Evaluation of Sulfide Inclusions before and after Deformation of Steel by Using the Electrolytic Extraction Method

Shuo Guo *, Andrey Vladimirovich Karasev, Anders Tilliander and Pär Göran Jönsson

Department of Materials Science and Engineering, KTH Royal Institute of Technology, Brinellvägen 23, 10044 Stockholm, Sweden; karasev@kth.se (A.V.K.); anders@kth.se (A.T.); parj@kth.se (P.G.J.)

* Correspondence: shuog@kth.se; Tel.: +46-(0)7-284-99591

Citation: Guo, S.; Karasev, A.V.; Tilliander, A.; Jönsson, P.G. Evaluation of Sulfide Inclusions before and after Deformation of Steel by Using the Electrolytic Extraction Method. Metals 2021, 11, 543. https://doi.org/10.3390/met11040543

Academic Editor: Lauri Holappa

Received: 1 March 2021
Accepted: 22 March 2021
Published: 26 March 2021

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Abstract: The characteristics of elongated MnS have a critical effect on fatigue anisotropy and all mechanical anisotropies. A comparative investigation of nonmetallic inclusions in both stainless steels and tool steels has been carried out in this study. The inclusion characteristics were investigated using electrolytic extraction (EE) followed by scanning electron microscopy combined with energy-dispersive spectroscopy (SEM-EDS). Overall, three types of MnS inclusions (type I (regular), type II (irregular) and type III (Rod)) were found in tool steels in as-cast samples, which had not been heat-treated. Furthermore, three types of MnS inclusions (Rod-like sulfide (RS), Plate-like sulfide (PS) and Oxysulfide (OS)) were found in samples taken after rolling. Based on the breakability of the elongated MnS, three types of inclusions, Type UU, UB and BB, where U represents the undamaged or unbroken edge of an inclusion and B represents the fragment or broken edge of an inclusion, were studied in both stainless steels and tool steels both before and after additional heat treatment. The effect of heat treatment and dissolving the metal layer during the EE process is also discussed. The results show that both processes have a limited effect on the breakability of inclusions in steels with carbon contents <0.42 mass%.

Keywords: steel; nonmetallic inclusions; MnS; electrolytic extraction; deformation; heat treatment

1. Introduction

Nonmetallic inclusions (NMIs) in steels and metals represent impurities that are most often harmful to steel’s mechanical properties. However, some reports show that sulfide (MnS) inclusions can improve the machinability of steels [1]. Despite this, these inclusions are still considered as detrimental to the final steel product after the steel has been deformed. Negative effects on the toughness, anisotropy, etc., will negatively impact the final steel properties and lead to structural failures [2,3]. The reason for this is that, compared to other inclusions such as oxides, sulfides (MnS) are softer and can be easily deformed during rolling [4].

It is well known that MnS inclusions can initially be classified into three types—namely, type I (globular), type II (dendritic), and type III (angular) inclusions. According to the results from Temmel et al. [5], a type I MnS inclusion is a globular oxysulfide with a wide range of sizes and a type III MnS inclusion is a monophase inclusion with an irregular or regular shape. After deformation, the MnS inclusions of type I and type III could be transformed into a pancake shape or an ellipsoidal geometry. This, in turn, could lead to anisotropy with respect to the steel properties in different directions [2]. Type II dendritic sulfides are rotated into the deformation plane when being deformed. According to T. J. Baker et al. [2], type II MnS inclusions show an entirely different starting situation during deformation and are present as fine needle shapes in an interdendritic eutectic distribution. This is similar to what has been found for alumina clusters. In this paper, these dendritic MnS inclusions are not included.

The characteristics of elongated inclusions play a critical effect on the fatigue anisotropy and all mechanical anisotropies (ductility, tensile strength, etc.) as the stress is concen-
treated at the site of elongated inclusions and such a concentration effect changes with the characteristics of the elongated inclusions [5]. Therefore, a characterization of these types of nonmetallic MnS inclusions is essential to understand how steel products’ properties can be improved. Characteristics such as the number, size, distribution, morphology, and composition of nonmetallic inclusions are essential as these parameters can help better understand the mechanisms of formation and growth of different nonmetallic inclusions as well as the behavior of the mechanical properties of the final steel product [6].

Currently, the most common method to characterize elongated inclusions is a two-dimensional (2D) method, where nonmetallic inclusions are examined on a polished cross-section (CS) of a steel sample using Scanning Electron Microscopy (SEM); moreover, this is sometimes combined with Energy Dispersive X-ray Spectroscopy (EDS) composition determinations. However, there is a large drawback by using the 2D method for studying these types of deformed particles. Specifically, a previous study [7] shows that the results obtained by 2D investigations often significantly differ compared to the real size of the particles. This is especially true for deformed inclusions such as elongated MnS. The reason for this is that the elongated inclusions’ real sizes are hard to determine on the polished metal sample surface. This is due to the fact that they are not always parallel to the polished cross-section. As a result, the cutting angle between the inclusions and the sample surface must be less than 1° to acquire acceptable results compared to the real length in the case of elongated inclusions [7]. However, this is not easy to achieve in practice. Therefore, the three-dimensional electrolytic extraction (3D EE) method has been judged to be more accurate than the 2D CS method to determine the real size of the inclusion [7,8]. Previously several studies [6–10] have presented a comparison of different investigation methods. Overall, the results show that to determine the regular sizes and morphologies of elongated inclusions, the 3D extraction method should be applied to acquire realistic results. However, after the EE process for the steel samples containing a higher carbon content, many inclusions can be partially or entirely covered by carbides, so accurate 3D investigations of NMIs are difficult in these steels. In order to remove the carbides, a short heat treatment at 900 °C with a following fast cooling is usually applied.

