

THE EFFECTS OF DEOXIDATION PRACTICE ON THE QUALITY OF THIN FOIL LOW-CARBON STEEL

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Abstract

In converter steelmaking of AISI 1006 steel for thin foil products, two tapping practices are used with respect to deoxidation: silicon and manganese additions during tapping and aluminum deoxidation after complete tapping ("semi-killed practice") and aluminum deoxidation during tapping, "fully killed practice". There is a perception that the semi-killed practice may be more economical and result in the same quality as the fully killed practice. In this work, the effects of the tapping practice on steel quality and cost variables were evaluated for thin foils of AISI 1006 steel. Oxygen and aluminum content, aluminum and ferro-alloy yield, the type of alumina inclusions formed, and the quality of the steel during thin foil rolling were evaluated and compared. It is shown that the fully killed practice leads to less reoxidation from slag, lower soluble oxygen, and lower total oxygen at the caster as well as better morphology of the remaining alumina inclusions than the semi-killed practice. Thus, the higher quality of the steel produced via the fully killed tapping deoxidation practice when compared with semi-killed tapping is demonstrated. It is also shown that a complete cost evaluation favors this practice in the case of products rolled for tin foil production.

Keywords: Low-carbon steel; Thin foils; Thermodynamics; Deoxidation; Aluminum.

1. Introduction

Steel for tin foil is cold rolled to very low thickness, typically in the range of 0.14mm. Although the cleanness requirements for tin foil may not be as stringent as those for high formability steels [1,2], large alumina inclusions or alumina clusters can cause rejection at the final stages of processing [3], with significant economic impacts associated to rejection and rescheduling of production. Figure 1 presents an example of the typical defects caused by alumina inclusions in cold rolled steel foil used for tin foil. Although steel product used for tin foil is aluminum killed, two different deoxidation practices are commonly used in flat steel mills for these low-carbon steels. In one practice, called "semi-killed tapping" in this work, manganese and some silicon are added during tapping and afterwards enough Al is added to fully deoxidize the steel and reduce some of the FeO and MnO contained in the slag passing to the ladle from the converter during tapping. In the second practice (called "fully killed tapping" in this work) sufficient aluminum is added during tapping to guarantee that the steel will remain fully killed during

the complete secondary metallurgy cycle. Since there is a significant difference in the amount of aluminum added and hence in the direct costs related to aluminum as well as in the sequence of oxides expected to form [4], some controversy prevails as to the economical and quality advantages of each deoxidation practice. The effects of deoxidation sequence on inclusion size and morphology, in particular, have been the subject of discussion for long time and significant discussion still prevail. Some authors propose that the deoxidants should be introduced starting with the lower deoxidation power silicon, followed by aluminum, while others recommend the complete addition of aluminum directly to the fully oxidized bath, as tapped [4-7]. The objective of this work is to compare quality and cost indicators for the two practices and to understand the processes occurring in each deoxidation practices using thermodynamics.

2. Experimental

A large number of heats of AISI 1006 are produced every month using either deoxidation

