Determination of Alloying Elements Ti, Nb, Mn, Ni, and Cr in Double-Stabilized Ferritic Stainless Steel Process Sample Using an Electrolytic Extraction Method and Separate Analysis of Inclusions

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Chromium, nickel, and manganese are common alloying elements in stainless steels. Additionally, titanium and niobium are added as microalloying elements to certain stainless steel grades. A double-stabilized stainless steel sample was dissolved in electrolyte using an electrolytic extraction method. Inclusions were separated from the electrolyte with vacuum filtration and put through a separate elemental analysis. Steel-soluble alloying elements were determined from the electrolyte after the extraction, and the elemental analysis of inclusions was performed. The results were compared to the ones obtained from the surface analysis commonly used in the steel industry. It was concluded that the alloying elements were distributed between inclusions and the steel matrix. Therefore, optical emission analysis from a solid steel sample can be misleading. The results might not accurately depict the composition of the steel matrix. Electrolytic extraction methods combined with elemental analysis provide accurate information about the real matrix composition of microalloying elements in steel. The method is also a tool for the simultaneous analysis of inclusions in 3D and soluble alloying elements.

I. INTRODUCTION

STAINLESS steel is in increasing demand. The trend is that there is also increasing demand for its quality and properties. New steel grades are being manufactured to achieve new quality standards. One of the main criteria for quality is steel cleanness which means that the steel should have a minimal amount of harmful inclusions that originate from different process stages and which may form during solidification. All steels contain inclusions as impurities. Zhang and Thomas reviewed several methods for the analysis of inclusions in steel.[1,2] These techniques face many challenges when it comes to simultaneous analysis of steel and inclusion compositions. So far, only optical emission spectrometry with pulse discrimination analysis (OES-PDA) has been tested for the simultaneous analysis of steel and oxide inclusions, but the results have not been consistent with other techniques.[3] Sometimes the surface analysis can be misleading, especially when large amounts of small inclusions are present. Another challenge is the analysis of microalloying elements due to their small quantities compared to the main components.

Only recent studies have combined inclusion studies with steel matrix chemical analysis. Depending on the composition and temperature of steel, alloying elements can occur either in the steel lattice or as a separate phase in the steel matrix. An electrolytic extraction method is used in 3D inclusion studies and also in the study of soluble and insoluble alloying elements from deoxidized ferrous materials and stainless steel.[4–8] The alkali fusion method has been used in the elemental analysis of inclusions.[5,9] The determination of alloying elements from the steel lattice and insoluble particles with acid digestion after sample dissolution using electrolytic extraction is fairly a new method of analysis for steel purity.[4] Precise information about steel's chemical composition is required when new, more intricate steels are manufactured. Steel composition studies are particularly interesting when rare and expensive alloying elements such as Nb and Hf are used. Detailed analysis of steel composition is also necessary for many industrial problems that are caused or aggravated by inclusions, such as clogging.[10]

Ti and Nb are used in stainless steel to stabilize the ferritic structure of steel as well as to remove nitrogen and oxygen. The influence of carbide-forming elements on the microstructure and mechanical properties as well as wear resistance of ferritic stainless steel has been studied.[11,12] Titanium and niobium precipitate in ferritic stainless steel as TiN, NbC, and Fe_2Nb.[13] Ti- and Nb-containing particles have been studied from Nb-modified SAE 8620 steel grades by dissolving the steel matrix with HCl electrolyte and studying the residue with a transmission electron microscope (TEM) and

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X-ray diffractometer (XRD)[14] and also for the precipitation behavior of Nb-Ti microalloyed HSLA steels.[15] The majority of ferritic stainless steel studies are executed on a laboratory scale, and information on real process samples is insufficient.

The purpose of this study was to analyze in which phase microalloying elements occur in industrial stainless steel process samples. Extracted inclusions were separated from the electrolyte by vacuum filtration. Waterless HCl electrolyte with tartaric acid was chosen for dissolution of the ferritic matrix.[16–18] A separate elemental analysis for inclusions was performed. The surface of a dissolved sample and inclusions on a polycarbonate (PC) filter were studied with a field emission scanning electron microscope (FESEM). The results were compared to the ones attained using a common surface analysis technique. Special attention is given to Ti and Nb as alloying elements. This relatively new method provides a great tool for analyzing steel cleanness and can be easily altered to be suitable for other steel grades and inclusions.

