

Research Article

Application of Different Extraction Methods for Investigation of Nonmetallic Inclusions and Clusters in Steels and Alloys

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The characterization of nonmetallic inclusions is of importance for the production of clean steel in order to improve the mechanical properties. In this respect, a three-dimensional (3D) investigation is considered to be useful for an accurate evaluation of size, number, morphology of inclusions, and elementary distribution in each inclusion particle. In this study, the application of various extraction methods (chemical extraction/etching by acid or halogen-alcohol solutions, electrolysis, sputtering with glow discharge, and so on) for 3D estimation of nonmetallic Al_2O_3 inclusions and clusters in high-alloyed steels was examined and discussed using an Fe-10 mass% Ni alloy and an 18/8 stainless steel deoxidized with Al. Advantages and limitations of different extraction methods for 3D investigations of inclusions and clusters were discussed in comparison to conventional two-dimensional (2D) observations on a polished cross section of metal samples.

1. Introduction

The characterization of nonmetallic inclusions (NMI) is of importance for the improvement of mechanical properties of steel products as well as for the production of clean steel. Some characteristics such as number, size and composition of inclusions are particularly important for understanding of the formation and growth mechanism of inclusions [1]. Previous studies [2, 3] have shown that three-dimensional (3D) investigations are more reliable regarding number and size of inclusion particles compared to conventional two-dimensional (2D) investigations on a polished cross section of metal samples. Moreover, the effect of matrix on composition analysis of small size inclusions is much higher with 2D compared to 3D investigations [4]. In this respect, a 3D investigation is significant for an accurate estimation of inclusion characteristics in steel. The 3D methods which have been used extensively for these purposes are so-called extraction methods. These include electrolytic extraction [5–8] as well as chemical extraction using halogen-alcohols and acids [5–7].

However, it is known that some nonmetallic inclusions in metal samples are dissolved during the chemical extractions. Inoue et al. [5] evaluated the possibility of dissolution of Al_2O_3 particles in acids ($HCl-HNO_3-H_2O$ and $H_2SO_4-HNO_3-H_2O$), halogen-alcohols (bromine-methanol and iodine-methanol), and in a 10% AA electrolyte (10 v/v% acetylacetone-1 w/v% tetramethylammonium chloride-methanol). More specifically, the standard fine Al_2O_3 powders with a known size distribution (average sizes are 0.06 or 1 μm) were charged in the solutions mentioned above and kept during a certain time. Thereafter, the contents of the dissolved Al in the solutions were measured at different time intervals. It was found that around 20% of the Al_2O_3 powder was dissolved in the acid solution after a holding time of 5 hours. The dissolution ratios in bromine-methanol and iodine-methanol are much lower, that is, about 0.5% and 0.3% after 10 hours, respectively. Especially, the dissolution ratio of the finer Al_2O_3 powder (<0.1 μm) was higher in both acid and halogen-methanol solutions. The lowest dissolution ratio of Al_2O_3 (approximately 0.1% after 11 hours) was obtained for the 10% AA electrolyte. Moreover, other inclusions such

as CaO and MgO have been shown to dissolve easily by acids and halogen-alcohols [5–7]. Therefore, the electrolytic extraction method using nonaqueous electrolytes was recommended for the investigations of nonmetallic inclusion particles containing CaO and/or MgO as well as for the studies of small size inclusion particles.

The purpose of the present study is to compare some available extraction methods applied for 3D investigations of inclusions and clusters in steel samples obtained during the deoxidation process in laboratory experiments and pilot plant trials. In addition, another purpose is to evaluate the possibility of using a short halogen-alcohol extraction time for the 3D investigations of Al₂O₃ clusters in metal samples. The application of various extraction methods, their advantages, and some limitations are compared with those of 2D investigations.

