Origin of the Inclusions in Production-Scale Electrodes, ESR Ingots, and PESR Ingots in a Martensitic Stainless Steel

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Abstract: The focus of the study was to define the origin of the inclusions in production-scale electro-slag remelting, (ESR) and electro-slag remelting under a protected pressure controlled atmosphere, (PESR), ingots. The inclusion characteristics in production samples were studied using both polished sample surfaces (two-dimensional (2-D) investigations) and inclusions extracted from steel samples by electrolytic extraction (three-dimensional (3-D) investigations) using SEM in combination with EDS. The results were compared to results from previously reported laboratory-, pilot-, and production-scale trials including electrode, remelted, and conventional ingots. The results show that primary, semi-secondary, and secondary inclusions exist in the remelted ingots. The most probable inclusion to survive from the electrode is a MgO-Al$_2$O$_3$ (spinel). It was also found that the ESR/PESR process slag acts in a similar way to a calcium treatment modification of alumina inclusions. On the whole, the most significant finding is that the overall cleanliness of the electrode including the inclusions in the electrode has an influence on the inclusion content of the ESR and PESR ingots.

Keywords: ESR; PESR; inclusions; electrolytic extraction; SEM; stainless steel

1. Introduction

Due to increased requirements on the final properties of high-quality steels, the limitations on the content of non-metallic inclusions (NMIs) and impurity elements in these steels are continually being tightened. The remelting techniques of electro-slag remelting (ESR) and electro-slag remelting under a protected pressure controlled atmosphere (PESR) produce clean steels with respect to non-metallic inclusion (NMI) content.

Previous studies on non-metallic inclusions and cleanliness in ESR or PESR remelted ingots are presented in Table 1 [1–25]. It can be seen that the majority of them are executed in laboratory- or pilot-scale furnaces (from 0.8 to 50 kg experimental trials) and with a focus on steel grades other than martensitic stainless tool steels, which is the focus of this investigation. The inclusions found in laboratory-scale trials are usually in the size range of 1–5 µm, but more often ≤2 µm. However, in industrial size ingots, significantly larger inclusions can be found. Therefore, for reliable evaluations of the characteristics of NMI (especially larger size inclusions) in industrial-scale ingots, investigations of NMIs carried out only in laboratory and pilot experiments are not sufficient.
Table 1. Previous studies on inclusions in electro-slag remelting (ESR) or electro-slag remelting under protective pressure controlled atmosphere (PESR) remelted.

| Year | Author          | Steel            | Scale | Diameter/Width | Inclusions Size | Ref. |
|------|-----------------|------------------|-------|----------------|-----------------|------|
| 1971 | D.A.R. Kay et al. | N.A.             | N.A.  | N.A.           | N.A.            | [1]  |
| 1980 | Z.B. Li et al.   | N.A.             | N.A.  | N.A.           | N.A.            | [2]  |
| 2012 | C-B. SHI et al.  | NAK80 die steel  | N.A.  | N.A.           | N.A.            | [3]  |
| 2012 | C-B. SHI et al.  | Die steel        | Laboratory | N.A.       | N.A.            | [4]  |
| 2012 | C-B. SHI et al.  | High-al steel    | N.A.  | N.A.           | <5 μm           | [5]  |
| 2012 | X.C. Chen et al. | Inconel 718     | N.A.  | N.A.           | CN 5–15 μm      | [6]  |
| 1969 | B.C. Burel       | steel, iron      | Laboratory | Mould 77 mm | <15 μm           | [7]  |
| 1974 | A. Mitchell et al. | oxygen containing iron, iron-OFC copper | Laboratory | Mould 76.2 mm | 1–5 μm           | [8]  |
| 1976 | J.C.F. Chan et al. | Stainless steel | Laboratory | Electrode 35 mm | N.A.           | [9]  |
| 2013 | C-B. SHI et al.  | Die steel, superalloys . . . Cold rolls steel | Laboratory | Mould 800 gr | N.A.            | [10] |
| 2013 | Y. Dong et al.   | Die steel CR-5A  | Laboratory | 800 gr      | N.A.            | [11] |
| 2013 | Y-W. Dong et al. | H13 die steel    | Laboratory, 50 kg | Electrode 90 mm | abt 2 μm       | [13] |
| 2015 | R. Scheinder et al. | Hot work steel abt H11 | Pilot | Electrode 101.5 mm | N.A.           | [14] |
| 2016 | C-B. SHI et al.  | High-Carbon 17% Cr Tool Steel | Pilot | ESR mould 170 mm | abt 5 μm       | [15] |
| 2017 | G. Du et al.     | H13 die steel    | Pilot | ESR mould 300 mm | 0–15 μm, >15 μm | [16] |
| 2014 | L.Z. Cang et al. | N.A.             | Pilot 15 kg | Mould abt 105 mm | N.A.          | [17] |
| 2019 | C-B SHI et al.   | Si-Mn killed steel ≈ H13 abt H11, H13 die steel, martensitic Cr-Ni steel | Pilot | PESR 95 mm | 1–3 μm, few >3 μm | [18] |
| 2013 | G. Reiter et al. | Martensitic stainless steel | Industrial | N.A.                   | ASTM E45 Heavy | [19] |
| 2014 | E.S. Persson et al. | Martensitic stainless steel | Industrial | Moulds 400–1050 mm | 8–30 μm       | [20] |
| 2016 | E.S. Persson et al. | Martensitic stainless steel | Industrial | Moulds 400–1050 mm | N.A.           | [21] |
| 2017 | H. Wang et al.   | H13 die steel    | Laboratory | Electrode 25 mm | abt 1–2 μm     | [22] |
| 2017 | E.S. Persson et al. | Martensitic stainless steel | Industrial | Moulds 400–500 mm | 8–45 μm       | [23] |
| 2017 | E.S. Persson et al. | Martensitic stainless steel | Industrial | ESR mould 300 mm | 8–20 μm       | [24] |
| 2018 | E.S. Persson et al. | Martensitic stainless steel | Industrial | ESR mould 300 mm | 8–20 μm       | [25] |