However, it is also well known that MnS inclusions can change their morphologies throughout the heat treatment process. The coarsening and spheroidization behaviors of elongated MnS inclusions after heat treatment have been studied in previous research [11,12]. After a homogenization at 1583 K (1310 °C) for up to 20 h, the morphology of elongated MnS inclusions changed from a rod-like to a spherical inclusion [12]. Additionally, the results of McFarland et al. [11] showed that the shape of elongated MnS inclusions, which had been heat-treated at temperatures between 815 and 1205 °C for up to 30 h, followed the transformation from a plate shape to a rod shape. The formation of a spheroid shape followed this until spherical inclusions were formed. Moreover, Shao et al. [13] investigated the shape changes of MnS inclusions in rolled resulfurized free-cutting steel (0.32 mass% of S) during heat treatment by in situ observations using confocal scanning laser microscopy. The obtained results showed that the elongated MnS can be split (or fragmented) into separate pieces during 5 min of heat treatment of metal sample at 1073 K (800 °C). In this case, an aspect ratio (ratio between length and width of inclusion) of elongated MnS drops quickly. In contrast, the total number of sulfide NMIs on the surface of the metal sample increases rapidly.

Moreover, a previous study has shown that [7] elongated sulfide inclusions might break at edges (one or both) of the elongated inclusions in rolled steel samples. Although the necessary deformation behavior of MnS inclusions is clear, not many studies show information with respect to plate-like sulfide (PS) inclusions. However, more systematical 3D investigations of deformed MnS inclusions are necessary for understanding the effect of preliminary heat treatment and electrolytic extraction process on breakability and morphology of investigated sulfides in various steel grades.

Therefore, the current study’s critical focus is to present a methodological approach to characterize sulfide inclusions in four different steels having various C and S contents
by using the 3D investigations in the EE method. Another focus of this study is to investigate the possible effect of a short preliminary heat treatment process of specimens and electrolytic extraction conditions on the characteristics of investigated sulfide inclusions (such as morphology, size and number) in selected steels before and after rolling.

2. Materials and Methods

2.1. Materials and Sample Preparations

The chemical compositions of the four studied steel grades that contain MnS inclusions are listed in Table 1. As shown in the table, the 42CrMo4 and 13HMF grades are tool steels with higher carbon contents (0.42% and 0.15%) and the 3R65 and 316L are stainless steels with low carbon contents (0.03% and 0.02%). It should also be noted that 42CrMo4 steel has a higher S content (0.025%) compared to the other samples. The 316L steel has the lowest S content (0.007%). All samples were cut from the center of a rolled bar obtained from production.

Table 1. The chemical compositions of the studied steel grades (mass%).

| Steel Grade | C   | Mn  | S   | O   | Cr  | Si  | P   | Ni  | Mo  | Al  | V   |
|-------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 3R65        | ≤0.03 | 1.70 | ≤0.015 | -   | 17.0 | 0.40 | 0.040 | 11.5 | 2.1 | -   | -   |
| 316L        | 0.02 | 1.60 | 0.007 | 0.002 | 17.0 | 0.40 | -   | 11.2 | 2.0 | 0.004 | -   |
| 42CrMo4     | 0.42 | 0.80 | 0.025 | <0.001 | 1.0 | 0.20 | ≤0.025 | -   | 0.23 | 0.019 | 0.004 |
| 13HMF       | 0.15 | 0.49 | 0.0012 | -     | 0.36 | 0.29 | 0.025 | 0.04 | 0.59 | <0.005 | 0.26 |

In this study, an additional heat treatment process was applied for the 42CrMo4, 13HMF and 3R65 steel samples. As mentioned above, MnS inclusions become spheroidized after a heat treatment, which lasts for hours. However, in this study, the purpose of the heat treatment was to dissolve the carbides in the metal matrix to enable better conditions to determine the inclusion characteristics. This is due to the fact that in a tool steel with a high carbon content, the MnS inclusions are all covered by carbides after applying the EE process to a steel sample.

The samples were heat-treated at a temperature of 900 °C. Initially, the furnace was preheated to 900 °C and thereafter it was held at this temperature until stable conditions were reached. After this, the samples were quickly placed in the furnace and kept there for the desired time. After being heated for the desired time, the samples were rapidly cooled (quenching in cold water) to avoid other carbides (such as cementite) precipitating. This heat treatment procedure has successfully been used to dissolve the carbides present in the original steel samples, as will be illustrated from SEM images presented later in the paper.

Table 2 shows information about the heat treatment process for the different steel samples. Only a 5 min heat treatment time was necessary to use to dissolve the carbides in the 42CrMo4 sample. After heat treatment, the inclusions could be observed. A 5 min heat treatment time was also used for the rolled 13HMF steel sample in order to be able to compare the results from the inclusion characterization. Finally, different holding times at 900 °C were applied for the rolled 42CrMo4 and 3R65 steel samples.

Table 2. Heat treatment parameters for different steel grades.

| Steel Grade | Heating Temperature | Atmosphere | Heating Time (Minutes) | Samples | Cooling       |
|-------------|---------------------|------------|------------------------|---------|---------------|
| 42CrMo4     | 900 °C              | Air        | 5 - 10 15 30           | As cast | Quenching in water |
| 13HMF       | 900 °C              | Air        | 5 - 15 30              | Rolled  |               |
| 3R65        | 900 °C              | Air        | 5 - 15 30              |         |               |
2.2. Electrolytic Extraction Method (3D EE)

After cutting the steel samples to proper sizes, grinding, extraction, and filtration were applied. Before carrying out electrolytic extraction, the samples were ultrasonically cleaned for 3 min by using organic solvents (first acetone and then benzene). Additionally, the sizes and weights of the samples were measured before the extraction process. In this study, only one side of each sample, which was parallel to the rolling direction, was used for the EE method.

A 10%AA (10% acetylacetone–1% tetramethylammonium chloride–methanol) electrolyte was used in the electrolytic extraction process. It has previously been reported that many oxides (Al$_2$O$_3$, TiO$_x$, MgO, etc.), carbides, sulfides, multicomponent inclusions, etc. have successfully been studied by using nonaqueous electrolytes in the EE method [10,14,15]. In this study, a soft 10%AA electrolyte was used for electrolytic extraction of all steel samples. According to results obtained by Inoue et al. [16], this electrolyte can be recommended for the extraction of different nonmetallic inclusions (including MnS) from metal samples without dissolving the inclusions. Moreover, an application of this electrolyte for extraction of thin plate-like or film-like MnS inclusions in deformed steels and in chips after machining did not show any dissolution of these inclusions during electrolytic extraction experiments [7,17]. These results have shown that a 10%AA electrolyte is suitable for safe extractions of MnS inclusions. The following parameters were used during the electrolytic extraction: an electric charge of 500 coulomb, electric currents varying from 40 to 60 mA, and a voltage of 3.5 V. In this study, different electric charges of 100, 200, 300, and 1000 coulombs were also applied for comparison. During the extraction process, the parameters’ current, voltage, and electric charges were recorded. Figure 1 shows the principle of the electrolytic extraction set up being used in this study.