2. Experimental

2.1. Etching and Extraction of Alumina Inclusion Particles and Clusters from a Stainless Steel. During a pilot plant trial, 350 kg of an 18/8 stainless steel (Fe-18 mass% Cr-8 mass% Ni) was melted at 1600 °C in an Al₂O₃ crucible using an induction furnace (600 Hz, 600 W) [9]. Argon was continuously added on a melt surface in order to prevent a possible reoxidation. Lollipop samples with dual thickness were taken from the melt at different holding times after an addition of 0.1 mass% Al. One of the sides of the thicker sample part (12 mm) was first ground and polished for 2D observation of clusters on the cross sections using a light optical microscope with low magnification (LOM) and a secondary electron microscope (SEM). By using LOM, cluster characteristics such as location and the average and maximum equivalent sizes were estimated. The equivalent size of nonspherical NMI (nonmetallic inclusions particles) and clusters was calculated as the average value of the measured maximum length and the perpendicular maximum width of clusters. Then, the polished sample surfaces were etched by using a 5–10 v/v% bromine-methanol mixture during 30–180 s for partial 3D investigations (3D*) of Al₂O₃ inclusion particles and clusters on the metal surface. Longer etching times (5–10 minutes) were used for extraction of Al₂O₃ inclusion particles and clusters for 3D investigations where the solution was filtered using polycarbonate (PC) film filter with an open pore size of 1 μm. The characteristics of inclusion particles and clusters such as size, number, morphology, and composition were evaluated using a SEM equipped with an EPMA (electron-probe microanalyzer).

2.2. Etching and Extraction of Alumina Inclusion Particles and Clusters from an Fe-10%Ni Alloy. An Fe-10 mass% Ni alloy (250–350 g) was melted at 1600 °C in a high purity Al₂O₃ crucible under Ar atmosphere using a laboratory high induction furnace (100 kHz, 20 kW) with graphite susceptor. Quartz tube samplers (diameter 10 mm) were used for sampling of the melt at different holding times after additions of varied amounts of Al (0.04, 0.08, 0.12, or 0.2 mass%). After sampling, the metal remaining in the Al₂O₃ crucible was cooled to

1400 °C (cooling rate ~0.65 °C/s) in the furnace, followed by rapid water quenching.

First, a horizontal disc with a 3 mm thickness was obtained from the height of about 15 mm of the ingot sample (total height 50 mm), and then specimens (20 × 10 × 3 mm) were prepared from the disc. They were polished for 2D observations in order to investigate inclusion characteristics such as composition and size distribution using SEM. The polished surface of the specimens was etched with a bromine-methanol mixture for 15 s for partial 3D observations (3D*). Then, the etched surfaces of these specimens were observed using a SEM for inclusion composition analysis. For 3D investigation of NMI and clusters, the same specimens obtained from the ingot and also quartz tube samples were dissolved by the potentiostatic electrolytic extraction method (current of 45–60 mA, a voltage of 150 mV, and a charge of 800 or 1200 coulombs) using a 10% AA electrolyte. The electrolyte after electrolytic extraction (EE), which contained undissolved nonmetallic inclusions, was filtered using a PC film with an open pore size of 0.05 μm. Thereafter, the characteristics of inclusion particles and clusters such as size, number, morphology, and composition were evaluated using SEM-EPMA.

The length (l), width (w), and height (h) of each metal specimen were measured before the dissolution experiments. In addition, the weight of each metal specimen was measured before and after extraction to enable the determination of the dissolution rate. An average dissolved depth, D_{dis} , of each metal sample was calculated by using the following equation:

$$D_{\text{dis}} = \frac{W_{\text{dis}}}{\rho_{\text{me}} \cdot A_{\text{sur}}}, \quad (1)$$

where W_{dis} and ρ_{me} are the weight and density (~0.0078 g/mm³ in this study) of dissolved metal, respectively. A_{sur} is the surface area of a metal specimen, which is exposed to the extraction solution.

