-situ observation of inclusion formation and evolution at high temperatures. Figure 4a gives an example of the melting sample surface and the immediate start of inclusion formation. With longer holding time above 1500 °C a growth and agglomeration of inclusions is observed. Moreover, as the comparison between Figure 4b and c shows (see the marked area), a change in wetting behavior of the inclusions in the liquid melt occurs within a few seconds. This can be attributed to a change in inclusion composition. Figure 5 demonstrates SEM-images of the analyzed sample: Next to some pure Al_2O_3, mainly AlTi-Oxides with varying Ti-content were detected. Different inclusion shapes were found for the AlTi-Oxide type, from nearly spherical to polygonal and also dendritic shape. A SEM-mapping of an almost spherical Ti-rich AlTi-Oxide is shown in Figure 5d. Al and Ti are homogeneously distributed over the whole inclusion; a layer formation could not be observed.

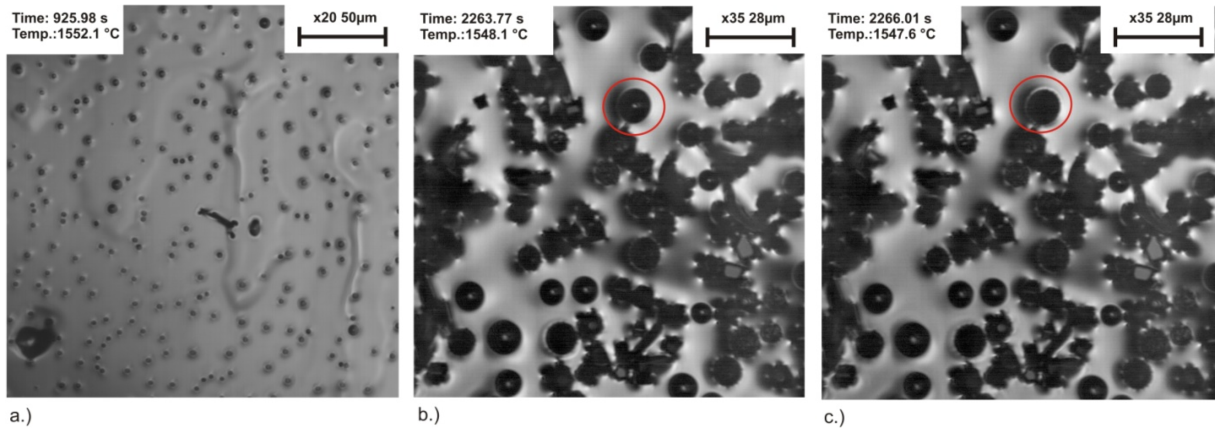

Fig. 4 Images from the HT-LSCM showing the evolution of AlTi-Oxides and their modification with longer holding time at experimental temperature.

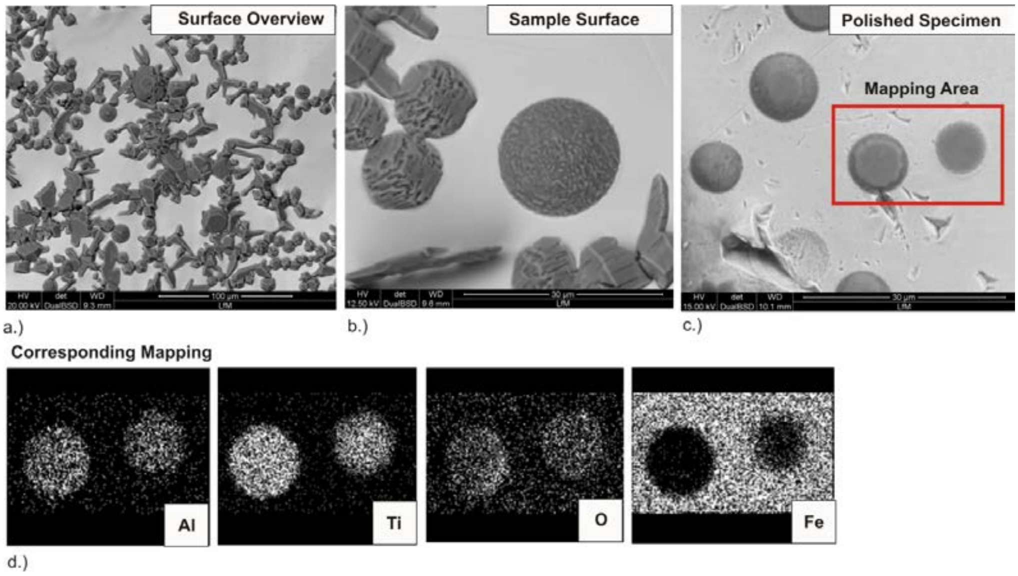

Fig. 5 a.) to c.) SEM-images from the samples surface and the metallographic specimen illustrating the morphology of Ti-rich AlTi-Oxides and d.) SEM-mapping of an Ti-rich AlTi-oxide.

4 Summary and Conclusions

Within the present study the influence of different alloying and deoxdation practices on the final inclusion landscape in ULC steels were investigated. Out of the obtained results the following conclusions can be drawn:

- The addition of Al and Ti to the reoxidised ULC steel (Series 1) results under the present conditions mainly in the formation of Alumina inclusions. However, also AlTi-Oxides form. In most inclusions of this category, Ti is evenly distributed over the entire inclusion and not enriched in a surface layer. This justifies the conclusion that the AlTi-Oxide type inclusions nucleate after the Ti-addition. The preexisting alumina inclusions seem to be largely unaffected. The latter was also confirmed by HT-LSCM experiments.
- The total oxygen content as well as the Ti/Al ratio in the steel changes the inclusion landscape significantly (comparison between Series 1 and 2).
- The morphology of multiphase inclusion is highly affected by the time between Al- and Ti-addition as well as the holding time after Ti-addition.
- The waiting time between Al- and Ti-addition seems to be a key parameter to control the number and composition of alumina inclusions containing Ti. However, although comparable results to industrial samples[8,9] have been obtained, conclusions on the industrial process have to be drawn very carefully.

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