The earlier and most generally accepted theories assume that the inclusions in the electrode will be rejected to the surface of the electrode tip to be incorporated into the liquid process slag [8,9,18,26–28]. The steel melt will then seek equilibrium with the process slag, so that new, different oxygen levels in the liquid steel pool will be obtained. With respect to the inclusion solution during ESR, in laboratory trials, Mitchell et al. [29] showed that the rate of solution of Al₂O₃ inclusions of 100 μm in a common ESR and PESR process slag (CaF₂ + 20–30 wt % Al₂O₃) should be dissolved within the predicted exposure time to the liquid slag at the electrode/slag interface. Li et al. [30] investigated the dissolution rate of Al₂O₃ into molten CaO-Al₂O₃-CaF₂ flux. In this study, it was seen that when the Al₂O₃ rod was immersed into molten flux, an intermediate compound of CaO-2Al₂O₃ was formed initially, before being dissolved in the flux. The dissolution rate of Al₂O₃ increased with an increased CaO/Al₂O₃ relation in the flux, a higher rotation speed of the rod in the flux, and a higher temperature.
In contrast to the accepted postulate of total inclusion removal by slag dissolution, an investigation using La$_2$O$_3$ as a tracer in the process slag showed that only 50% of the inclusions contained La [24,25]. This finding illustrated that only 50% of the inclusions had been in contact with the slag, either by total or partial solution. The remaining inclusions, which did not contain La, either survived from the electrode, precipitated without containing La, or without a detectible amount of La. The above examination shows that the most likely inclusion path from an electrode to an ingot involves two distinct routes, i.e., a direct transfer without a change of the inclusion characteristics and a solution/re-precipitation reaction. It was seen that the inclusions containing Mg spinels (MgO-Al$_2$O$_3$) were the ones most likely to be found without La. The share of the total number of oxide inclusions, consisting of Al inclusions containing >3% Mg of the total number of oxide inclusions, did not depend on the specific melting rate (melting rate per area) [25]. However, neither did it depend on the exposure time at the electrode/slag interface. The spinel proportion increases with increased ingot and inclusion sizes. Thus, spinel inclusions found without La were assumed to have been trapped within steel drops falling from the liquid film on the electrode tip [25]. Burel [7] already proposed this entrapment mechanism, even though it could not be seen in his experimental work. Another reason for primary inclusions could be that they were contained in solid steel fragments falling directly into the pool from the porous central region of the cast electrode. This latter effect would not be seen in small-scale experiments using rolled or forged electrodes and may account for the absence of large or unaltered inclusions in those results.