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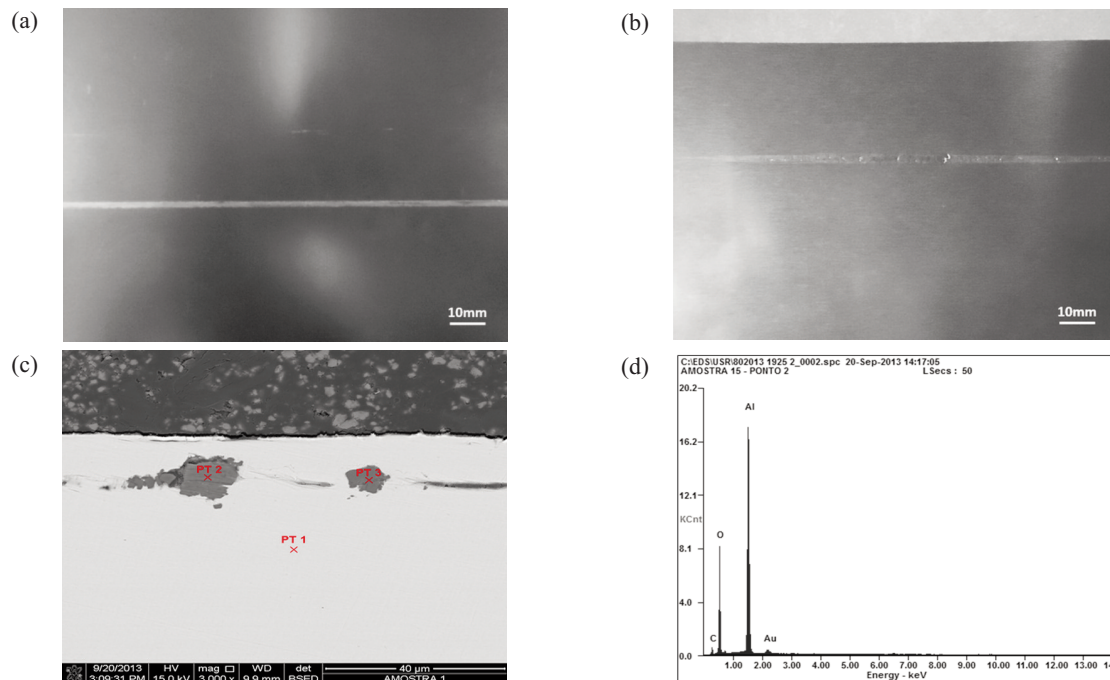


Figure 1. (a) and (b) examples of defects on cold rolled foils caused by alumina inclusions (without or with perforation, respectively). (c) Cross section image (SEM, BE) of a region of defective foil. (d) EDS spectrum of the large alumina inclusion to the left Figure 1(c) (PT 2). Alumina inclusion were all identified using EDS and had similar spectra to Figure 1(d).

practice. All the data was collected on heats of this grade of steel. The two practices are schematically presented in Figure 2. The deoxidation practice is selected based on operational variables: before this study, the main reason for selecting the semi-killed practice for this low carbon steel was the lower possibility of phosphorous reversion. In general, for low carbon steels in which lower nitrogen pickup during tapping is important, this practice is also preferred. In both cases, the favorable effects of the high oxygen content dissolved in the steel are explored [8,9]. In more than 15 heats deoxidized according to each practice, sampling of the metal and of the slag were taken at the end of tapping, at the arrival at the argon stirring station and at the release of the heat from the argon stirring station. Complete chemical analysis of the steel and slag samples were performed using X-Ray spectrometry. Total oxygen content was determined from steel pins taken at the caster with TOS® samplers from Heraeus using inert gas fusion in graphite crucibles (LECO® system). Furthermore, temperature and oxygen activity were measured, using commercial solid zirconia electrolyte disposable cell and S-type (Pt-Pt10%Rh) disposable thermocouples. In selected heats, samples from the TOS pin taken at the caster were dissolved in acid, and the resulting residue was filtered for scanning electron microscope (SEM) observation of inclusion morphology using secondary electrons (SE). The dissolution process was performed in the following

way: the samples with around 3g of steel were ground to remove surface oxides. They were then dissolved in 100mL of hot hydrochloric acid dissolved in water (1:1) (80-100°C). After 3h in the solution all iron was dissolved. 150mL of hot deionized water were then added to the solution. The final solution was filtered in polycarbonate fiber filter with average pore size of 1.2µm. The residue was then washed alternating a hot hydrochloric acid solution in water (1:25) and hot deionized water, five times with each liquid to remove iron salts. The residues were then dried in a dust free chamber, gold coated and taken to the SEM for examination.