![Experimental setup for electrolytic extraction](image)

Figure 1. Experimental setup for electrolytic extraction (a) and filtration (b).

After finishing the extracting of the inclusions, a filtration was applied as seen in Figure 1b. A 0.4 μm aperture polycarbonate film filter was used for the collection of the inclusions on the film filter as the liquid was drained through the filter. After the whole process was finished, the filter was carefully removed and placed in a dry clean plastic sample box. In addition, the weight of the steel sample after the electrolytic extraction was determined. After this, the filter was kept in the box until the SEM investigations were made.

The depth of the dissolved sample layer ($D_{\text{dis}}$) during electrolytic extraction can be calculated as follows:

$$D_{\text{dis}} = \frac{W_{\text{dis}}}{\rho_{\text{metal}} \times A_{\text{surface}}}$$

(1)
where $W_{\text{dis}}$ is the weight loss (in g) of the sample during the extraction process, $A_{\text{surface}}$ is the reaction surface area (in mm$^2$) of the steel sample, and $\rho_{\text{metal}}$ is the steel density (0.0078 g/mm$^3$).

### 2.3. Scanning Electron Microscope (SEM) Determinations

Before observing the characteristics of nonmetallic inclusions (NMIs) from the EE process by using SEM, a part of the sample filter was pasted on an aluminum holder by using carbon tape. In order to investigate the composition of the typical NMIs, an Energy Dispersive X-ray Spectroscopy (EDS) determination was carried out. The voltage was set to 15 kV and the working distance was set to approximately 11 mm. In addition, the Back-scattered electron (BSE) mode was applied for observation of the inclusions and to avoid interferences from impurities.

**Method 1**

To investigate the typical NMIs in each sample, Method 1 (M1) was applied. Here, SEM photos were randomly captured on the film filter to observe the inclusions of both small sizes (less than 10 $\mu$m) and large sizes (larger than 100 $\mu$m). Additionally, different SEM magnifications were used depending on the sizes and the morphologies of the typical NMIs.

**Method 2**

For evaluating the characteristics of NMIs more systematically, another method was used, which was named Method 2 (M2). In this method, $\times 500$ and $\times 1000$ magnifications (depending on the sample) were used to determine the fractions of different types of NMIs as well as number of inclusions per volume ($N_v$) for each sample. Typically, 10 to 50 photos at $\times 500$ magnification were captured continuously throughout the film filter at the fixed magnification for each specimen. The data were mainly gathered to determine the $N_v$ values of the inclusions. For each sample, a minimum of 100 inclusions was investigated to obtain a statistically reliable amount of data.

For elongated sulfides, the maximum lengths ($L_s$) and widths ($W_s$) were measured on SEM images by using the digital calliper as well as using the image software “ImageJ”, as shown in Figure 2.

![Figure 2. Definitions of determining the sizes of elongated inclusions.](image)

To evaluate the deformability and classification of the sulfide inclusions, the aspect ratio (AR) was applied. This was calculated as follows:

$$AR = \frac{L}{W}$$

The number of NMIs per unit volume of a metal sample ($N_v$) was also calculated as follows:

$$N_v = \frac{n \times A_f}{\sum A_{\text{obs}} \times \rho_{\text{metal}} / W_{\text{dis}}}$$
where \( n \) is the number of investigated inclusions in the selected size range, \( A_t \) is the whole area of the film filter with inclusions (=1200 mm\(^2\)), and \( A_{\text{obs}} \) is the observed area on a film filter.

3. Results

3.1. Application of EE for Studies of Deformed NMIs in Different Steels

3.1.1. Data for Stainless Steels (<0.1% C)

For stainless steels with carbon contents less than 0.1% (mass percent), the NMIs (including MnS) can easily be extracted. Both of the steels (3R65 and 316L) had been rolled before the study. No additional sample treatment was applied before the electrolytic extraction. The parameters used in the extraction method and the SEM observations when using Method 1 are presented in Table 3. The overall size range as well as the average size and standard deviation of each sample are also listed in Table 3. The units of the main parameters are listed in the brackets.

Table 3. Main parameters of electrolytic extraction (EE) and scanning electron microscopy (SEM) observation of Nonmetallic inclusions (NMIs) in the 3R65 (0.03% C) and 316L (0.02% C) steels when using Method 1.

| Sample | Coulomb (C) | \( W_{\text{dis}} \) (g) | \( D_{\text{dis}} \) (μm) | \( A_{\text{obs}} \) (mm\(^2\)) | Num. (NMIs) | Size (L, μm) |
|--------|-------------|-----------------|-----------------|-----------------|------------|-----------|
| 3R65   | 500         | 0.1158          | 66.7            | 1.1229          | 96         | 19 ± 27.5 (3.2–273.3) |
| 316L   | 500         | 0.0878          | 104.2           | 1.1229          | 71         | 15 ± 16.7 (2.9–210.7) |

The typical classification of sulfides with respect to their morphologies is presented in Figure 3. As shown in the figure, the elongated inclusions are classified into three types—namely, Type RS—rod-like sulfides, Type PS—plate-like sulfides, and Type OS—oxy sulfides.

| Type   | RS        | PS        | OS        |
|--------|-----------|-----------|-----------|
| Typical photo | ![Typical sulfide inclusions observed in steel samples.](image) |

The characteristics of the elongated NMIs after electrolytic extraction when using Method 2 are presented in Table 4. It should be pointed out that the plate-like inclusions (such as separate sulfide plates as well as two or more sulfides sintered together during the deformation process) have significantly larger widths compared to the widths of typical rod type elongated inclusions. In the 316L steel, most of the MnS inclusions (~97%) are of the RS type. In the 3R65 steel, almost 46% of the inclusions are of the RS type and 51% are of the PS type. In addition, both of the steel samples contain small amounts of OS type inclusions—namely, around 3 and 1% in the 3R65 and 316L steels, respectively. As shown in the table, the OS type inclusions have smaller aspect ratios and the solid oxide (\( \text{Al}_2\text{O}_3–\text{SiO}_2 \)) parts are barely deformed. This is because of the deformation behavior difference between the different inclusion types. Matsuoka et al. [18] have presented a model to simulate the complex oxysulfides’ deformation behavior after hot rolling. The result showed that if the ratio of (soft) sulfide inclusions increases, this will lead to an increased difference between...
the aspect ratios of these inclusions before and after deformation of a steel sample. The units of the main parameters are listed in the bracket next to the units. The overall size range, the average size and standard deviation for each sample are also listed in Table 4.

