CHARACTERIZATION OF NONMETALLIC INCLUSIONS IN Ti STABILIZED Al-KILLED ULTRA-LOW CARBON STEEL*

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Abstract

The present work is based on the characterization of nonmetallic inclusions in Ti stabilized ultra-low carbon steel, produced in a large steel mill. Due to a large incidence of submersed valve clogging in a continuous casting, the study is important in order to know the characteristics of the inclusions which are causing the problem. Total of 24 heats were sampled in the tundish and manually analyzed with a scanning electron microscope. The results revealed that 98.65% of the 3183 inclusions analyzed were solid in steelmaking temperature and 66.54% were alumina. The solid inclusions of alumina have low wettability for the iron bath, showing a high tendency of agglomeration in the submersed valves, affecting the castability. It has been concluded from the results and literature that some alternative measures such as the application of the treatment with calcium, precautions to avoid steel re-oxidation and the total or partial replacement of the pre-deoxidized element; would reduce the obstruction problem.

Keywords: Nonmetallic inclusions; Clogging of submersed valves; Manual analysis of inclusions.

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1 INTRODUCTION

Inclusions can be defined as nonmetallic phases and sometimes intermetallic, inserted in the steel matrix [1]. These can be originated basically from the following sources: steel deoxidation, slags, refractories, chemical heating and steel reoxidation. Consequently, there should be an adequate inclusion characteristics, so in case there is an improper quantity, morphology and/or chemical composition of these contents, problems may occur such as: Clogging of submersed valves, cracks induced by hydrogen, fragility in low temperatures, wire break during cold drawing, etc [1, 2, 3].

Aluminum is the deoxidizer most applied as it promotes an efficient deoxidation at a satisfactory cost. It is effective in the control of austenitic grain and in the formation of nitrides, enabling the removal of nitrogen solution [3]. In this type of deoxidation, the product solid alumina (Al_2O_3) is typically found [4]. Inclusions of solid alumina are frequently related to the obstruction of valves during the continuous casting. The problem is caused by the high angle of contact of the inclusion of alumina with liquid steel. Therefore, these inclusions anchor themselves along the refractory surface of the submersed valves and tend to cluster [4].

Spinel inclusions (Al_2O_3-MgO), are also possible causes of obstruction of submersed valves [5]. Just like alumina, the spinels have a high angle of contact with steel liquid [6]. Magnesium is not intentionally added, the main sources of magnesium during steel manufacturing are: impurities in the addition of Al with the deoxidizer, deterioration of the refractory and the slags [7]. MgO-base refractories and MgO bearing slags both have the potential sources of Mg for molten steel which subsequently leads to the formation of spinels [8].

Addition of titanium in Al-killed steel forms aluminum-titanate inclusions [9, 10]. The insertion of Ti has shown to accelerate the clogging tendency of low carbon steel deoxidized to aluminum [11]. The re-oxidation can worsens the castability of Al-killed Ti-steels as it forms inclusions rich in Ti which cause large-scale melt freezing inside the nozzle deposits [12]. The possible reasons for nozzle clogging during the casting of this kind of steel. First Al-Ti-O inclusions are formed due to reoxidation by air or molten slag, which acts as bonds among the inclusions of Al_2O_3 and after, the addition of Ti increases the wettability between the nozzle refractory and molten steel [13].

The application of the treatment with calcium has the objective to control the shape and composition of the oxides and sulfides inclusions in Al-killed steel [14]. The principle of the transformation of solid Al_2O_3 inclusions is the reaction between the dissolved calcium in the molten metal and the alumina to produce liquid inclusions of CaO-Al_2O_3 [15]. Liquid inclusions have a small angle of contact with steel liquid and tend not to agglomerate [16]. These liquid inclusions avoid obstructions [17].

This work presents the main inclusions found in an Ti stabilized Ultra-Low Carbon (ULC) steel with high tendency of valve clogging, indicating possible alternatives from literature for a good castability.

2 MATERIALS AND METHODS

Samples of Al-killed ULC steel without calcium treatment were obtained from the tundish in 24 heats, through a lollipop sampler. The average chemical composition of this steel, obtained from an optical emission spectrometer is presented in Table 1 and its steelmaking route is illustrated in Figure 1.