Cross sections of foils were examined in SEM using backscattered electrons (BE). Energy-dispersive X-Ray spectroscopy (EDS) was used in the SEM to confirm inclusion compositions. When EDS was used, the samples were coated with a fine film of gold to enhance electrical conductivity and avoid charging effects. The rolled steel foils are 100% inspected automatically and visually for the occurrence of the infrequent defects presented in Figure 1. The data on tin foil quality and use of aluminum and ferro-alloys was collected over a period of ten months and related to the deoxidation practice. A statistical analysis of the level of oxidation (FeO content in slag, and dissolved oxygen in steel at the end of converter process) indicated that there was no significant difference in oxidation between the heats processed according to each deoxidation practice. To evaluate

the heat losses (and gains) associated with each deoxidation process, temperatures were measured at various points of the processing of the heats (minimum: before tapping from the converter, right after tapping, upon arrival at the argon stirring station and on leaving the argon stirring station).

Thermodynamic calculations were performed using Thermo-calc [10] and SLAG3 [11] database. Previous work has confirmed the excellent description of Fe-Al-O equilibrium by this database [12,13].

3. Results and Discussion

Figures 3 and 4 present the main quality indicators selected for evaluation in this work. In Figure 3 the total rejection percentage (on a weight of steel basis) is classified according to deoxidation practice and according to the disposition of the rejected material. The most frequent disposition, in both cases, is the change of grade of the steel heat to a less demanding application. However, scrapping is the only possible disposition in some cases. The incidence of the disposition “change of grade” is higher for the fully killed practice. The change of grade is usually decided as the final heat composition is known. On the other hand the incidence of rejection leading to scrapping is significantly higher in the semi-killed practice than in the fully killed practice. Typically, these rejections occur after some processing, which adds significantly to the cost of the rejection. The cost of scrapping is thus significantly higher than the cost of change of grade, evidently. The cost of change of grade is evaluated on a heat by heat basis, since it

depends on the grade to which the material is classified, and the costs of rescheduling production which are always much less than the cost of rescheduling scrapped material that has been already processed to some extent.

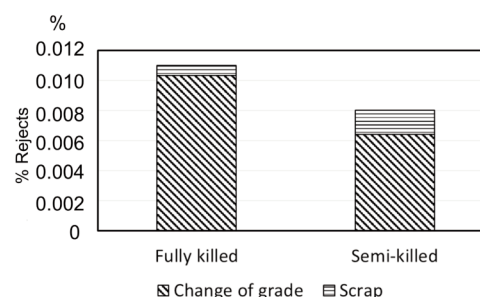


Figure 3. Incidence of rejections classified according to the type of deoxidation used and to the disposition of the rejected material.

The data presented in Figure 4 shows clearly that the incidence of rejections leading to scrapping associated with alumina inclusions is much higher in steel produced according to the semi-killed practice. As these rejections occur, usually, after cold rolling, the total losses associated with the scrapping are very significant. Evidently, the cost of rescheduling is usually higher, as the time “lost” in processing material that is scrapped normally increases the rescheduling costs.

In order to better understand the evolution of the deoxidation during the two practices, the values of oxygen in solution in the steel were compared at