II. MATERIALS

A. Ti-Nb-Stabilized Stainless Steel Process Sample

The sample of this study was taken from Ti-Nb-stabilized stainless steel. The process sample was taken from a corner of a slab. The slab contains inclusions that were formed during solidification and are therefore important in this study. A suitable piece of the sample was cut from the slab sample for the electrolytic extraction and inclusion studies. Same sample was used in both studies. A composition analysis from the solid process sample was done with optical emission spectrometry using a spark excitation source (spark-OES). The chemical composition of the studied sample is presented in Table I. It is known that there is a difference in inclusion abundance and their composition in different parts of a slab. In this study, the corner was the most convenient part for further analysis.

B. Reagents

All reagents used in the electrolytic extraction were *pro analysis* purity grade provided by VWR: HCl (32 pct, EMSURE), tartaric acid, and methanol (EMPARTA ACS). The water used for diluting the standards and samples was Milli-Q produced. Primary standards were used in the calibration of spectrometers in the elemental analysis.

III. INSTRUMENTAL

The electrolytic extraction was controlled using a BioLogic SP-150 potentiostat. The dissolution of the inclusions in the HNO₃–HF media was performed in a SYSTEC autoclave in gently closed PTFE containers.

A. FESEM

An FESEM equipped with energy-dispersive X-ray spectroscopy (EDS) and a backscattered electron detector was used in the inclusion analyses. Separate studies were performed on the film filter after vacuum filtration of the electrolyte and on the surface of the steel sample after electrolytic extraction. Operating parameters are presented in Table II.

B. ICP-OES

A PerkinElmer Optima 5300 DV ICP-OES equipped with an AS-93plus autosampler was used in the determination of alloying elements from the filtrated electrolyte and for the dissolved inclusions after electrolytic extraction. Successful ICP-OES analysis is very dependent on the sample matrix. For this study, the iron content and the amount of methanol in samples and the calibration standards were matched. Methanol matching ensures similar nebulization of the samples and compensates for intensity changes. The samples were diluted properly to a working range. Blank samples were also prepared and measured for their analyte content. The operating parameters are presented in Table III.

Table II. Parameters for Determination of Chemical Composition of Inclusions on Film Filter with FESEM

Operating Parameters	
EHT	15 kV
Current	2.3 nA
Aperture	60.0 μm
Working distance	8.5 mm

Table III. Operating Conditions for the Determination of Soluble Alloying Elements Ti and Nb from Filtrated Electrolyte and Ti and Nb from Dissolved Inclusions

Operating parameters	
RF power	1300 W
Plasma gas flow	15 L min⁻¹
Auxiliary gas flow	1.0 L min⁻¹
Nebulizer gas flow	0.50 L min⁻¹
Sample flow	1.50 mL min⁻¹
Replicates	3
Emission lines (nm)	
Ti	334.94 (II)
Nb	269.703 (II)

Table I. Chemical Composition of the Ferritic Stainless Steel Process Sample

	Ni	Mn	Ti	Nb	Cr	Fe	S	C
Weight pct	0.17	0.38	0.15	0.42	18	80	0	0.03

Table IV. Operating Conditions for the Determination of Ni and Mn from Filtrated Electrolyte and Dissolved Inclusions

	Operating Parameters					
	Ni					Mn
Wavelength	232.0 nm					279.5 nm
Lamp	HCL					HCL
Energy	56					50
Current	20 mA					30 mA
Slit	0.2 nm					0.2 nm
Injected sample	20 μl					20 μl
Modifier	—					Pd-Mg
Injected modifier	—					10 μl
						(10 μg Pd; 1 μg Mg)

Heating Program	K (°C)	Ramp (s)	Hold (s)	K (°C)	Ramp (s)	Hold (s)
Step 1	343/383* (70/110*)	10	30	343/383* (70/110*)	10	30
Step 2	403 (130)	25	30	403 (130)	25	30
Step 3	1373 (1100)	10	20	1573 (1300)	10	20
Step 4	2573 (2300)	0	5	2173 (1900)	0	5
Step 5	2723 (2450)	1	3	2723 (2450)	1	3

*383 K (110 °C) was used in step 1 for the elemental analysis of dissolved inclusions. 343 K (70 °C) was used for methanol-containing samples.