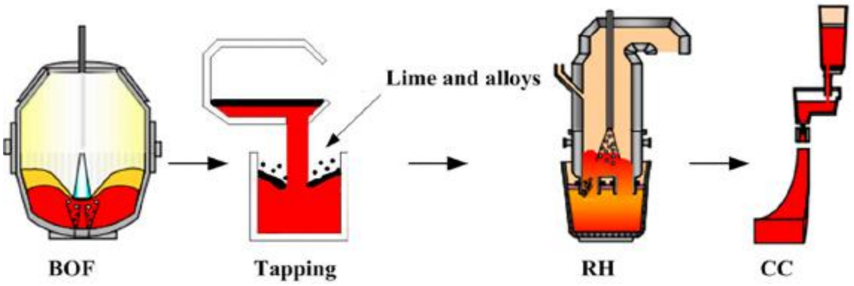

Figure 1. Steelmaking route [18].

Table 1. Chemical composition of the ULC steel investigated.

C	Si	Mn	S	Al	Cr	Nb	Ti	V	Ca
0.0018	0.007	0.135	0.0067	0.0407	0.008	0.018	0.0414	0.002	0.0001

The preparation of the samples was made by cut through a cut-off. Following, the samples were built-in and went through metallographic preparation with the objective of removing superficial scratches. The latter consisted of sanding with sandpapers size 100, 220, 340, 400, 600 and 1200 mesh and polishing with diamond paste with size 6, 3 and 1 µm. No superficial attack was applied.

After metallographic preparation, an area for analysis of 75 mm² was selected for each sample, using a permanent marker to demarcate the area of interest.

A manual analysis of inclusion occurred in a Tesca Scanning Electronic Microscope (SEM) of model Vega XMU coupled with an energy dispersive x-ray spectrometer. Sizes, elementary compositions and quantity of inclusions were acquired enclosed in the selected areas. The analysis in SEM-EDS was performed with an acceleration voltage of 20KV and an scanning gain of 500x.

The elementary chemical compositions of inclusions with more than one element were normalized and balanced to the form of oxides. Subsequently, the compositions were plotted in ternary diagrams for the obtainment of their melting point which were compared to the steelmaking temperature.

3 RESULTS AND DISCUSSION

3.1 Classification by size

A total of 3183 inclusions of the 24 samples analyzed were found. Generating an average of 132.6 inclusions per sample. They were classified by a size range as presented in figure 2. 60.98% of the inclusions were in a range lower than 5 µm. This can be an evidence of the characteristics of agitation in the degasser [19]. In the beginning of the agitation, the inclusions coalesce and increase in size; therefore, these are easily removed, along with the big inclusions by floatation. For the smaller remaining inclusions, the colisions are difficult due to their lower quantities and also having difficulties in floating due to the size. Hence, in the molten metal the smaller inclusions are conserved [19].

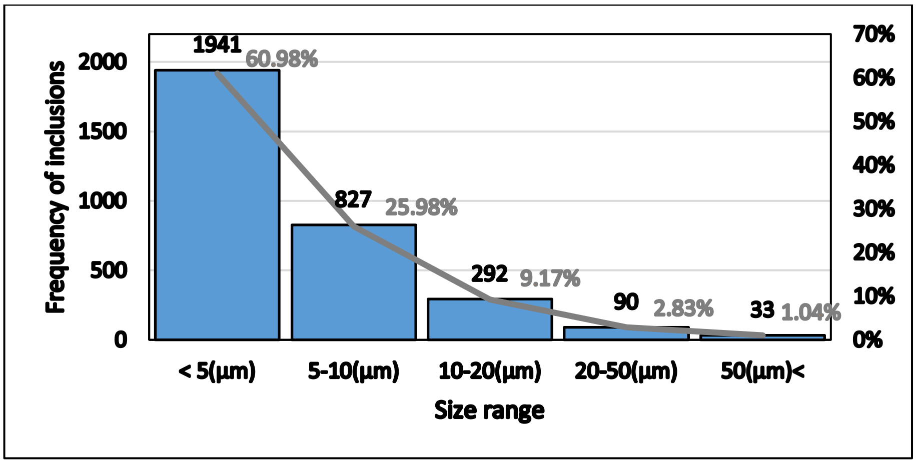

Figure 2. Distribution of the number of inclusions per size.