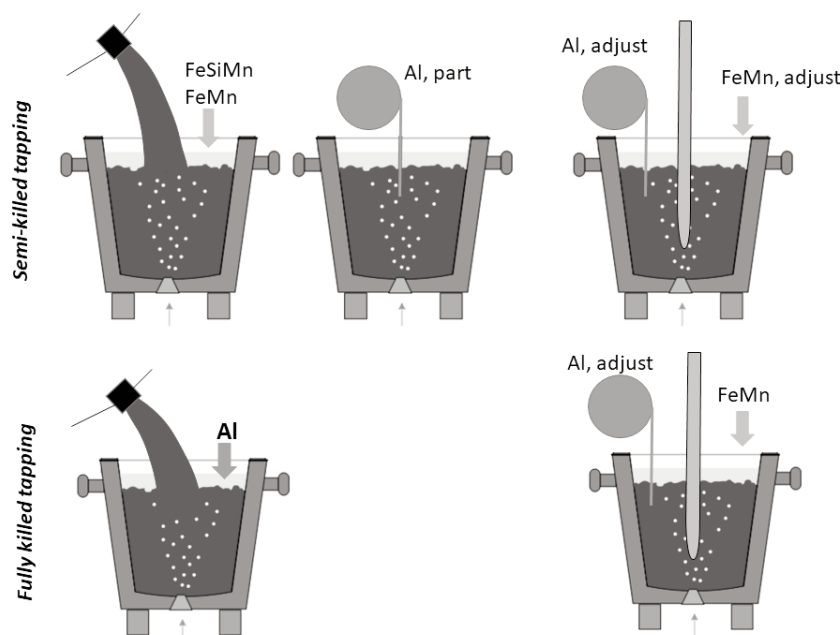


Figure 2. Schematic presentation of the two deoxidation practices. From tapping of the converter (left) to the argon stirring station (right).

different stages of the process. Furthermore, the differences in total oxygen in the product -an indirect measurement of steel cleanliness [14] - was also evaluated, as shown in Figure 5.

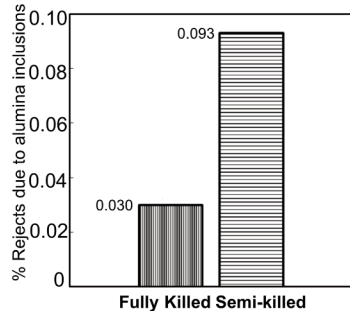


Figure 4. Incidence of rejections associated to alumina inclusions classified according to the type of deoxidation.

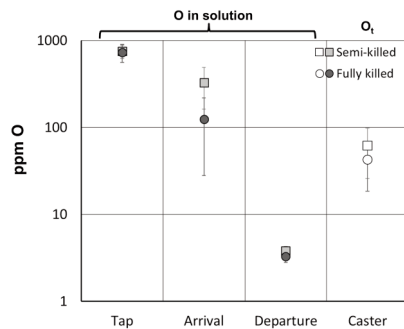


Figure 5. Overview of the evolution of the oxygen content along the steelmaking process depending on the deoxidation practice. The values for tap, arrival and departure from the argon stirring station are of soluble oxygen while the value at the caster corresponds to the total oxygen content in the steel.

To present the various stages of the process in a single graph, a logarithm scale must be used for the oxygen content. This masks some important differences that will be discussed in the following paragraphs. However, even in a log scale, the large difference in dissolved oxygen on arrival at the argon stirring station for both practices is clearly visible as is the difference in total oxygen in the product. The indirect implication of the lower dissolved oxygen at arrival in the argon stirring station is that, in the fully killed practice, a significantly larger amount of alumina is formed before this stage. This means more time for coalescence and entrainment of these inclusions in the slag when this practice is used [15]. A direct result is the lower total oxygen in the final product observed when the fully killed practice is used.

Examining in more detail the oxidation level of the steel at the end of the process in the argon stirring

station, the important differences are more evident, as presented in Figure 6. First, it is evident that the residual oxygen in solution in steel is lower in the average in the fully killed practice. Second, the slag deoxidation, as indicated by its FeO content is also more effective in this practice. This seem to indicate that deoxidation of the steel is more effective in the case of the fully killed practice. The FeO content of the slag is crucial since the slag can be an important source of oxygen for reoxidation [8,16-18], when it is not in equilibrium with the steel, in accordance with Equation 1:



Where the underlined element is dissolved in steel.

In Figure 7 the difference in final total oxygen contents for both deoxidation practices are compared. The higher cleanliness of the fully killed steel and the lower dispersion observed in this deoxidation practice is evident.

The question of whether Equation 1 reaches equilibrium or not in these processes can be addressed by thermodynamic calculation. When there is equilibrium between FeO in slag and oxygen dissolved in steel, the ratio given by Equation 2 should equal a constant value (considering the steel to be sufficiently dilute so that $a_{Fe} \cong 1$), depending only on temperature.

$$\frac{a_{FeO}}{\%O} = K(T) \quad (2)$$

In Equation 2, $K(T)$ is the equilibrium constant for Equation 1 and a_{FeO} is the activity of FeO in the slag.