3. Results and Discussion

It is predicted that the size range and maximum size of inclusions obtained by different extraction methods increase with an increased weight of dissolved metal sample. For the different extraction methods, the relations between inclusion size and weight of dissolved metal sample are schematically shown in Figure 1. It can be seen from this figure that the chemical extractions by using acid and halogen-alcohol solutions dissolve inclusions in comparison to the EE method. However, as was reported by Inoue et al. [5–7], small inclusions of chemically stable oxides (such as Al₂O₃) as well as inclusions containing unstable oxides (such as CaO and MgO) are dissolved during the chemical extractions. As a result, some clusters constructed by such type of oxide inclusions are considered to be broken by using these extraction methods. Thus, the application of chemical extraction methods could introduce errors when investigating the 3D characteristics of nonmetallic inclusion particles and clusters in steels. On the contrary, the EE method is a much softer dissolution method, which can

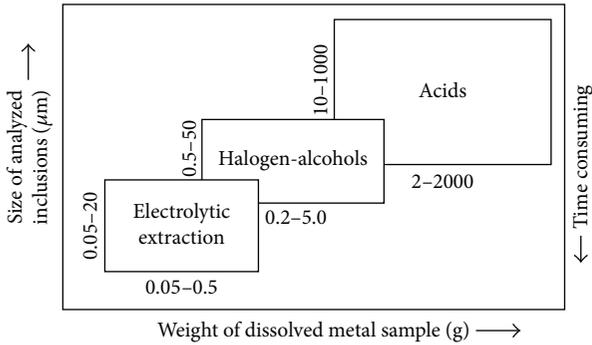


FIGURE 1: Application of different extraction methods for investigation of nonmetallic inclusions in metal sample.

be successfully used for extraction of various nonmetallic inclusions [5–7]. However, the EE method shows a relatively slow extraction and is usually used for the dissolution of small amounts of metal samples (0.05–0.5 g).

In this study, the main extraction parameters such as dissolution rate and dissolved depth of stainless steel and Fe-10 mass% Ni samples were determined for different extraction methods. Figure 2 presents dissolution rates of metal samples determined in this study for the halogen-alcohol solutions (such as 5 v/v% bromine-methanol and 14 w/v% iodine-methanol) and for the nonaqueous electrolytes such as 10% AA, 4% MS (4 v/v% methylsalicylate-1 w/v% tetramethylammonium chloride-methanol), or 2% TEA (2 v/v% triethanolamine-1 w/v% tetramethylammonium chloride-methanol). It is clear from this figure that the bromine-methanol solution has a much higher dissolution rate (0.006–0.015 g/min) compared to the other solutions. These results indicate that the bromine-methanol is a chemically stronger solution. However, it should be noted that the values of the dissolution rates obtained by using bromine-methanol and iodine-methanol are more scattered even though the values are obtained for the same stainless steel samples under the same conditions. Clearly, a more stable dissolution rate is preferred in order to give a more reliable prediction of the aimed dissolved weight of the sample. Therefore, in this case, the EE method, which shows much slower dissolution rates and a narrow range of dissolution rate (0.0004–0.001 g/min), can be recommended. The bromine-methanol solution is still recommended for short time dissolutions, for example, etching of the sample surface. It should be pointed out that the values of dissolution rate for the given stainless steel and Fe-10% Ni alloy samples did not show a drastic difference at the given conditions for each extraction method. Therefore, the results in this and the following figures are shown without a distinction between different steel grades.

Figure 3 shows a comparison of the average depth for a dissolved layer of metal specimens as a function of time for different extraction solutions. For dissolutions of certain thicknesses of the metal layer on a surface of metal specimens, the extractions of metal samples were performed by using both one-side (1-sd) and two-side (2-sd) dissolutions. The metal samples, in which only one side of the sample is