Only 1.04% of the inclusions were above 50 µm, however among these, inclusions above 1000 µm were observed and all of them had titanium oxide in their composition, in addition to a complex morphology.

3.2 Classification by chemical composition

Figure 3 presents a quantity of inclusions found in accordance with the type of inclusion, according to its chemical composition. Based on the results obtained, a greater quantity of alumina was found, followed by inclusions of spinels and entitled inclusions as uncommon. The latter is incorporated mainly by inclusions containing oxide of titanium and aluminum, in addition to the inclusion of complex compositions. Sulfide were not found.
Figure 4 presents, in bars, the total quantity of inclusions and in the lines, the percentage of each type of inclusion found in each heat analysis. These were identified with letters. It is also possible to identify in almost all heats, that alumina was most dominant followed by spinels and uncommon inclusions. These three types represent 87.4% of the identified inclusions and will be displayed during this work. Few calcium-aluminates were found which reflects the fact that the use of the treatment of inclusions with calcium was not applied in these heats.

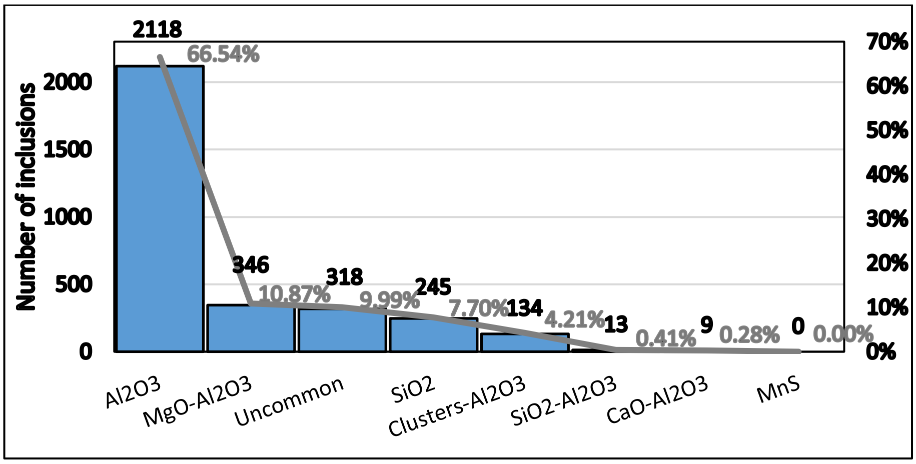

Figure 3. Distribution of the number of inclusion per chemical composition.

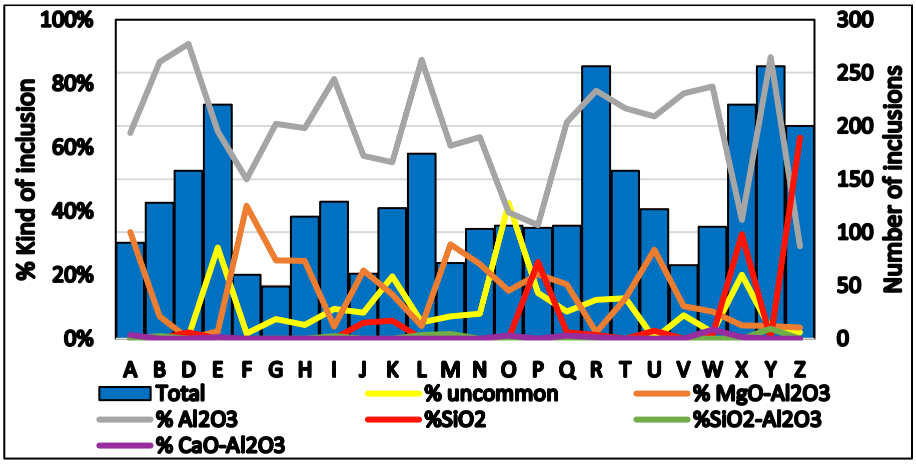

Figure 4. Distribution of the total number of inclusions and the type of inclusions per heat.