Table 4. Classification of different nonmetallic inclusions in 3R65 and 316L samples when using Method 2.

| Steel  | Type | RS   | PS   | OS |
|--------|------|------|------|----|
| 3R65   | Num. (NMI) | 79   | 87   | 6  |
|        | L (µm)   | 34.9 ± 25.2 | 16.2 ± 16.1 | 27.1 ± 24.5 |
|        | AR       | 20.7 ± 10.6 | 9.8 ± 7.4 | 12.6 ± 5.6 |
|        | Composition | MnS<sub>(pure)</sub> | MnS<sub>(pure)</sub> | MnS-(Al,Si)O |
|        | Frequency (%) | ~46 | ~51 | ~3 |
| 316L   | Num. (NMI) | 167  | 3    | 2  |
|        | L (µm)   | 15.9 ± 16.7 | 12.7 ± 5.8 | 10.1 ± 5.5 |
|        | AR       | 8.7 ± 6.6 | 6.7 ± 2.3 | 4.2 ± 1.7 |
|        | Composition | MnS<sub>(pure)</sub> | MnS<sub>(pure)</sub> | MnS-(Al,Si)O |
|        | Frequency (%) | ~97 | ~2  | ~1 |

The SEM investigations showed that the elongated inclusions (MnS) can be fragmented or broken. In this study, U represents the undamaged or unbroken edge of an inclusion and B represents the fragment or broken edge of an inclusion. Therefore, the elongated inclusions can be classified as follows: UU, UB, and BB. If the inclusion is broken (BB and UB), the end part of inclusion has an angular sharp broken edge while the unbroken inclusion (UU) has a smoothly rounded or elongated end part. This can easily be observed on SEM photos when using larger magnifications. The precise morphologies of each group of inclusions are shown in Table 5. It is apparent that these broken inclusions cannot be used for an accurate determination of the real sizes of elongated sulfides.

Table 5. Typical SEM images of elongated MnS inclusions with broken (B) and unbroken (U) edges in the steel samples after a completed EE.

Table 6 shows the characteristics of different shapes of inclusions (both unbroken and broken inclusions) in the 3R65 and 316L steel grades. As can be seen, both steel samples contain more than 97% of elongated undamaged (UU) RS inclusions (MnS), which have retained their original sizes and morphologies. Only around 3% of the inclusions have either been damaged on either side or on both edges. Therefore, the obtained sizes and aspect ratios were judged to be reliable.

Overall, for the steels in which the carbon content is less than 0.1% (mass percent), the results show that the electrolytic extraction method can successfully be applied without any additional heat treatment of the samples. Furthermore, the percentage of UU particles is high enough (>97%) to enable accurate determinations of deformed MnS inclusions.
Table 6. The classification of elongated inclusions in the 3R65 and 316L steel grades when using Method 2.

| Steel | Type | UU (µm) | UB (µm) | BB |
|-------|------|---------|---------|----|
| 3R65  | L    | 3.2–150.2 | 6.1–48.4 | -  |
|       | AR   | 6.5–47.9 | 3.9–17.5 | -  |
|       | Frequency (%) | ~97 | ~3 | - |
| 316L  | L    | 2.0–210.7 | 4.9–35.0 | 8.9–20.9 |
|       | AR   | 2.0–76.4  | 1.2–5.6  | 3.5–8.8  |
|       | Frequency (%) | ~97 | ~2 | ~1 |

3.1.2. Data for Steels Containing 0.15% C and 0.42% C

In steels containing a larger amount of carbon compared to the steels discussed in Section 3.1.1, more carbides precipitate during solidification of the steel melt. As can be seen in the left column of Table 7, a large number of iron carbides were extracted from the carbon steel samples in the case when a preliminary heat treatment was not performed. These carbides covered almost all the other inclusions on the film filter, which made a detailed inclusion investigation impossible. In this case, the results of the determination of the inclusion characteristics such as the sizes and morphologies will be incorrect. However, after an additional heat treatment was carried out (5–30 min at 900 °C in an air atmosphere followed by water quenching), the carbides were mostly dissolved. Additionally, as mentioned above, it can be assumed that the separate regular (type I) and rod-like (type III) inclusions in ingots can be deformed during rolling to mostly form elongated rod-like sulfides (RSs), while irregular sulfides (type II) and any sulfides located close each other can form during deformation the plate-like sulfides (PSs) [5]. By this treatment, inclusions (such as sulfides and oxides) can clearly be seen on the film filter after electrolytic extraction, as can be seen in the right column of Table 7. The inclusions shown in Table 7 from the ingot sample are classified as regular (type I) sulfide, and the inclusions from the rolling sample are classified as rod-like sulfide inclusions (type RS). The detailed information for the inclusion classification can be seen in the text below.

Table 7. Typical SEM images of inclusions on film filter after electrolytic extraction of 42CrMo4 steel samples (0.42% C) without and with heat treatment.

| Samples | Before Heat Treatment | After Heat Treatment |
|---------|-----------------------|---------------------|
| (42CrMo4) Ingot | ![Image](42CrMo4_Ingot_Before.png) | ![Image](42CrMo4_Ingot_After.png) |
| (42CrMo4) Rolling | ![Image](42CrMo4_Rolling_Before.png) | ![Image](42CrMo4_Rolling_After.png) |
To compare the characteristics of sulfide inclusions before and after deformation, the morphologies of MnS inclusions in steel samples were determined. Based on the results of the SEM images, the morphologies of the MnS inclusions in ingot sample (before rolling) were classified into the following three types: (i) type I (regular), (ii) type II (irregular), and (iii) type III (rod). As is shown in Table 8, 64% of the MnS inclusions are of type I and their maximum size is 20.1 μm. Additionally, 16 μm and 20% of the inclusions belong to type II and type III inclusions, respectively. The maximum size (length) of type III MnS inclusions is 49.5 μm, which is significantly larger than the maximum size of type II sulfides (23.3 μm).