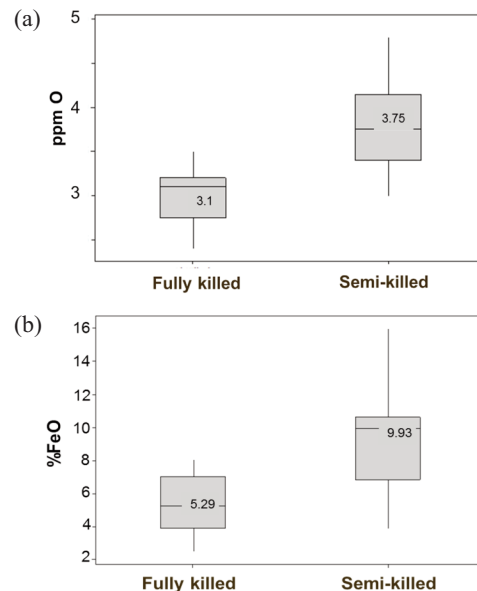


Figure 6. Boxplots of (a) dissolved oxygen content and (b) FeO content of slag, as the steel ladle leaves the argon stirring station, for the two deoxidation practices.

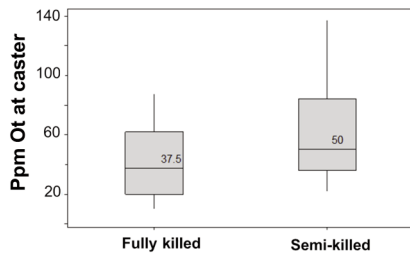


Figure 7. Boxplot of total oxygen in the steel sampled at the caster, depending on the deoxidation practice.

To evaluate if equilibrium indeed occurred, the FeO activity was calculated for each heat, using the slag analysis and temperature data as input for the computational thermodynamics software and database described in item 3, above. With this information, it was also possible to calculate the dissolved oxygen that would be in equilibrium with this slag, in accordance with Eq. 2. While the oxygen content in the steel is roughly proportional to the calculated FeO activity, as shown in Figure 8(a), in both cases the values deviate significantly from the calculated oxygen content in equilibrium with the slag, as shown in Figure 8(b). Thus, there is no equilibrium between the oxygen potentials associated to the FeO in the slag and to the oxygen dissolved in steel in either deoxidation practice. Hence, there is a potential for slag reoxidation of the steel in both cases. The driving force for reoxidation is the difference in oxygen chemical potential between the slag and the steel. This can be indirectly expressed via the difference between the oxygen content that would be in equilibrium with the slag and the actual oxygen content of the steel, so that, the oxygen flux from slag to metal, responsible for reoxidation, would be given as in Equation 3.

$$j_o = k_o \left(\frac{a_{FeO}}{K(T)} - \%O \right) \quad (3)$$

where j_o is the flux of oxygen from the slag to the metal, (in mass/area.time) and k_o is the mass transfer coefficient for the transport of oxygen.

The above-mentioned differences can be observed in Figure 8(b) and were calculated to be, on the average, 213 ppm oxygen in the case of the fully killed practice, and 299 ppm in the case of the semi-killed practice. This confirms that the driving force for reoxidation by slag is less when the fully killed practice is used.

The morphology of the alumina inclusions in the samples taken from the caster was also evaluated. Figure 9 presents typical morphologies observed in samples taken from the caster obtained with both deoxidation practices. While fully dendritic structures and some structures where “arms” are still visible are present in the steel produced via the semi-killed practice, the fully killed practice resulted in