The two-dimensional (2-D) and three-dimensional (3-D) investigations of NMI on the electrode and remelted ingots [23], as well as the tracer element investigations, showed that many of the inclusions contained an inner core of spinel, covered by a layer corresponding to the chemical composition of the process slag. This result supports a more recent theory [24], that proposes that two ESR ingot inclusion types exist; first, secondary inclusions, which have gone through some form of solution/re-precipitation reaction where they reacted with the slag and finally acted as nucleates to grow in the ingot pool and solidifying region; second, primary inclusions from the electrode, which have not been influenced by the melting. Studies indicate that the inclusions in the second category that are most likely to survive are pure Mg spinels [23–25]. Some of the spinel inclusions were found to contain a layer corresponding to the ESR/PESR process slag composition (denoted below as semi-secondary inclusions). They are assumed to have survived due to their higher melting point and hence lower solution rate in either the slag or metal; therefore they may have acted as nucleus during cooling and solidification in the liquid steel pool [25]. With nuclei present, the semi-secondary inclusions would have the possibility to grow larger as the liquid metal pool cooled compared to if they were simply re-precipitated during the solidification.

According to Wang et al. [22], the original oxide inclusions in a Mg-free H13 consumable electrode are Al$_2$O$_3$ and the original oxide inclusions in a Mg-containing H13 steel consumable electrode are Mg spinels. After an ESR remelting, the oxide inclusions in the Mg-free ESR ingot are still Al$_2$O$_3$, while both Al$_2$O$_3$ and MgO-Al$_2$O$_3$ inclusions exist in the Mg-containing ESR ingot. Related studies [31] on the removal of large inclusions from a cast steel electrode made with a deliberately-high content of inclusions larger than 500 µm have also indicated that not all large inclusions were removed by an ESR remelting, identifying some large inclusions that have survived into the ingot without change. A similar study reported by Paton et al. [32] indicates that approximately 20% of the large inclusions in the ESR ingot have the same composition as those found in the electrode.

Mg spinel inclusions can be formed by reactions during the ESR process. Shi et al. [18] remelted vacuum-induction remelting (VIM)-produced electrodes (Si-Mn killed steel) containing only MnO-SiO$_2$-Al$_2$O$_3$ inclusions in a pilot PESR using a process slag containing 3–4% MgO. The inclusions found in the remelted ingot (Ø95 mm), were only Mg spinel inclusions containing ≈3 mass% Mg, readily formed in the liquid pool as a result of the reactions between the alloying elements and the dissolved oxygen that dissociated from the MnO-SiO$_2$-Al$_2$O$_3$ inclusions in the liquid steel.
Laboratory results, obtained by Dong et al. [12] indicate that most non-metallic inclusions in an ESR remelted Cr-5A die steel, using a multi-component process slag, are MgO-Al_2O_3 inclusions. Based on a laboratory study of H13 steel remelting, Shi et al. [14] also found that MgO-containing inclusions survive from the electrode. Specifically, they found that all the inclusions in the consumable electrode were Mg spinels, occasionally surrounded by an outer (Ti, V)N or MnS layer. Their study showed that when only Al-based deoxidant additions or no deoxidants are used, all the oxide inclusions remaining in the PESR ingots are Mg spinels. After a PESR refining combined with a proper calcium treatment, the ingot inclusion population was modified to mainly consist of CaO-MgO-Al_2O_3 inclusions but also including some CaO-Al_2O_3 inclusions. The size range of the inclusions in the PESR ingots of this laboratory study was approximately <2 µm, suggesting that the inclusions were predominantly precipitates formed during solidification or cooling.

Many research studies [33,34], have reported on the physical removal of inclusions during steelmaking processes, with a focus on the influence of buoyancy forces on the removal. The ESR ingot pool presents a similar case, but with significant differences in the liquid flow patterns and residence times. The terminal velocity of a Mg spinel inclusion 50 µm in diameter rising in a liquid steel is approximately 5 × 10^{-4} m/s given the computed ingot pool pattern [35]. This implies that any inclusion removal is determined by a balance between the probabilities of being exposed to the slag/ingot interface or being trapped in the solidifying metal as dictated by the bulk metal flow of the liquid ingot pool. Inclusions (depending on their size and density) will be trapped in the flow pattern, many never reaching the steel/slag interface. According to this model, the contribution of inclusion refining though flotation is much smaller than what has previously been estimated.

The oxygen content in ESR and PESR remelted steels is discussed in several articles [5,9,16,18,36–41]. The overall finding is that the system moves towards equilibrium directed by the slag/metal equilibria. However, the reported oxide inclusion contents contribute for only a very small fraction (<1%) of the total analyzed oxygen content. Therefore, the reduction in the oxygen level often reported between the electrode and ingot cannot be allocated to a removal of inclusions to the slag. The oxygen level in the investigated high-chromium steel is normally between 5–10 ppm. While oxygen reductions during ESR are indicative of a refining process, they are not in themselves indicators of whether inclusion removal or formation of new inclusions have taken place.