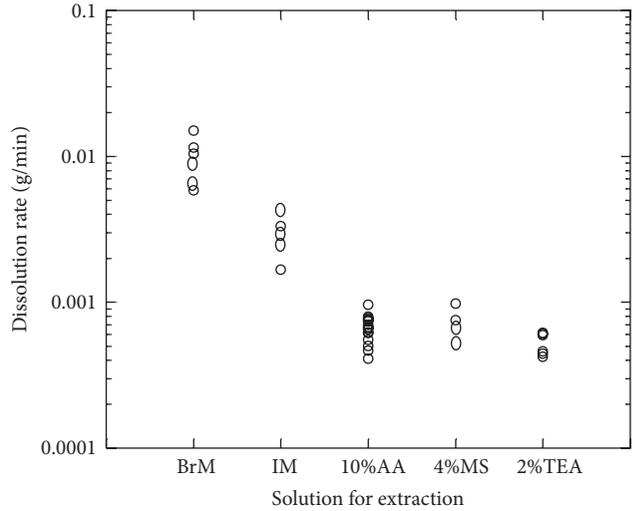


FIGURE 2: Dissolution rates of metal samples during the chemical (using 5 v/v% bromine-methanol and 14 w/v% iodine-methanol) and electrolytic (using 10% AA, 4% MS, and 2%TEA electrolytes) extractions.

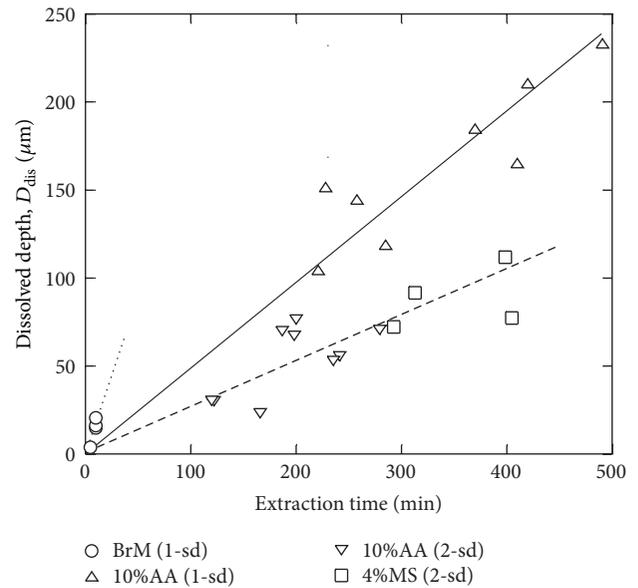


FIGURE 3: Dissolved depth of metal samples during one-side (1-sd) and two-side (2-sd) chemical and electrolytic extractions.

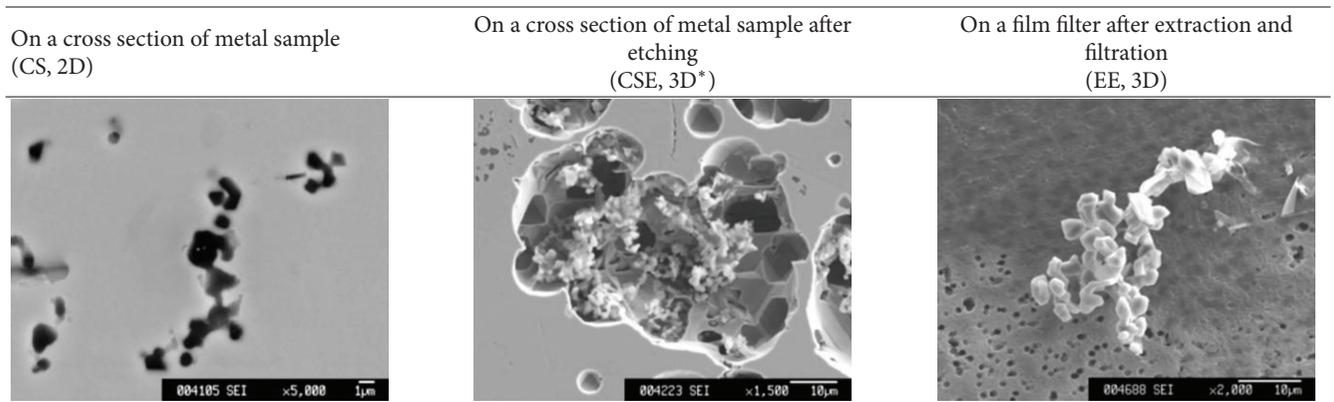
exposed to the extraction solution (1-sd extraction), are dissolved two times deeper on average, as follows from Figure 3. Thus, obtaining a certain depth can be achieved faster using the 1-sd extraction procedure compared to the 2-sd extraction procedure. It can be seen that the bromine-methanol solution has the highest dissolution rate, as also mentioned previously. On average, it takes about 5–10 times longer to dissolve a certain layer thickness by using the EE method with a 10% AA electrolyte compared to the extraction with bromine-methanol.