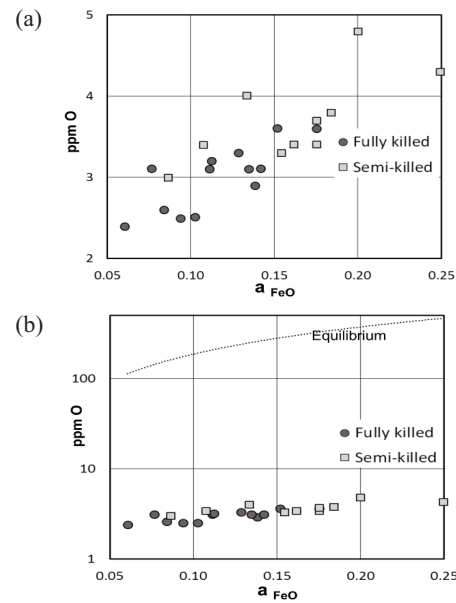


Figure 8. (a) Dissolved oxygen as a function of FeO activity and (b) dissolved oxygen and equilibrium dissolved oxygen (dashed line) as a function of FeO activity. FeO activity calculated from slag chemical analysis and temperature, using Thermo-calc and SLAG3 database.

more compact and polygonal inclusions, consistent with the observations of refs. [19-23] where the changes of alumina morphology with supersaturation and time in the deoxidation of liquid steel were evaluated. The inclusions in the fully killed practice are consistent with longer residence time in the steel, as also indicated in the analysis of the results of Figure 5, above. Thus, not only a lower content of inclusions but also a more favorable morphology is obtained in the fully killed practice than in the semi-killed practice.

Most deoxidation reactions are exothermic, but the overall process, including the dissolution of the deoxidant in the steel can have different thermal effects [24]. Thus, the temperature loss for each practice was also evaluated. The temperature losses in the heats processed according to the fully killed practice averaged approximately 2.5°C/min against a loss of 5.5°C/min for the semi-killed practice.

Finally, in order to evaluate the relative costs of the aluminum, ferro-alloy and other additions the averages were computed over the ten-month period for the same steel grade for each deoxidation practice. The results of this evaluation are shown in Table 1 where the additions performed in the fully killed practice are taken as the basis for comparison. It is evident that, depending on the cost of different materials, the cost of additions can be higher in one or the other practice, there being no way to directly indicate if one practice will always be cheaper. When the cost of rejections is included in the evaluation, the

fully killed practice can become significantly advantageous in various situations.

Table 1. Average amount of additions performed in the semi-killed deoxidation practice using the fully killed deoxidation practice as basis for comparison.

Material Added	Fully killed (basis)	Semi-killed to fully killed practice ratio
Al wire	1	2.9
Granulated Al	1	0.75
Bulk Al	1	0
FeMn M/C	1	1.1
FeMn H/C	1	0.13
FeSiMn	1	936
Graphite wire	1	1.1
FeMn M/C wire	1	1.04

As mentioned in the introduction, in some cases the semi-killed practice has operational advantages. Tapping with a higher oxygen content has two benefits: as the converter slag that passes into the ladle contains phosphorous, improved deoxidation will result in more phosphorous reversion in accordance with Equation 4: [8,25]



Furthermore, since oxygen is a strong surfactant in iron [9] it restricts the flow of nitrogen through the air/steel interface, thus reducing or avoiding nitrogen pickup during taping [24].

The evaluation of the heat effect of the two practices in this study also indicates that, in case of high end-of-blow temperatures, the semi-killed practice may also present advantages.