**Table 8.** Typical SEM images of MnS inclusions in an ingot sample and a rolled steel samples after heat treatment when using Method 1.

| Steel         | Type      | I (Regular) | II (Irregular) | III (Rod) |
|---------------|-----------|-------------|----------------|-----------|
| 42CrMo4 (Ingot) | Typical photo | ![Image](image1) | ![Image](image2) | ![Image](image3) |
| Size (μm)     | Frequency (%) | 4.3–20.1 | 7.1–23.3 | 18.9–49.5 |
| Frequency (%) | 64 | 16 | 20 |
| Type          | RS | PS | OS |
| 42CrMo4 (Rolling) | Typical photo | ![Image](image4) | ![Image](image5) | ![Image](image6) |
| L (μm)        | AR | Frequency (%) | 6.6–216.3 | 7.4–81.2 | 96 |
|               |     |               | 15.5–98.3 | 3.3–9.0 | 4 |

Elongated MnS inclusions with rod-like shapes can also clearly be seen in the rolled steel samples. In Table 8, 96% of the elongated inclusions are rod-like sulfide inclusions (type RS) with a maximum length of 216.3 μm. Only less than 4% of the inclusions correspond to plate-like sulfides (type PS), which have much smaller maximum sizes (<100 μm) compared to type RS inclusions. Additionally, the oxysulfide inclusions (OS) were not observed in this rolled steel sample.

As mentioned above, the elongated MnS inclusions in the rolled steel sample have been classified into three groups depending on the broken edges as described above—namely, UU, UB, and BB. However, a large number of elongated inclusions in the 42CrMo4 rolled steel sample have one or two broken edges.

The parameters used for the heat treatment of the 42CrMo4 sample and the characteristics of the elongated sulfides after heat treatment for different heating times are presented in Table 9. In all the samples, both small inclusions (less than 10 μm) and large inclusions (larger than 150 μm) were found. The number of sulfides per volume of steel (Nv) for each sample is similar and corresponds to approximately 4500 inclusions per cubic millimeters.
Table 9. Main parameters of EE and SEM observations of elongated sulfides in different steel samples of 42CrMo4 steel grade after heat treatment using Method 2.

| Sample        | Time (min) | Coulomb (C) | \( W_{\text{dis}} \) (g) | \( D_{\text{dis}} \) (µm) | \( A_{\text{obs}} \) (mm\(^2\)) | Num. (NMIs) | Size (L, µm) | \( N_v \) (mm\(^{-3}\)) |
|---------------|------------|-------------|---------------------------|---------------------------|---------------------------------|-------------|-------------|---------------------|
| 42CrMo4/05    | 5          | 500         | 0.1159                    | 102                       | 2.0081                          | 112         | 6.6–200.3    | 4510                |
| 42CrMo4/10    | 10         | 500         | 0.1291                    | 104                       | 2.0081                          | 127         | 9.1–216.9    | 4576                |
| 42CrMo4/15    | 15         | 500         | 0.1240                    | 103                       | 2.0081                          | 123         | 10.8–207.3   | 4623                |
| 42CrMo4/30    | 30         | 500         | 0.1221                    | 104                       | 2.0081                          | 119         | 9.1–185.6    | 4542                |

The detailed characteristics of broken and unbroken inclusions in the 42CrMo4 steel after heat treatment are given in Table 10. The percentage of UU type inclusions for each sample was relatively low for all samples—namely, less than 40%. It can also be seen in the table that most of the largest inclusions correspond to broken particles. From a previous study [19], it is known that the short crack in steel was initiated at the site of elongated MnS inclusions. There is high stress concentrated at the edge of the deformed MnS inclusions, especially for plate-like pancake-shaped inclusions. Therefore, this geometry can result in a significant mechanical anisotropy. Additionally, when the stress ratio increased, the short crack growth increased during the propagation stage around the MnS inclusions. Therefore, it is believed that the stress concentration on the elongated inclusions in the metal matrix and the stress ratio is the reason for the presence of broken particles before the electrolytic extraction of these steel samples.

Table 10. Classification of different nonmetallic inclusions in rolled 42CrMo4 steel samples using Method 2.

| Sample        | Type * | UU  | UB  | BB  |
|---------------|--------|-----|-----|-----|
| 42CrMo4/05    | L (µm) | 6.6–169.6 | 9.5–200.3 | 9.7–148.8 |
|               | AR     | 3.2–81.2 | 3.3–66.7 | 3.7–52.3 |
|               | Frequency (%) | ~39 | ~30 | ~31 |
| 42CrMo4/10    | L (µm) | 9.1–139.4 | 10.7–216.3 | 26.7–151.5 |
|               | AR     | 4.1–47.1 | 5.0–71.9 | 5.6–44.2 |
|               | Frequency (%) | ~36 | ~39 | ~25 |
| 42CrMo4/15    | L (µm) | 10.8–207.3 | 11.2–165.0 | 12.5–118.5 |
|               | AR     | 6.3–51.2 | 5.7–47.4 | 5.4–35.6 |
|               | Frequency (%) | 34  | 34  | 32  |
| 42CrMo4/30    | L (µm) | 9.1–164.5 | 21.7–161.6 | 15.2–185.6 |
|               | AR     | 6.8–49.5 | 7.2–43.2 | 6.3–54.7 |
|               | Frequency (%) | ~35 | ~32 | ~33 |

* (UU = unbroken–unbroken inclusions, UB = unbroken–broken inclusions, BB = broken–broken inclusions).

For the other 13HMF steel sample, the fraction of unbroken/broken inclusions is quite different compared to the 42CrMo4 steel samples. Specifically, 88% of the inclusions are unbroken particles, and the rest have either one broken edge or two broken edges. Some parameters used in the electrolytic extraction experiments and characteristics of deformed MnS inclusions in the 13HMF metal samples are given in Table 11. Note, that the 13HMF sample, which was not heat-treated, could not be studied due to the presence of carbides which covered the inclusions after extraction, as discussed previously.