TABLE 1: Comparison of main parameters of different extraction methods for investigation of nonmetallic inclusions in metal sample.

Dissolution parameters	Reference	Extraction method					
		Acid	Halogen-alcohols		Electrolytic extraction		
			5% Bromine-methanol	14% Iodine-methanol	10% AA	4% MS	2% TEA
Dissolution ratio of Al_2O_3 (%)							
(i) Particles $< 0.1 \mu m$	[5]	4.0–6.7	0.4–0.5	0.10–0.13	0.006–0.007	—	—
(ii) Particles $\sim 1 \mu m$	[5]		0.021	0.016	< 0.003	—	—
Dissolution rate (g/min)	ps		0.006–0.015	0.002–0.006	0.0004–0.001	0.0004–0.001	0.0004–0.0007
Depth dissolution rate ($\mu m/min$)	ps		2.07–5.17	0.69–2.07	0.14–0.35	0.14–0.35	0.14–0.24

ps: present study.

TABLE 2: Typical SEM images of clusters obtained by different methods applied in this study for 2D and 3D investigations of nonmetallic inclusion particles and clusters in metal samples.



Figures 2 and 3 can be used for planning and controlling of future extraction experiments, in which the required depth of a metal specimen should be dissolved during a given time. Furthermore, the main parameters of different extraction methods for investigation of nonmetallic inclusions in metal samples are summarized in Table 1. Values of dissolution ratio of Al_2O_3 inclusions were determined based on previous results [5].

In this study, techniques of etching and extraction were applied for the 3D investigations of inclusion particles and clusters in both a stainless steel grade and an Fe-10 mass% Ni alloy deoxidized with Al. The characteristics of clusters and inclusion particles in clusters were investigated on a cross section of metal specimens after etching (3D*, CSE method) and on a surface of film filter after electrolytic or chemical extraction (EE method). Moreover, the 2D observations on a polished cross section of metal specimens (CS method) were carried out to enable a comparison of the results obtained from the CSE and EE methods. Typical SEM images of clusters in these methods are shown in Table 2. It was found that the time consumption for sample preparation before SEM investigation increased in the order from CS to EE method. However, the morphology, size, and number of inclusion particles and clusters can be determined more precisely by the 3D investigations. Although the sample preparation by the CSE method for 3D investigations is much

faster than that by the EE method, the estimations of the number and size of inclusion particles and clusters are not as precise as using the EE method. This might be explained by the reason that there is a possible risk of incomplete removal of inclusion particles and clusters from the metal surface during etching, because inclusions remain in holes on the metal surface. This phenomenon causes an error when the etched surface is studied. From another side, the size and number of inclusion particles and clusters, which are not completely extracted from the metal matrix, cannot be determined precisely. Therefore, this method is called a “partial 3D investigation” (3D*) in the present study. By using the CS method, only sections of clusters and inclusion particles can be investigated on a surface of metal sample. Hence, the extraction method (EE) followed by observations on a film filter is the preferred method for determination of the real size and number of inclusion particles and clusters in metal samples.

Figure 4 shows an example of estimated size distributions of inclusion particles in clusters in stainless steel samples taken from the melt at different holding times after Al deoxidation. The inclusion particles in the clusters were investigated by SEM after extraction with bromine-methanol and filtration, as described in Section 2.1. As can be seen, the Al_2O_3 inclusion particles in clusters grow during the holding time. The peaks of particle size distributions become wider