3.3 Characteristics of the principal identified inclusions

The alumina was shown in various sizes and morphologies as illustrated in figure 5. The origin of alumina has, as its main source, aluminum in the deoxidation phase, refractory particles and can also be incorporated from the impurities along with other ferroalloys [20]. 134 clusters of alumina were also found as shown in figure 6, along with an elementary map. Small particles of alumina are formed during deoxidation which can agglomerate creating clusters [21, 22]. Tiekink et al (2010) found various rough clusters of alumina in a steel intentionally reoxidized by air revealing that clusters can be an evidence of reoxidation.

The spinels ($MgO-Al_2O_3$) are presented with a globular morphology and in small diameters with an average of 3 µm. These are presented in figures 7 and 8. Refractory of Al_2O_3 rarely causes influence in the inclusions of Al-killed steel, while MgO refractory and glazed Al_2O_3 refractory can help in the formation of spinel inclusions from alumina inclusions [24]. In contrast to ladle glaze, MgO refractory can generate more Mg dissolved in liquid steel [24].

These MgO-base refractories, as those that have MgO-C, can provide Mg for the bath by the reduction reaction of oxide of manganese with the Al of bath and/or by the proper refractory carbon [8]. In terms of the mechanism of the supply of

Mg to steel liquid, the reactions of reduction with Al and C may occur. However, the most predominant occurs through carbon [8].

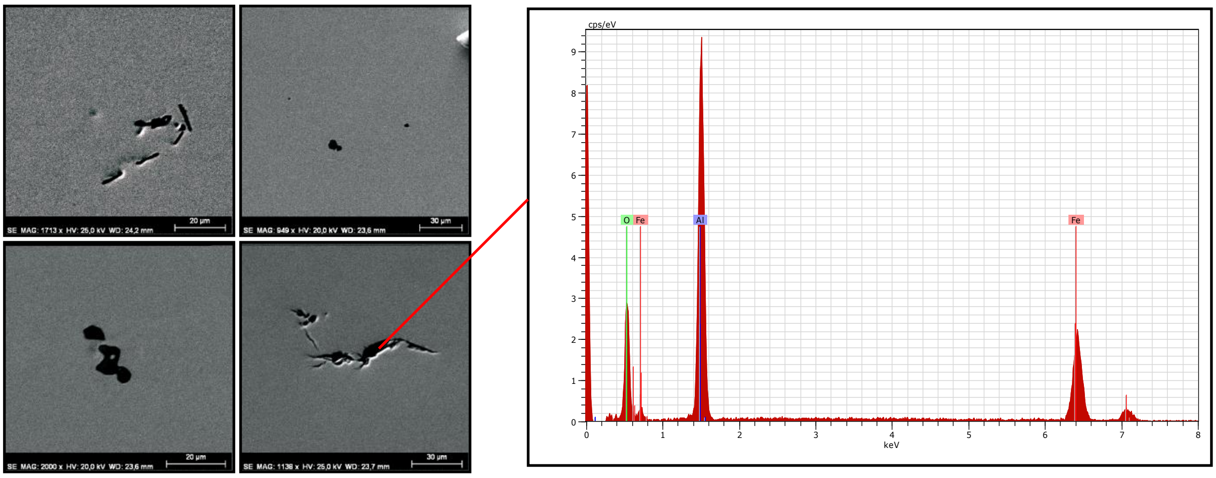

Figure 5. Inclusions of alumina with varied morphologies and sizes. Images and EDS obtained by SEM.