Higher amounts of oxygen in the electrode (about 30–100 ppm) lead to a decreased oxygen content in a remelted steel [5,36,37,40]. In contrast, a lower amount of oxygen (about <10–15 ppm) leads to an oxygen pick-up in the remelted ingot [18,19,37–40].

The current study, as well as some conference presentations by the same author, focused on a different steel grade than ones presented in previously reported studies in the literature, see Table 1, namely a martensitic stainless steel. A production-scale electrode, an ESR ingot, and a PESR ingot, all from the same electrode heat, were investigated in order to verify the results from earlier theoretical, laboratory, and pilot studies presented above. This study focused on investigations of larger inclusions (≥8 µm) and their behavior during the ESR and PESR remelting processes, since this size range is more meaningful with respect to the influence of inclusions on various mechanical properties compared to the smaller inclusion sizes.

## 2. Materials and Methods

The material studied was from one ingot-cast consumable electrode 300 mm × 300 mm (denoted as the CE-300 sample), one ESR remelted ingot 400 mm × 400 mm (denoted as the ESR-400 sample), and one PESR remelted ingot Ø500 mm (denoted as the PESR-500 sample). All electrodes were cast from the same initial steel charge. A typical composition of martensitic stainless steel used in this study is as follows: C 0.38%, Si 0.9%, Mn 0.45%, Cr 13.6%, and V 0.28%. The difference between the ESR and PESR processes is that the ESR process here represents a multiple-electrode remelting process (involving electrode changes), which is performed in a moving mold, in an open furnace under an air atmosphere and using a continuous aluminum deoxidation. In contrast, the PESR process is a
single-electrode remelting process using a static mold and an inert pressure controlled atmosphere. In the ESR and PESR trials, a common process slag was used containing about one third each of CaO, CaF₂, and Al₂O₃, and including ≈3% MgO and ≈1.5% SiO₂.

The steel samples were taken from horizontal slice/slices of the electrode and ingots as follows: top (T), middle (M), and bottom (B) for the electrode, two samples taken at positions in between the top and bottom for the ESR ingot and one middle sample for the PESR ingot, as shown in Figure 1. The samples for the SEM investigations were taken from corner to corner on the electrode (3 × 5 samples), the central sample as close to the center as possible due to the secondary pipe/dense area in the electrode), from the ESR ingot (2 × 7 samples), and from side to side from the PESR ingot (1 × 9 samples).

Figure 1. Schematic illustration of horizontal slices and sample positions on the consumable electrode (a) CE-300, (b) ESR, and (c) PESR remelted ingots.

The characteristics of the non-metallic inclusions were studied using both a common two-dimensional (2-D) investigation of NMI on polished cross sections of metal samples [20,21,24] and by using three-dimensional (3-D) investigations of NMIs on the surfaces of metal samples after electrolytic extraction (EE) combined with SEM + EDS [23].

The 2-D studies were performed on a larger area of sample surface. More specifically, the field of view per sample was about 6500 mm². The samples were first analyzed using a scanning electron microscope (FEI Quanta 600 Mark II, Thermo Fisher Scientific, Waltham, MA, USA). The number, size, and chemical composition of the inclusions larger than 8 µm were analyzed using the “Inca features” software from Oxford Instruments. Afterwards, the inclusions were divided into four size classes, namely 8–11.2 µm, 11.2–22.4 µm, 22.4–44.8 µm, and larger than 44.8 µm. The observed inclusions
were also classified, according to their composition, as follows: (1) Duplex oxysulfides (OSs)—oxide containing MnS and/or CaS sulfide, (2) Type AM—Al₂O₃-MgO oxides with 10–35% MgO and <10% CaO, (3) Type A—almost pure Al₂O₃ oxides with <10% MgO and <10% CaO, (4) Type AC—Al₂O₃-CaO oxides with 50–90% Al₂O₃, 10–50% CaO, and <10% MgO, (5) Type ACM—Al₂O₃-CaO-MgO oxides containing 45–80% Al₂O₃, 10–40% CaO, and 10–25% MgO, and (6) MnS inclusions—almost pure Mn sulfides.