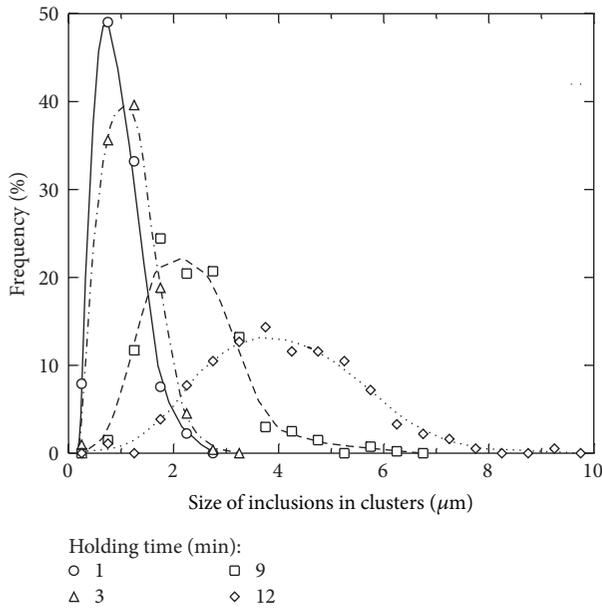


FIGURE 4: Particle size distributions of inclusions in clusters in stainless steel samples obtained from EE method.

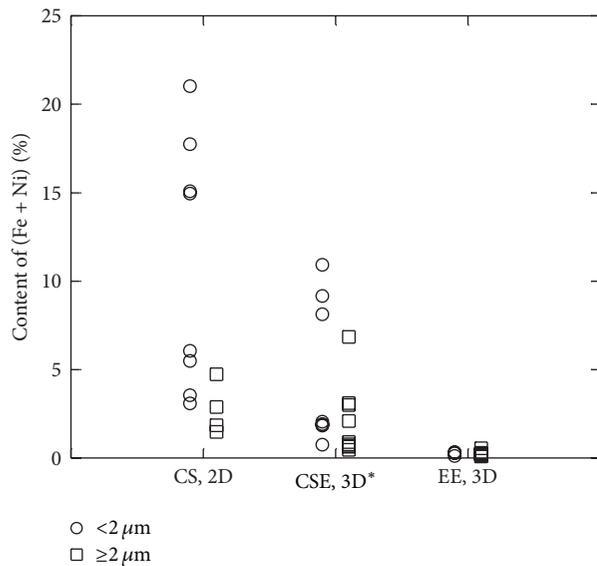


FIGURE 5: Effect of the metal matrix (Fe + Ni content) on analysis of alumina inclusions in an Fe-10 mass% Ni alloy for different evaluation methods.

and lower with the holding time. This experimental finding indicates that the variation of inclusion particle size increases during the process.

The composition of inclusions can also be more accurately determined by 3D investigations (CSE and EE methods) due to the decreasing or elimination of the effect of Fe-Ni metal matrix (in terms of Fe and Ni contents) on the results for composition determined by EPMA, as shown in Figure 5. This is of particular importance in analyzing small inclusions (<2 μm). Even though the etching method gives

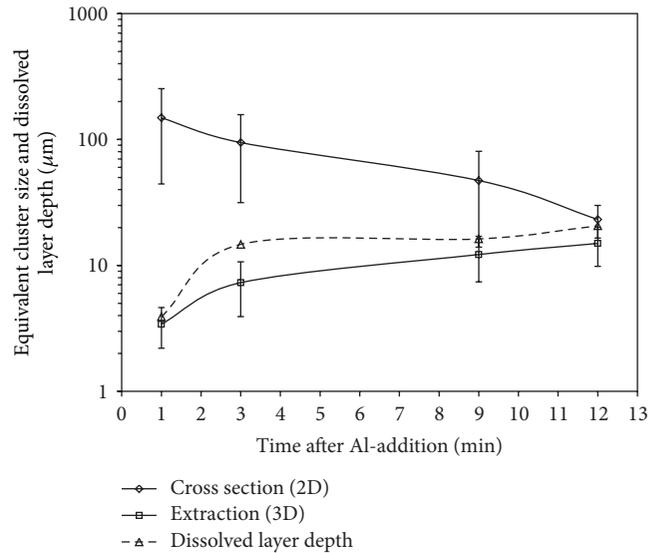


FIGURE 6: Equivalent cluster size obtained from the CS (2D) and EE (3D) methods and dissolved layer depth as a function of holding time.

higher matrix effect compared to extraction methods, it is still used because it is a faster technique for assessment of the characteristics of some inclusion particles and clusters (such as morphology, composition, location, and dispersion).