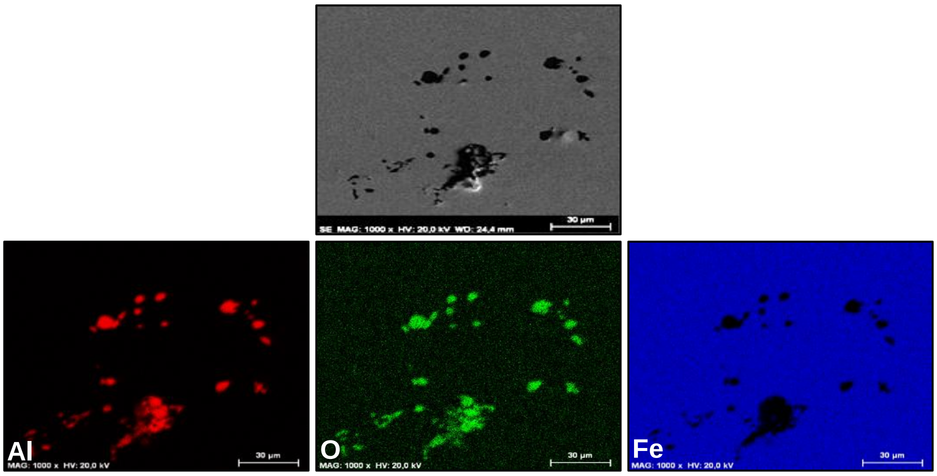

Figure 6. Cluster of alumina and elemental maps for Al, O and Fe. Image obtained by SEM with increase of 1000x.

The largest inclusions found were the ones containing oxides of titanium and aluminum. Figures 9 and 10 illustrate these types of inclusions. These inclusions displayed a very distinct morphology. It is also possible to observe smaller globular inclusions in the proximity of the larger inclusions.

Ti-aluminate inclusions aggregate and become larger from the RH furnace to the tundish. Thus, the distribution of the size of the inclusions from samples of the ladle or the tundish is not a function of deoxidation practice [25]. The average size of the ti-aluminate inclusions increases with increasing the levels of Ti in ULC steel stabilized with titanium [25].

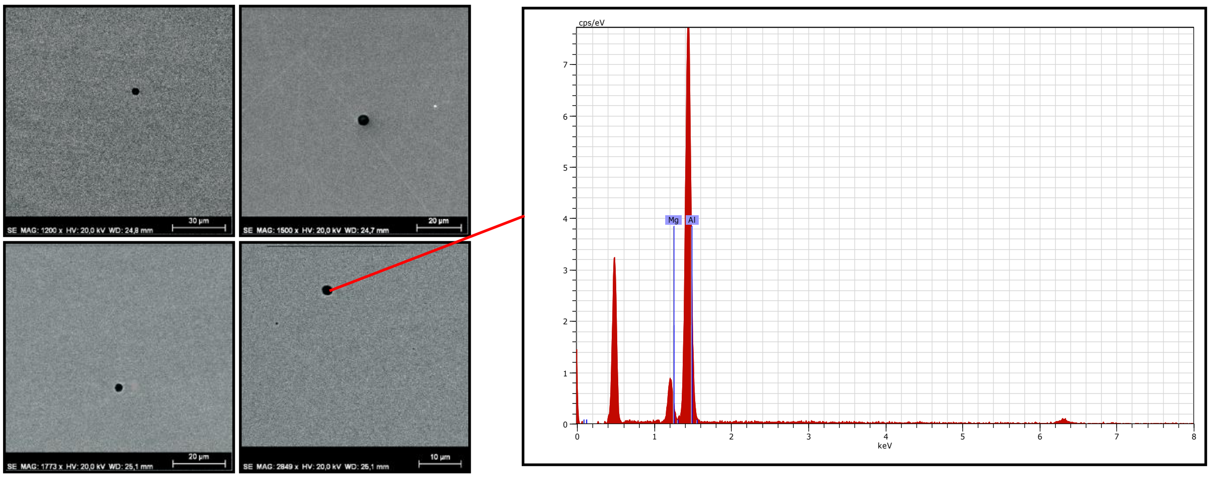

Figure 7. Globular inclusions of spinel. Images and EDS obtained by SEM.

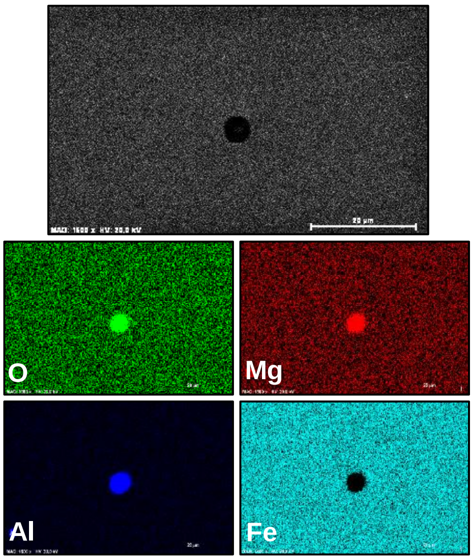

Figure 8. Inclusion of spinel and elementary maps for O, Mg, Al and Fe. Image obtained by SEM with an increase of 1600x.