Table V. Operating Conditions for Cr Measurements with FAAS

	Parameter
Wavelength	Cr 357.87 nm
Flame	C_2H_2 3.3 l/min
	Air 10.0 l/min
Slit (mm)	2.7/0.8
Lamp	HCL
Current (mA)	25

C. GF-AAS

A PerkinElmer AAnalyst600 atomic absorption spectrometer equipped with an AS-800 autosampler and THGA Graphite Tubes was used in the determination of nickel and manganese from filtrated electrolyte and dissolved inclusions after electrolytic extraction. Zeeman-effect background correction was used. Standards and matrix modifiers were prepared in methanol. The methanol content was taken into account when the heating program was modified for each element. The operating conditions are presented in Table IV.

D. FAAS

A Perkin Elmer AAnalyst 400 coupled with an S10 autosampler flame atomic absorption spectrometer was used in the determination of chromium. The amount of Cr is relatively large compared to other determined elements, and the dilution of samples was necessary. The operating conditions for the determination of Cr from filtrated electrolyte and dissolved inclusions are presented in Table V.

IV. EXPERIMENTAL

A. Cutting and Grinding of Steel Samples

Samples were cut into rectangle shapes with measurements of approximately $7 \times 7 \times 4$ mm. The samples were ground *in situ* with an SiC disk, and finishing polishes were done with a diamond disk. The steel sample was exposed to ultrasound in methanol, rinsed with methanol, and allowed to dry in a desiccator from a few hours to overnight. Next, the samples were weighed and stored in methanol before electrolytic extraction and further procedures.

B. Electrolytic Extraction and Filtration

Figure 1 presents the experimental design used in this study. The experimental design included steps that are divided into electrolytic extraction (1), filtration (2), sample preparation from filtrate (3), collection of inclusions or the analysis of inclusions with FESEM (4), dissolution of inclusions (5), sample preparation from dissolved inclusions (6), and elemental analysis of alloying elements from filtrate and inclusions (7). Detailed procedures for the inclusion dissolutions are described in Sections IV–B–1 and IV–B–2.

It should be noticed that glassware used for this type of analysis should be properly cleaned with acid baths and rinsed with Milli-Q water. Because the reaction itself is water free, all containers were rinsed at least once with methanol prior to any stages of this method.

The amount of electrolyte in the reaction was approximately 200 mL HCl electrolyte (10 V/V pct concentrated HCl and 1 w/V pct tartaric acid in methanol). Potentiostatic controlling is necessary for monitoring the sample for even dissolution and possible changes in the current. An applied voltage 0.150 V *vs* standard
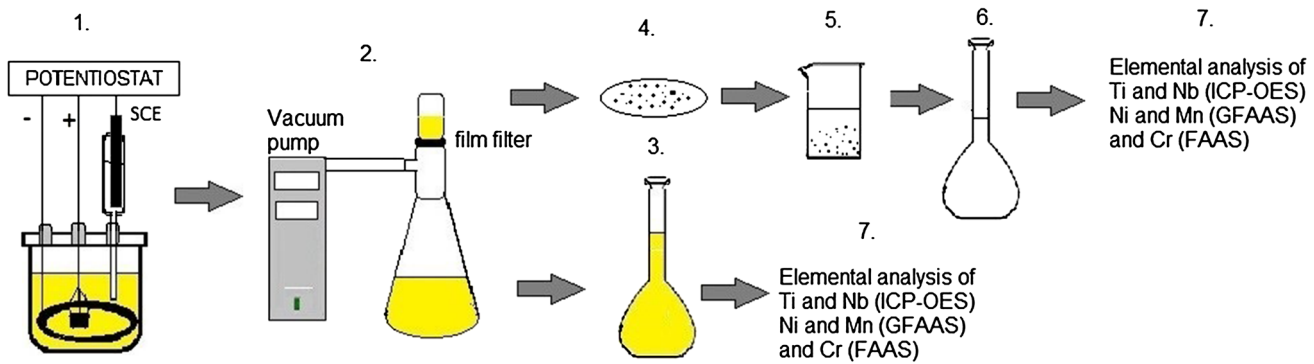
Fig. 1—Apparatus and procedure for electrolytic extraction of steel samples in 10 V/V pct HCl electrolyte and the experimental procedure that followed.

calomel electrode (SCE) was applied for this sample. The sample was weighed before and after the extraction. The correct amount of dissolved sample for this study is 1 to 1.5 g for the determination of soluble alloying elements and elemental analysis of inclusions. The maximum amount of 0.2 g was enough for closer examination of inclusions on the film filter and steel surface. If the steel sample contained sulfur, and manganese sulfides were expected to be present, then the use of another electrolyte than 10 pct HCl is advised.