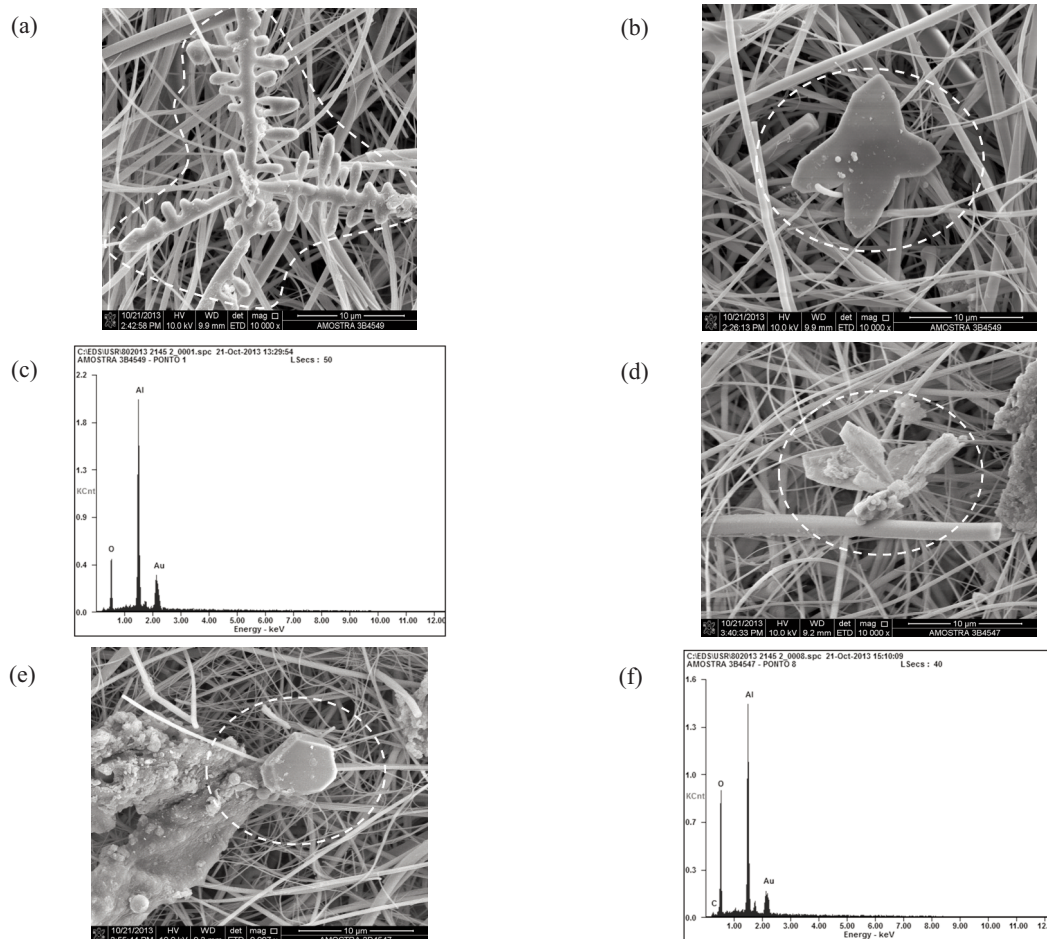


Figure 9. Alumina inclusions retained during filtering after acid dissolution of steel sample (filter fibers visible in the background, dashed lines indicate particles identified as alumina. Steel samples taken at the caster. (a) and (b) semi-killed practice. (c) EDS spectrum from inclusion in (a). This spectrum is representative of the one obtained from the inclusion in (b), too. (d) and (e) fully killed practice. (f) EDS spectrum from inclusion in (e). This spectrum is representative of the one obtained from the inclusion in (d), too. Note: The large piece under the alumina inclusion in (e) is undissolved steel. All images: SEM, SE.

4. Conclusions

The fully killed teeming practice results in lower dissolved oxygen, lower total oxygen and thus cleaner steel than the semi-killed teeming practice. The alumina inclusions remaining in steel produced according to the fully killed practice are less harmful for cold rolled thin products of low carbon steel, probably due to their earlier formation in the ladle, compared to the semi-killed teeming practice. This leads to better elimination and better morphology of the remaining alumina inclusions. Rejections and deviations in thin products are lower when the fully killed teeming practice is used than when the semi-killed teeming practice. The lower potential for reoxidation from slag during the fully killed route probably also contributes to these better results. When all costs are compared (not only the cost of additions but the also the costs of rejection) the semi-killed teeming practice can be more expensive than the fully killed teeming practice for foil products. Depending on the relative cost of additions at a given time, the fully killed practice may be more economical independent of the final product and rejection costs. Nonetheless, in some cases the semi-killed teeming practice may still be needed, to avoid excessive nitrogen pick-up and phosphorous reversion and to process hot heats. In this case, special attention should be given to the destination of these heats.

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