In the 3-D studies, 0.1–0.3 g of steel samples were dissolved in a 10% AA electrolyte (10%w/v acetylacetone—1%w/v tetramethylammonium chloride—methanol). Thereafter, the solution was filtrated and the inclusions were collected on a film filter. After electrolytic extraction, the NMIs were investigated on a surface of metal sample. However, due to the high amount of intermetallic inclusions (IMIs) in the martensitic stainless ingot, the NMIs could not be investigated precisely on the film filter under a layer of extracted IMIs after the filtration of electrolytes. Therefore, the non-metallic inclusions, which appeared completely on a surface of metal sample after electrolytic extraction, were also investigated on the sample surfaces.

3. Results

The total number of inclusions per unit area (Nₐ) for each size class and ingot type obtained from the 2-D studies is displayed in Figure 2. Additionally, the Nₐ values for different inclusion compositions are displayed in Figure 3a–c. The most common inclusion types in the size range 8-44.80 µm in the electrode (field of view of 312,300 mm²) are almost pure MnS inclusions followed by almost pure Al₂O₃ and Al₂O₃-CaO oxides containing <10% MgO (Types A and AC inclusions). For the ESR and PESR ingots (using a field of view of 36,380 and 19,800 mm², respectively), Al₂O₃ and Al₂O₃-CaO oxides followed by Al₂O₃-CaO-MgO oxides (Type ACM), are the most common inclusions. In addition, approximately 30% fewer inclusions are present in the PESR ingot compared to the ESR ingot. The compositions of various types of oxide inclusions in different samples observed by 2-D investigations on polished sample surfaces are shown in Figure 4 in an Al₂O₃-MgO-CaO diagram. Since the sulfide inclusions are fully dissolved during electrode melting and mostly accumulated by the liquid technological slag, the present investigation focused primarily on the oxide components.

![Figure 2](image-url)  
*Figure 2. Number of (a) oxide and (b) sulfide inclusions per unit area (Nₐ) for the C-300, ESR-400 and PESR-500 samples. The amounts of sulfur in the steel [%S] in the ESR-400 and in the PESR-500 are 68% respectively 76% of the amount of sulfur [%S] in the CE-300.*
Figure 3. Number of different non-metallic inclusions (NMIs) per unit area ($N_A$) observed by two-dimensional (2-D) investigations on different polished steel samples: (a) CE-300 M (b) ESR-400, and (c) PESR-500.

Figure 4. Compositions of oxide inclusions in different samples observed by two-dimensional (2-D) investigations on polished sample surfaces, (a) CE-300 M (b) ESR-400, and (c) PESR-500.

Examples of the typical largest oxide inclusions observed in different investigated samples are shown in Figures 5 and 6 [23]. The results show that neither of the ESR-400 and PESR-500 samples contain large sulfides. The Mg spinel core that is found in many of the inclusions, is about 1-10 µm. In addition, it was found that most of the inclusions in the ESR-400 and PESR-500 samples have spherical (or almost spherical) morphologies. It can be concluded that the total composition or the composition of the surface layer of those inclusions corresponds to the liquid CaO$_2$Al$_2$O$_3$ phase, as can be seen in Figure 7.
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**Figure 5.** Typical large-sized oxide inclusions in different samples observed by two-dimensional (2-D) investigations on polished sample surface; (a) Types A and AM: Al₂O₃, Al₂O₃-MgO; (b) Type ACM: Al₂O₃-MgO + CaO-Al₂O₃ + (CaS); (c) Type AC: Al₂O₃-CaO + (CaS); (d) Type AC: Al₂O₃-CaO + CaF₂.

**Figure 6.** Typical oxide inclusions in different samples observed by three-dimensional (3-D) investigations on surfaces of steel samples after electrolytic extraction; (a) Type A: Al₂O₃; (b) Type AM: Al₂O₃-MgO; (c) Type ACM: Al₂O₃-MgO + CaO-Al₂O₃ + CaF₂; (d) Type AC: CaO-Al₂O₃ + (CaF₂ + CaS).
| Type of NMI                                                                 | Mapping of main elements in NMI |
|---------------------------------------------------------------------------|---------------------------------|
| **Type AM, Al₂O₃-MgO**                                                    | ![Image](image1.png)             |
| **Type ACM, Al₂O₃-MgO + CaO-Al₂O₃ + CaF₂**                                | ![Image](image2.png)             |
| **Type AC, Al₂O₃-CaO-SiO₂ + CaS**                                        | ![Image](image3.png)             |
| **Type AC, CaO-Al₂O₃ + CaF₂ + CaS**                                       | ![Image](image4.png)             |

**Figure 7.** Mapping of main elements in different inclusions observed by three-dimensional (3-D) investigations on the surfaces of steel samples after electrolytic extraction.