The addition of Al and Ti resulted initially in Al_2O_3 particles; afterwards, oxides of Ti were formed in the existent particles and finally, these oxides changed to the composition of Al_2O_3 but contained up to 20 mol% Ti [26]. When Ti is added to the Al-deoxidized melt, the following reactions are possible to occur [27]:

$$\mathrm{m[Ti] + nAl2O3 = AlxTimO3n(s) + [Al]2n\text{-}x} \qquad (1)$$

$$\mathrm{x[Al] + y[Ti] + z[O] = AlxTiyOz(s)} \qquad (2)$$

Prediction has been made that when free oxygen in the bath is low due to the high addition of Al, Al-Ti-O inclusion is formed in accordance to equation 1. The reduction reaction of the solid is considered slow and induces the formation of an inclusion with phases in two different layers. However, with a high level of free oxygen, Ti tends to react to the O and Al dissolved in the bath as in equation 2 and pure Al-Ti-O inclusion of Al-Ti-O is rapidly formed. A reoxidation in Al-killed steel containing Ti, generates inclusions with characteristics of structures with double layer consisting of a core of Al_2O_3 surrounded by oxides of the Al-Ti-O complex [28].

In figure 10, it is not possible to observe signs of cores or double layers, indicating that these inclusions are possibly pure. However, this steel was degassed resulting in low dissolved oxygen. For this reason a hypothesis of a re-oxidation of the bath is not discarded. As already mentioned**,** 87.4% of inclusions are of pure alumina or alumina based, being that all of them can worsen the castability. An alternative would be the partial or total modification of the pre-deoxidizer applied, this way alternating the formed product. Li et al (2015) replaced the element pre-deoxidizer Al for Si, resulting in a better stability of cleaning in the slabs and a lower quantity of complex inclusions.

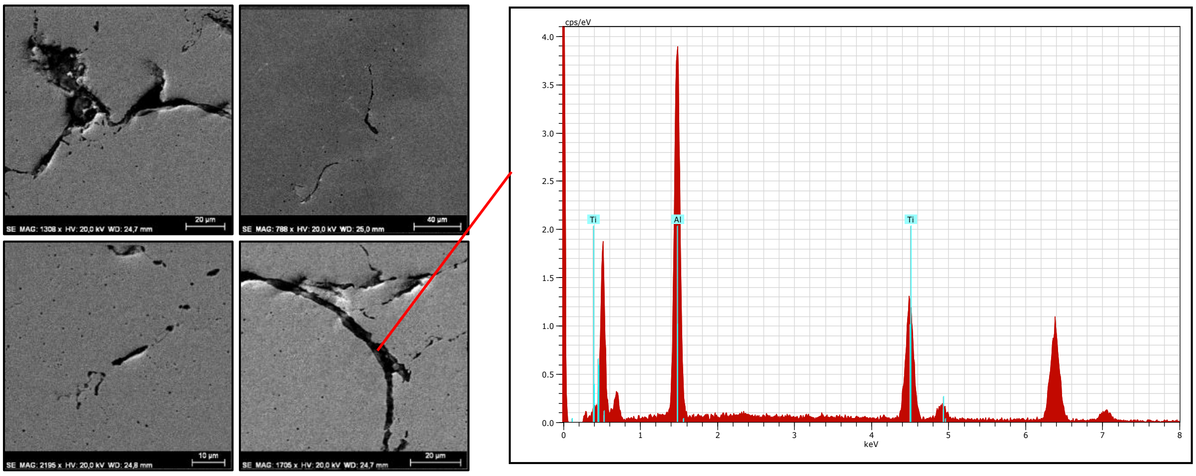

Figure 9. Ti-Al-O inclusions. Images and EDS obtained by SEM.