Figure 6 shows the equivalent cluster size estimated by the CS (2D) method and after bromine-methanol extraction (3D) in the same set of steel samples as a function of holding time after Al addition. Error bars represent the standard deviations of observed cluster sizes. It can be seen that the CS (2D) method shows a significantly larger cluster size compared to the EE method. This unexpected fact may be explained by the consideration of the depth of the dissolved metal layer during extraction, which is also presented in this figure. Since the depths of dissolved layers in most extractions in this study were smaller than 20 μm, it was not expected to obtain clusters larger than 20 μm with the EE and CS methods. Therefore, the size of the largest clusters in steel samples can be estimated on polished cross sections of metal samples (2D, CS method) and on metal surface after etching (3D*, CSE method). For 3D investigation of large clusters by using the EE method, the depth of dissolved layer should be increased to values comparable with the expected size of the largest clusters. In this case, the EE method can be recommended because the halogen-alcohol solutions cannot be used due to the significant increase of the extraction time and dissolution of inclusions.

Based on the results obtained in the present study, the main advantages and limits for applications of the CS, CSE, and EE methods for 2D and 3D investigations of nonmetallic inclusion particles and clusters in metal samples are qualitatively summarized in Table 3. It is concluded that the CS method can be applied for fast 2D estimations of the following characteristics: (i) location of inclusion particles and clusters in steel samples and (ii) estimation of the largest

TABLE 3: Application of three methods for 2D and 3D investigations of nonmetallic inclusion particles and clusters in metal sample.

Characteristics of inclusions and clusters	On a cross section of a metal sample (CS, 2D)	On a cross section of a metal sample after etching (CSE, 3D*)	On a surface of a film filter after extraction and filtration (EE, 3D)
Time for sample preparation before investigation	Short	Short/moderate	Long
Morphology	Possible	Good	Very good
Size			
(i) Inclusions	Possible (rough)	Possible/good	Very good (precise)
(ii) Clusters	Possible (rough)	Possible/good	Very good (precise)
Number	Possible (rough)	Possible (rough)	Very good (precise)
Composition			
(i) Inclusions	Possible/good	Good	Good
(ii) Effect of metal matrix	High effect	No/small effect	No effect
Location in metal specimen	Very good	Good	Impossible

*Partial 3D investigations.

cluster size. Moreover, the CSE method by using halogen-alcohol solutions for etching can be applied for fast partial 3D investigations (3D*) of the following characteristics: (i) location of inclusion particles and clusters in steel samples, (ii) estimation of the largest cluster size, and (iii) morphology, composition, and size of inclusion particles in cluster. Finally, the EE method can be successfully applied for the precise 3D investigations of the morphology, composition, size, and number of clusters and inclusion particles in clusters although it requires the most extensive sample preparation time compared to the CSE and CS methods.

4. Conclusions

The following three methods for inclusion characterization were evaluated: (i) conventional 2D observations on a polished cross section of metal specimens (CS method), (ii) partial 3D investigations on a cross section of metal specimen after light etching (CSE method), and (iii) 3D investigations on a surface of film filter after extraction and filtration (EE method). According to the results obtained in this study the following conclusions were summarized.

- (1) The CS method can be applied for fast 2D investigations of the location of inclusion particles and clusters in steel samples and for estimation of the largest cluster size.
- (2) The CSE method by using halogen-alcohol solutions for etching can be applied for fast partial 3D investigations of the location of inclusion particles and clusters in steel samples, the largest cluster size, and morphology, composition, and size of inclusion particles in cluster.
- (3) The EE method can be successfully applied for precise 3D investigations of the morphology, composition, size, and number of both clusters and inclusion particles in clusters.

- (4) The method using bromine-methanol solution has approximately a 10 times higher dissolution rate compared to the EE method. However, it has shown to be more unstable which in turn can make the estimation of the time to dissolve a certain layer depth more difficult.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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