### 4. Discussion

#### 4.1. Contrast between a Conventional Cast Electrode and Remelted Ingots

The results show that the number of smaller oxide inclusions is less in the electrode, (CE-300), than in the remelted ingots, (ESR-400 and PESR-500), see Figure 2a. The number of larger oxide...
inclusions is approximately similar in the electrode and the remelted ingots. However, it should be noted that the electrodes have a loose central structure, which contains most of the large-sizes inclusions. This population of large inclusions in the center of the electrode cannot be fully counted by the conventional NMIs determination due to the large porosity of the central region of the electrode. In this study, the determination of NMIs in the central region was done in dense steel obtained as close to the center as practical. As a possible result, apparently anomalous effects can be observed in Figure 2a. The number of sulfide inclusions, mainly MnS, is more than ten times larger in the electrode than in the remelted ingots, see Figure 2b. Altogether, the electrode contains approximately 50% more inclusions than the remelted ingots. An explanation for the larger number of small oxide inclusions in the ESR and PESR ingots compared to the electrode is that primary, semi-secondary, and secondary inclusions are present in the ESR and PESR ingots.

The primary inclusions, often $\text{Al}_2\text{O}_3$-$\text{MgO}$ inclusions containing $>10\%$ MgO and $<10\%$ CaO (Type AM), are assumed to be electrode inclusions that have been trapped in steel drops or particles that have fallen from the electrode tip, through the slag bath to the steel pool, without having been overheated and dissolved, as can be seen in Figure 8. According to the literature, the diameter of the droplets leaving the electrode is generally in the range of 1–10 mm but usually about 5 mm [42,43], i.e., much larger than the individual inclusion size range.

The semi-secondary inclusions, which often are almost pure $\text{Al}_2\text{O}_3$ and $\text{Al}_2\text{O}_3$-$\text{CaO}$ oxides containing $<10\%$ MgO (Types A + AC), are assumed to be small Mg spinel inclusions ($<8 \mu\text{m}$) that have survived from the electrode. The Mg spinel inclusions already exist in the electrode, either as a solitary

![Figure 8. Schematic illustrations of different oxide inclusions in the melted metal layer on the surface of electrode, liquid slag, melted metal bath, and solidified ingot during the ESR process.](image-url)
spinel inclusion or as an inclusion with a core of a Mg-spinel and an outer layer corresponding to the top slag composition in the final treatment ladle. When the coated Mg spinel reaches the electrode tip, the outer layer melts, leaving the spinel. Thereafter, the corresponding ESR or PESR process slags potentially coat the spinel inclusions (Type ACM). This explanation is also confirmed by the detection of some amounts of CaF$_2$ in the outer CaO-Al$_2$O$_3$ layer of inclusions (see Figure 6c,d and Figure 7), since the ESR or PESR process slags contain CaF$_2$ and the ladle slag does not. Moreover, the slag inclusions (Type AC) can be carried into the liquid steel pool with metal droplets, which passed down through the ESR or PESR process slags, as shown in Figure 8c. An alternative is the novel evolution mechanism using both thermodynamic and kinetic techniques, presented by Xuan et al. [44]. In this case, this type of inclusion can have an origin from a coalescence-collision between a solid Mg spinel and a liquid (Ca-Al oxide) inclusion in the liquid steel, that is (1) at the electrode tip, (2) in the process slag or, (3) in the molten steel pool, which in cases (2) and (3) would be the ESR/PESR process slag acting as an infinitive source of a Ca-Al oxide inclusion. However, further studies are needed to evaluate this alternative inclusion mechanism in the ESR/PESR processes.

The secondary inclusions, for example, Al$_2$O$_3$-MgO (with a low content of MgO) and Al$_2$O$_3$, are formed in the liquid metal pool as a result of the reactions between alloying elements and dissolved oxygen [41]. Calcium aluminates are also assumed to precipitate in the molten steel pool. The generation of these oxide inclusions during solidification of liquid steel in the mold is assumed to be driven entirely by the amount of silica in the process slag.

The discussion above assumes that the content of [Ca] is probably high (accounting for the greater part of the inclusion-accountable oxygen content), but has not been determined in this study. Their composition is driven entirely by the ESR slag/metal reactions. A schematic over the three inclusion types is displayed in Table 2.