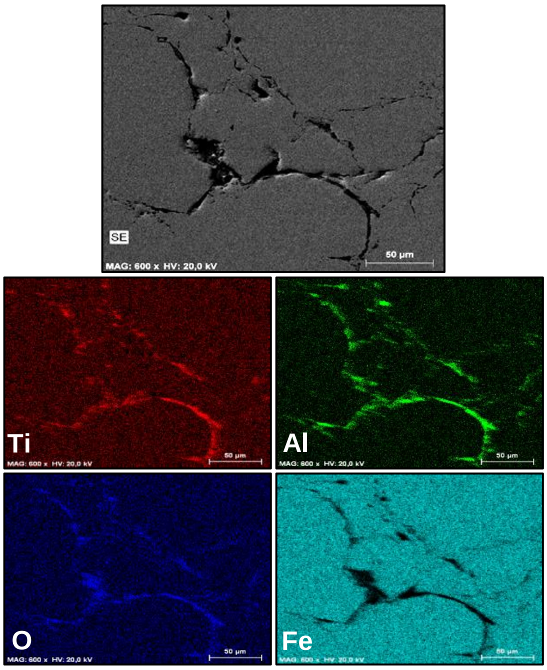

Figure 10. Ti-Al-O inclusion and elementary maps for Ti, Al, O and Fe. Image obtained by SEM with an increase of 600x.

3.4 Physical state of the inclusions in the steelmaking temperature

The balanced compositions of the inclusions with two or three oxides were plotted in ternary diagrams containing liquidus lines in the systems: Al_2O_3-MgO-CaO, TiO_2- Al_2O_3-CaO, TiO_2-Al_2O_3-MgO, SiO_2-Al_2O_3-CaO and SiO_2-TiO_2-Al_2O_3. The diagrams are presented in Figure 11 and Table 2 shows the quantity of inclusions found for each system.