Table 11. Main parameters of EE and SEM observations of elongated sulfides in the steel of 13HMF after heat treatment for 5 min at 900 °C using Method 2.

| Sample        | Coulomb (C) | \( W_{\text{dis}} \) (g) | \( D_{\text{dis}} \) (µm) | \( A_{\text{obs}} \) (mm\(^2\)) | Num. (NMIs) | Size (L, µm) | \( N_v \) (mm\(^{-3}\)) |
|---------------|-------------|---------------------------|---------------------------|---------------------------------|-------------|-------------|---------------------|
| 13HMF/05      | 500         | 0.1344                    | 85                        | 0.504                           | 147         | 1.7–110.3    | 20,313              |
For the 13HMF steel sample 92% of the elongated inclusions are type RS inclusions, with a maximum length of 92.8 μm and only 8% of the inclusions are type PS inclusions, as shown in Table 12. It can also be seen in the table that 88% of the inclusions are UU inclusions. It can be concluded that the amount of broken elongated MnS inclusions depends on the steel grade, parameters of deformation, and heat treatment procedure. The maximum length of the inclusions in each group of the U/B particles decreased from 110.3 μm for the “UU” inclusions to 44.5 μm for the “BB” inclusions.

Table 12. The classification of different types of sulfide NMIs in the sample of 13HMF by using Method 2.

| Type   | RS            | PS            | OS            |
|--------|---------------|---------------|---------------|
| Typical photo | ![Typical photo](image) | ![Typical photo](image) | -            |
| L (μm) | 1.7–92.8      | 3.2–110.3     | -             |
| AR     | 2.6–40.6      | 6.6–30.0      | -             |
| Composition | MnS\textsubscript{(pure)} | MnS\textsubscript{(pure)} | -            |
| Frequency (%) | 92     | 8             | -             |

| Type   | UU            | UB            | BB            |
|--------|---------------|---------------|---------------|
| Typical photo | ![Typical photo](image) | ![Typical photo](image) | ![Typical photo](image) |
| L (μm) | 1.7–110.3     | 18.2–82.3     | 19.6–44.5     |
| AR     | 2.6–37.9      | 5.5–19.3      | 3.0–12.9      |
| Composition | MnS\textsubscript{(pure)} | MnS\textsubscript{(pure)} | MnS\textsubscript{(pure)} |
| Frequency (%) | 88    | 8             | 4             |

The main finding is that an additional heat treatment is required in order to be able to study carbon steel samples (0.15–0.42% C) by using the electrolytic extraction method. The purpose of the heat treatment is to enable a reliable determination of the presence of elongated inclusions. However, a large number (61–66%) of elongated inclusions in the 42CrMo4 steel sample taken after heat treatment and electrolytic extraction were broken. Several possible reasons could have caused this. First, in the steelmaking process, the temperature and the rolling process are essential factors that influence the results. The steel is rolled in a temperature range that the sulfide inclusions can easily break. Second, the electrolytic extraction procedure (cutting of sample, grinding, ultrasonic cleaning, extraction, filtration, and film filter preparation for SEM observation) may cause the problem. Third, the heat treatment may cause the MnS inclusions to transform, leading to the MnS inclusions being broken during the heat treatment.

3.2. Effect of the Dissolved Metal Layer during the EE Process

For determination of the effect of cutting and grinding on the number of broken sulfides, the 316L steel sample without heat treatment was extracted to acquire the different depths of the dissolved metal layer (D\textsubscript{dis}).

Table 13 shows the overall fractions of size (length), ARs, fractions of unbroken particles, etc., for the 316L steel samples for which no heat treatment was performed. The
percentage of unbroken particles is larger than 97% in all samples. This means that the results obtained from these samples are very reliable. Additionally, the \( N_v \) values do not change too much between the samples. Thus, it seems that the dissolved layer of the samples varying from 26 to 237 \( \mu \)m did not affect the results in the present study.

| Sample | Coulomb (C) | Num. (NMIs) | \( W_{\text{dis}} \) (g) | \( D_{\text{dis}} \) (\( \mu \)m) | \( A_{\text{obs}} \) (mm\(^2\)) | \( N_v \) (mm\(^{-3}\)) | Size (L, \( \mu \)m) | AR | UU% |
|---------|-------------|-------------|-----------------|-----------------|-------------------|-----------------|-----------------|-----|-----|
| 316L    |             |             |                 |                 |                   |                 |                 |     |     |
| 100     | 45          | 0.0218      | 26              | 1.1229          | 17,207            | 2.68–82.40      | 3.23–37.30      | ~98 |     |
| 200     | 77          | 0.0422      | 50              | 1.1229          | 15,210            | 2.19–210.72     | 0.03–62.39      | ~97 |     |
| 300     | 131         | 0.0608      | 72              | 1.1229          | 17,960            | 2.63–171.54     | 2.18–33.68      | ~98 |     |
| 500     | 172         | 0.0878      | 104             | 1.1229          | 16,330            | 2.19–210.72     | 0.04–62.39      | ~97 |     |
| 1000    | 365         | 0.1995      | 237             | 1.1229          | 15,251            | 2.06–154.43     | 1.93–76.42      | ~98 |     |

The largest size (length) of inclusions and the dissolved layer’s depth during the extraction were compared for all samples. However, it should be pointed out that extracted inclusions were parallel to the metal sample’s extracted surface. The results show that the elongated inclusions’ largest size increased with an increased depth of the dissolved metal layer. Almost all the samples have inclusion sizes far larger than the dissolved layer’s depth in each sample, except for the 1000C experiment. That is because, for the 1000C extraction, the depth of the dissolved layer was 237 \( \mu \)m. This number is far larger than the size of typical inclusions that exists in the current steel samples.

In this study, the size ranges of inclusions have been classified into four groups, which are: (i) less than 10 \( \mu \)m, (ii) 10–50 \( \mu \)m, (iii) 50–100 \( \mu \)m, and (iv) larger than 100 \( \mu \)m. Figure 4 shows \( N_v \) values for all samples in each size range. Most of the inclusions have a size that is smaller than 50 \( \mu \)m. In the group consisting of inclusions smaller than 10 \( \mu \)m, the number of sulfide inclusions tends to increase with an increased charge value. However, inclusions belonging to the 10–50 \( \mu \)m size group shows an opposite tendency with an increased charge value.