### Table 2. Characterization and a general schematic of the three described inclusion types.

| Inclusion | Primary Inclusions (PI) | Semi-Secondary Inclusions (SSI) | Secondary Inclusions (SI) |
|-----------|-------------------------|---------------------------------|--------------------------|
| Schematic illustration | Al$_2$O$_3$-CaO | MgO-Al$_2$O$_3$ | Al$_2$O$_3$-CaO |
| Type of NMI | AM | ACM, A and AC | A, AC |
| Size on NMI | Large, see below | Medium (normally $< 30 \mu$m) | Small ($< 10 \mu$m) |
| Source or formation mechanism | From the electrode, the size depends on the size of the inclusions in the electrode and the size of the steel droplets. In the ingot the spinels are often found in inclusion clusters with complex shapes, often together with other inclusions and elements (C, Cr, Si, Mn, S, Ca). | Primary AM oxides covered by process slag, sometimes with CaF$_2$ attached. If CaF$_2$ is found, it is proof that the inclusion has been in contact with the ESR/PESR process slag. | Precipitated in the ingot during solidification of the liquid steel |
In the slag/metal reaction scheme, Ca and Mg can be introduced into the metal due to a reduction with an Al deoxidant according to the following reactions:

$$3(MgO) + 2[Al] = 3[Mg] + (Al_2O_3)$$  \hspace{1cm} (1)

$$3(CaO) + 2[Al] = 3[Ca] + (Al_2O_3)$$  \hspace{1cm} (2)

The driving force for Mg and Ca in the steel (reactions (1) and (2)), should lead to a higher amount of $[Mg]$ and a lower content of $[Ca]$ in the conventional ingot and a higher amount of $[Ca]$ and a lower content of $[Mg]$ in the ESR/PESR ingot. The reason is that the content of silica ($SiO_2$) is higher in the ladle slag compared to the process slag in ESR/PESR. According to laboratory investigations by Shin et al. [45] the direction of the driving force in equations 1 and 2 is controlled by the amount of silica in the process slag. However, the difference in $[Mg]$ and $[Ca]$ contents could not be determined, or was considered to be in the margin of error, from the total composition results of the samples from the conventional ingots, electrodes, and ESR/PESR ingots.

The discussion above assumes that the Mg spinel, both in the electrode and in the ESR/PESR ingots is formed due to a reaction taking place in the liquid steel slag. According to Kiessling [46], non-metallic inclusion nucleus with MgO as one component may be formed as a product due to reactions between the furnace refractories and the furnace or ladle slag, or with the molten steel itself. Magnesium has both a very low solubility in iron and a Mg-spinel has a high melting point of 2135 °C [46]. According to the low amount of MgO in the ESR process slag (about 3%) and the lack of refractory in the remelting processes, these results indicate that the primary MgO containing inclusions from the electrode should survive the ESR/PESR remelting processes. As a comparison, the melting points for common inclusions are presented in Table 3, the data of which are taken from [46].

**Table 3.** Melting points of inclusions occurring in electrode charges and ESR/PESR ingots, data from [46].

| Type of Inclusion               | Melting Point     |
|--------------------------------|-------------------|
| MgO-$Al_2O_3$ spinels           | 2135 °C           |
| CaO-$Al_2O_3$ calcium aluminates| 1455–1850 °C      |
| CaO-$SiO_2$ calcium silicates   | 1475–2070 °C      |
| MnS manganese sulfide           | 1610 °C           |
| CaS calcium sulfide             | about 2500 °C     |

Yang et al. calculated stability diagrams of the Mg-Al-O system in molten steel at 1873 K and 1773 K [47]. According to them, as well as from our observations the measured amounts of Mg, O and Al, Mg spinel is stable both in the electrodes as well as in the ESR/PESR ingots. The working temperature on the electrode tip is assumed to be about 25 °C higher than the melting point of the steel, which is approximately 1798 K [13,18,41,48]. Yang et al. [47], (as well as Shi et al. [13]) also presented a mechanism that could explain the modification of Mg-spinel inclusions into MgO-$Al_2O_3$-CaO-CaS inclusions, during calcium treatment. However, the inclusions obtained by calcium treatment are very similar to the inclusions seen in this and previous investigations [12,23–25]. This indicates, to a certain level, that the ESR process slag itself acts in the same way as a conventional calcium treatment of a steel melt.

Xuan et al.’s theory regarding attachment behavior on evolution mechanism of Mg-Al oxides particles in steel [44] describes two possibilities to obtain an inclusion with one or more Mg spinel particles as a core and with a coating layer of Ca-Al-(Mg) oxide. The inclusion evolution can take place by either a chemical reaction or a coalescence-collision behavior. This idea may explain the appearance of this kind of inclusions in the electrode, and possibly also in the ESR/PESR processes.