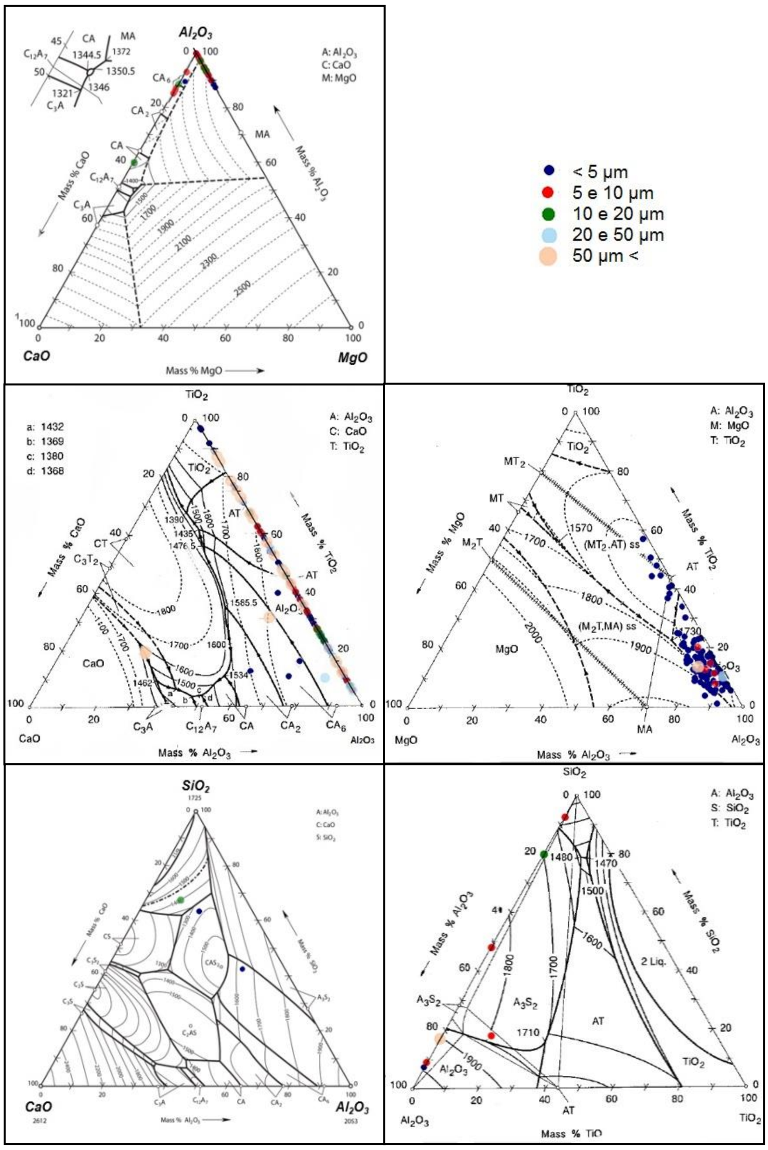

Figure 11. Size distribution of inclusions in ternary diagrams with liquid lines, for the systems: Al_2O_3-MgO-CaO, TiO_2-Al_2O_3-CaO, TiO_2-Al_2O_3-MgO, SiO_2-Al_2O_3-CaO e SiO_2-TiO_2-Al_2O_3 [30].

Tabela 2. Number of inclusions for each oxide system.

Ternary system	Number of inclusions
Al_2O_3-MgO-CaO	308
TiO_2-Al_2O_3-CaO	225
TiO_2-Al_2O_3-MgO	107
SiO_2-TiO_2-Al_2O_3	7
SiO_2-Al_2O_3-CaO	3

For alumina and silica which are pure inclusions with only one oxide, their melting points are respectively 2050 °C and 1710 °C [20]. Now it is possible to know the quantity of solid and liquid inclusions during the process. This result is presented in figure 12.

Only 1.16% of the inclusions were not evaluated for having more than three types of oxides. On the whole, 98.65% of the inclusions were solid during the process and only 0.19% in liquid state.

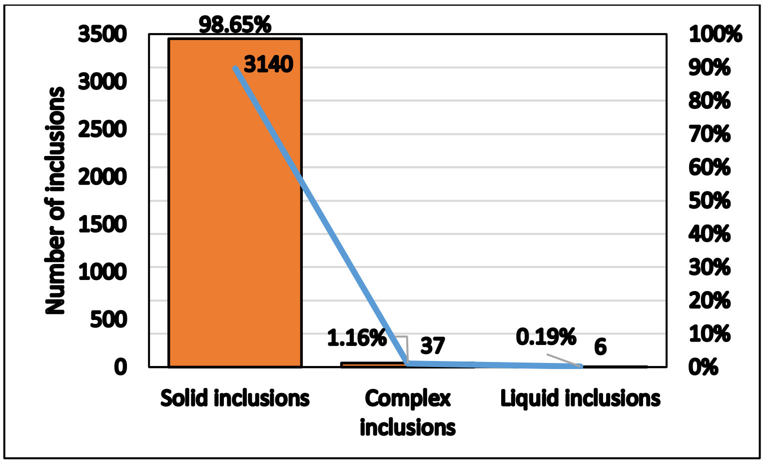

Figure 12. Physical state of the inclusions at the steelmaking temperature.

Bielefeldt (2009), affirms that the treatment with calcium is a mechanism considerably used in the steel plants in order to promote the transformation of inclusions of solid alumina in inclusions of liquid calcium aluminates benefiting the castability of the process.

4 CONCLUSION

The analysis of the inclusions evaluated showed that 60.98% of the inclusions were in the lower size range of 5 µm exhibiting in accordance to the effects of the bath agitation.

As for the chemical composition, evaluating the three types of inclusions with greater frequency (87.4% of the total), these possess negative influences for the obstruction in submersed valves. 66.54% are alumina, 10.87% are spinels and 9.99% are uncommon or mainly oxides of titanium and aluminum. All of them have alumina as a base and a partial or total change of pre-deoxidized element could improve problems related to the cleaning of steel.

It was found that 98.65% of the inclusions were solid during the process and an application of the treatment with calcium would be favorable to liquid inclusions during the continuous castability.

Inclusions greater than 50 µm contained oxide of titanium in their composition and can be considered as indications of re-oxidation of the molten metal demanding attention and precautions with re-oxidations.

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