Table 14 shows that all samples have a relatively high frequency of UU inclusions (85–100% in different size ranges), which means that most inclusions have an actual size. The average length and the average AR values show similar tendencies. In addition, the small size inclusions have small aspect ratios and large inclusions show large aspect ratios. As seen in Table 14, when using electric charge values of 100 and 200 coulombs, no inclusions larger than 100 \( \mu \)m could be found. This can be explained by the depth of

**Table 14.** The number of inclusions per volume (\( N_v \)) values of sulfides in the 316L steel grade in the different size groups.

**Figure 4.** The number of inclusions per volume (\( N_v \)) values of sulfides in the 316L steel grade in the different size groups.
the layer being dissolved ($D_{\text{dis}} \leq 50 \ \mu m$) being quite small, which makes it hard to extract large size inclusions (>100 µm) at the surface of the metal sample which is parallel to the rolling direction. As shown in Table 14, the average sizes of inclusions that are smaller than 10 and 10–50 µm are 5–7 µm and 18–25 µm, respectively. For the 50–100 µm size group, the average size of inclusions varies in the range of 63 to 68 µm. For all samples, 96% of all inclusions are of an RS type. Furthermore, very few inclusions belong to the PS and OS inclusion types.

Table 14. The characteristics of elongated sulfides in the steel of 316L in different sized groups using Method 2.

| Sample | Size Range (µm) | $\bar{L}$ (µm) | $\bar{AR}$ | UU% | RS% | PS% | OS% |
|--------|----------------|----------------|-------------|-----|-----|-----|-----|
| 100C   | <10            | 6.63 ± 1.97    | 6.37 ± 2.10 | 100 |    |    |    |
|        | 10–50          | 24.93 ± 10.83  | 11.66 ± 4.82 | ~95 | ~98 | ~2  | -   |
|        | 50–100         | 67.57 ± 11.16  | 22.49 ± 10.27| 100 |    |    |    |
|        | >100           | -              | -            |    |    |    |    |
| 200C   | <10            | 7.06 ± 1.76    | 6.43 ± 2.18  | ~85 |    |    |    |
|        | 10–50          | 17.65 ± 8.32   | 10.18 ± 4.57 | 100 |    |    |    |
|        | 50–100         | 64.01 ± 8.82   | 20.53 ± 2.91 | 100 | ~96 | ~3  | ~1  |
|        | >100           | -              | -            |    |    |    |    |
| 300C   | <10            | 5.73 ± 2.01    | 4.88 ± 1.62  | 100 |    |    |    |
|        | 10–50          | 20.93 ± 9.47   | 10.40 ± 3.88 | ~97 |    |    |    |
|        | 50–100         | 62.84 ± 8.62   | 17.79 ± 9.26 | 100 | ~97 | ~2  | ~1  |
|        | >100           | 135.43 ± 25.53 | 24.86 ± 8.78 | 100 |    |    |    |
| 500C   | <10            | 5.33 ± 2.12    | 4.84 ± 2.09  | ~99 |    |    |    |
|        | 10–50          | 23.68 ± 11.96  | 13.13 ± 7.28 | ~90 |    |    |    |
|        | 50–100         | 67.79 ± 13.41  | 27.26 ± 11.47| ~95 | ~99 | ~1  | -   |
|        | >100           | 152.63 ± 31.51 | 46.92 ± 9.32 | 100 |    |    |    |
| 1000C  | <10            | 5.42 ± 1.94    | 4.53 ± 1.70  | ~99 |    |    |    |
|        | 10–50          | 22.49 ± 11.01  | 10.34 ± 5.68 | ~98 |    |    |    |
|        | 50–100         | 66.69 ± 13.60  | 17.92 ± 7.56 | 100 | ~97 | ~2  | ~1  |
|        | >100           | 143.06 ± 11.37 | 51.31 ± 25.11| 100 |    |    |    |

In summary, by investigating the characteristics of inclusions by using the electrolytic extraction method and by using different electric charges for the 316L steel samples without heat treatment, it is clear that most inclusions are elongated MnS inclusions. Specifically, 96–99% of the RS inclusions are unbroken particles. The depth of the dissolved layer has a limited effect on the characteristics of the elongated MnS inclusions. Additionally, the inclusions’ size range was not affected by the electric charge of the EE process. However, if the dissolved layer’s depth after the EE process is too small (<50 µm), it can be difficult to detect larger size (>100 µm) elongated inclusions. Thus, it can be concluded that the sample preparation and electrolytic extraction with the selected parameters of this study can have a very small or negligible effect on the number of broken MnS inclusions.

3.3. Effects of Heat Treatment on the Fraction of U/B and Morphology of Inclusions

The results above show that after additional heat treatment (at 900 °C for 5–30 min) of a 42CrMo4 sample, sulfide inclusions can be observed and measured after EE. However, there are also many elongated inclusions (up to 61–66%), which have either one or two broken edges. In order to study the influence of a short heat treatment process on the morphology and breakability (fragility) of elongated inclusions (MnS), the low carbon rolled steel of 3R65 ($\leq 0.03%$C, $\sim 0.015%S$), containing about 97% undamaged inclusions, was selected. The steel composition, classification of inclusions, and their characteristics in the 3R65 steel sample without heat treatment are presented in Table 1, Table 4, and Table 6, respectively.
In Table 15, four samples with different holding times at 900 °C have similar N_v values corresponding to approximately 6500 inclusions per cubic millimeter. In addition, large size inclusions (>100 µm) were found in all samples. The maximum length of the inclusions in the heat-treated samples is larger than in the samples that were not heat-treated. These results show that this short heat treatment at 900 °C has no noticeable effect on the largest size of the elongated inclusions.