The results presented above correspond to the results from the trials using a tracer in the ESR process slag [24,25]. More specifically, approximately 50% of the inclusions in an ESR ingot are primary inclusions, with an origin from the electrode, and the most common type is a Mg spinel inclusion.
4.2. Difference between ESR and PESR Remelted Ingots

The difference in inclusion characteristics (morphology, composition, size, and number) between the ingots from the open-air furnace and the ingots from the PESR process is probably both due to the difference, which comes from electrode changing, the extra chemical reactions taking place between air and slag bath, and the aluminum deoxidation during the ESR process. The aluminum deoxidant, dissolved in the slag pool reacts with FeO in the process slag as follows [10,49]:

$$2[\text{Al}]_{\text{in slag}} + 3(\text{FeO}) = (\text{Al}_2\text{O}_3) + 3[\text{Fe}]$$  (3)

Schematic illustrations of the mechanisms of oxygen transfers and Al deoxidation in an open ESR process are shown in Figure 9. Due to the reactions, the feasibility for nucleation of a larger number of inclusions exists. According to Li et al. [30] an $\text{Al}_2\text{O}_3$ rod immersed in a $\text{CaO}-\text{Al}_2\text{O}_3-\text{CaF}_2$ flux led to the formation of an intermediate coating compound of $\text{CaO}-2\text{Al}_2\text{O}_3$. This could explain why more than a double amount of Al-Ca oxides (Type AC) were found in the ESR ingot as compared to the PESR ingot.

Another critical point is that, in order to prevent a liquid breakout, a smaller electrode/ingot ratio is often used in ESR furnaces with movable molds or baseplates. A smaller electrode/ingot ratio concentrates the heat more towards the center of the ingot, which leads to a deeper pool of molten steel in the ingot. A deeper pool results in a longer longest solidification time (LST), i.e. a longer residence time in the liquid pool. This, in turn, promotes more nucleation and inclusion growth. According to Cao et al. [43], a larger filling ratio (electrode/ingot diameter) also leads to more and smaller droplets as compared to a smaller filling ratio. More and smaller droplets increase the contact area between the slag and steel, which promotes the removal of non-metallic inclusions from the original electrode material.

5. Conclusions

The following conclusions can be drawn based on the results from this study:

- Both larger inclusions (up to 44.8 $\mu$m) and an approximatively two times higher number of oxide inclusions per area were found in the ESR ingot compared to the PESR ingot. This is believed to be caused by the remelting under air atmosphere, the Al deoxidation, the lower filling ratio between the electrode and the ingot, and an unintentional uneven melting during the electrode changes.
- According to the recent classification of inclusions, primary, semi-secondary and secondary inclusions exist in the remelted ingots as explained below.

**Figure 9.** (a) Schematic illustration of the mechanisms of oxygen transfers and Al deoxidation in ESR process (lsp-liquid steel pool). (b) Numbering of reactions in the figure is given according to [10].
• The primary inclusions (such as Al₂O₃-MgO oxides, Type AM) are assumed to have survived from the electrode because they were trapped inside a steel drop or a fallen steel fragment, without having contact with the ESR/PESR process slag.

• The most common inclusion type in the remelted ingots has a core of MgO-Al₂O₃ with an outer layer that corresponds to their corresponding process slag (Type ACM). However, inclusions containing MgO are characterized by having an exogenous origin, where the main sources of MgO are refractories or the furnace or ladle slags. Due to the low solubility of Mg in iron and the high melting point of MgO, it is more likely that at least the majority of the Mg spinel inclusions in the remelted ingots are primary inclusions, which survived from the electrode. This kind of inclusion is denoted as semi-secondary inclusions.

• The secondary inclusions are assumed to be formed in the liquid steel pool as a result of the reactions between alloying elements and the dissolved oxygen.

• According to the literature, the inclusions after a calcium treatment modification, (used to modify MgO-Al₂O₃ to softer inclusions with a lower melting point of the outer layer of inclusions) are very similar to the inclusions found in the ESR/PESR ingots. This observation indicates that the ESR process slag acts in some way like a calcium treatment modification. This hypothesis is supported by the observed appearance of the inclusions described above.

• The results presented above correspond to the results from previous trials, made using a tracer (La₂O₃) in the ESR process slag, which indicates that the most probable inclusion to survive from the electrode is a Mg-spinel.

• On the whole, we find that the overall cleanliness of the electrode (and also the composition of the inclusions in the electrode) has a direct bearing on the inclusion content of the ESR and PESR ingots.

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