Table 15. The characteristics of elongated sulfides in different steel samples of 3R65 after heat treatment using Method 2.

| Sample  | Temperature (°C) | Time (min) | W_{dis} (g) | D_{dis} (µm) | A_{obs} (mm²) | Num. (NMI) | Size (L, µm) | N_v (mm⁻³) |
|---------|-----------------|------------|-------------|-------------|--------------|-------------|--------------|-----------|
| 3R65/00 | 25              | 0          | 0.1079      | 74          | 2.2458       | 172         | 3.2–150.2    | 6643      |
| 3R65/05 | 900             | 5          | 0.1097      | 69          | 2.2458       | 170         | 3.7–273.3    | 6458      |
| 3R65/15 | 900             | 15         | 0.1070      | 66          | 2.2458       | 167         | 4.2–217.2    | 6504      |
| 3R65/30 | 900             | 30         | 0.1081      | 69          | 2.2458       | 169         | 5.0–197.5    | 6515      |

As shown in Table 16, all of the samples have a high percentage of UU particles (larger than 97%). It can also be seen that the largest sizes (length) of the inclusions all belong to the UU type. Additionally, the average size and average aspect ratio (AR) of UU rod-like sulfides in all samples did not change so much and did not show a relation between the morphology of sulfides and the heat treatment time. More specifically, the average length of UU sulfides varied from 28.0 to 32.6 µm and the average AR values ranged between 12.8 and 15.9. Thus, the obtained results indicate that the heat treatment under the given conditions (using a temperature of 900 °C for 5–30 min) has no effect on the fragility (tendency to break) and on splitting (fragmentation) of elongated inclusions during heat treatment.

Table 16. The classification of different types of NMIs in the sample of 3R65 using Method 2.

| Steel  | Type | UU | UB | BB |
|--------|------|----|----|----|
| 3R65/00 | Size (L, µm) | 29.8 ± 28.4 (3.2–150.2) | 19.7 ± 14.7 (5.6–48.3) | - |
|        | AR   | 12.8 ± 8.1 (3.5–49.2) | 9.7 ± 5.0 (3.8–17.5) | - |
|        | Frequency (%) | ~97 | ~3 | - |
| 3R65/05 | Size (L, µm) | 32.6 ± 23.9 (3.7–273.3) | 18.6 ± 9.6 (6.1–29.1) | - |
|        | AR   | 15.9 ± 10.8 (3.2–49.6) | 10.1 ± 6.5 (4.0–20.7) | - |
|        | Frequency (%) | ~97 | ~3 | - |
| 3R65/15 | Size (L, µm) | 28.0 ± 31.2 (4.2–217.2) | 14.9 ± 9.9 (3.5–65.6) | - |
|        | AR   | 13.6 ± 9.8 (3.9–49.1) | 8.1 ± 3.9 (3.4–13.6) | - |
|        | Frequency (%) | ~98 | ~2 | - |
| 3R65/30 | Size (L, µm) | 29.0 ± 21.6 (5.0–197.5) | 19.1 ± 10.8 (10.2–72.8) | - |
|        | AR   | 15.2 ± 8.9 (4.0–47.7) | 10.8 ± 11.7 (5.1–32.2) | - |
|        | Frequency (%) | ~98 | ~2 | - |

4. Conclusions

Elongated sulfide inclusions (MnS) in deformed 316L, 3R65, 42CrMo4, and 13HMF steels containing different carbon (0.02–0.42%) and sulfur (0.007–0.025%) contents were studied. The characteristics of inclusions were determined by using 3D investigations of NMIs after electrolytic extraction of steel specimens using SEM in combination with EDS.
For dissolution of carbides and evaluation of the effect on sulfide characteristics, a set of steel samples were preliminarily heat-treated for 5–30 min at 900 °C. According to the obtained results, the following main conclusions can be made:

1. The electrolytic extraction method can successfully be applied for stainless steels containing less than 0.1 mass% carbon and for tool steels containing 0.15 mass% C and 0.42 mass% carbon by using a 10% AA electrolytes.

2. For tool steels containing more than 0.15% C, carbides were extracted from the steel matrix during the EE process and they covered other inclusions. Therefore, an additional heat treatment is needed to investigate the inclusions after EE. The results show that a heat treatment at 900 °C for 5 min can successfully dissolve the carbides during phase transformation in steel samples so that the inclusions (MnS) can then be precisely investigated after EE.

3. The sulfide inclusions from the as-cast sample (42CrMo4) can be classified into three main groups—namely, (i) type I (regular), (ii) type II (irregular), and (iii) type III (rod-like), corresponding to 64, 16 and 20% of the total number of sulfide inclusions, respectively. Depending on the morphology of deformed MnS inclusions, the sulfides in the rolled steel samples were classified as rod-like (RS), plate-like (PS) and oxysulfides (OSs). The RS and PS inclusions’ compositions correspond to pure MnS and the OS inclusions are complex MnS-(Al,Si)O particles. It was found that the rolled 316L stainless steel (0.02% C and 0.007% S) contains about 97% of RS inclusions and only 2% of PS and 1% of OS inclusions. The 3R65 stainless steel (≤0.03% C and ≤0.015% S) contains about 46% of RS, 51% of PS and only 3% of OS inclusions. In the 13HMF (0.15% C and 0.012% S) and 42CrMo4 (0.42% C and 0.025% S) tool steels, most of observed deformed sulfides correspond to RS (~92% and 96%, respectively) and PS (~8 and 4%, respectively).

4. In the rolled and heat-treated steel, 42CrMo4, having 0.42% C, only ~34–39% of the inclusions correspond to undamaged (unbroken–unbroken—UU) inclusions. For the stainless steel having a lower content of C, the frequency of undamaged sulfides significantly increased by up to 88% in the 13HMF steel and up to 97% in the 3R65 and 316L stainless steels.

5. The sample preparation, EE process and the thickness of the metal layer dissolved during electrolytic extraction (~26–237 μm) have a negligible effect on the morphology and frequency of the undamaged (UU) sulfides observed in deformed low-carbon steels.

6. The preliminary heat treatment for 5–30 min at 900 °C did not practically affect the morphology and fragility of deformed sulfides in both groups of steels containing less than 0.1 mass% C and steels having carbon contents ranging between 0.15 and 0.42 mass%.

**Author Contributions:** Conceptualization, A.V.K.; formal analysis, S.G.; investigation, S.G.; writing—original draft preparation, S.G.; writing—review and editing, A.V.K., A.T. and P.G.J.; supervision, A.V.K., A.T. and P.G.J. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Informed Consent Statement:** Informed consent was obtained from all subjects involved in the study.

**Data Availability Statement:** Not applicable.

**Acknowledgments:** Shuo Guo would like to acknowledge the financial support from China Scholarship Council (CSC) and all other colleagues who participated in this study.

**Conflicts of Interest:** The authors declare no conflict of interest.
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