After electrolytic extraction, the electrolyte was filtrated through a polycarbonate film filter with a pore size 0.05 μm assisted with a vacuum pump. The filtrated electrolyte was diluted to a fixed volume.

1. Dissolution of inclusions aqua regia

The filter with inclusions was transferred to a small container with 20 mL of methanol. The container was placed in an ultrasound bath until inclusions were separated from the filter. The filter was rinsed once with methanol before removing from the container.

The container with inclusions and methanol was put into an oven overnight until the methanol was completely evaporated. Then 5 mL of concentrated nitric acid and 15 mL of concentrated HCl were added. The container was put on a warm heating plate and mixed well with a glass stirrer. The acid mixture was diluted to a volume with water in a glass volumetric flask and stored in an LDPE bottle.

An elemental analysis of Ti, Nb, Mn, Ni, and Cr was performed with ICP-OES, GF-AAS, and FAAS. A blank sample was also prepared with the same experimental design without a sample. The blank sample was measured for the same elements as the steel sample.

2. HNO_3/HF dissolution of inclusions

A film filter with inclusions went through a dissolution in a PTFE vessel with 5 mL HNO_3 and 2 mL HF in an autoclave [393 K (120 °C), 30 minutes]. The vessel was gently closed with a PTFE cap before starting the heating program. After the heating program the residue was transferred into a plastic volumetric flask with ultrapure water and the film filter was rinsed properly before disposal.
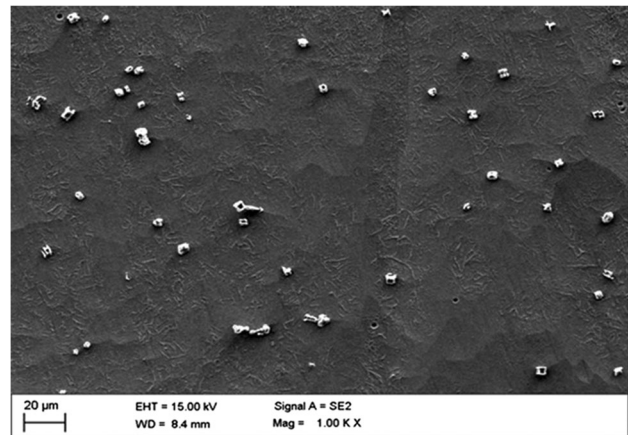

Fig. 2—Inclusions on the steel sample surface after electrolytic extraction. The extraction procedure should dissolve steel, so that the extracted alloying elements give accurate results.

An elemental analysis of Cr, Mn, Ni, Ti, and Nb was performed on the sample and a blank sample. The blank sample was prepared using a clean, weighed film filter that was put through the same autoclave program than the actual sample went through.

V. RESULTS

A. Inclusions on Steel Surface

The dissolved steel matrix revealed the Ti- and Nb-containing inclusions. Figure 2 presents the surface of the steel sample after extraction in HCl electrolyte.

B. Inclusions on Film Filter

Inclusions were studied from the film filter after the vacuum filtration using FESEM. A piece of the film filter was cut on a carbon tab and coated with a carbon layer.

A clear majority of the studied particles was Ti-Nb-containing cubic or acicular crystals with an equivalent circle diameter (ECD) of 1 to 3 μm. Titanium and niobium were the main elements in the studied inclu-

w-%
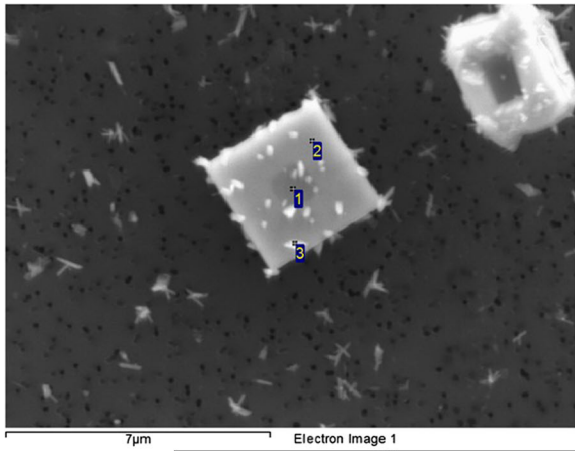
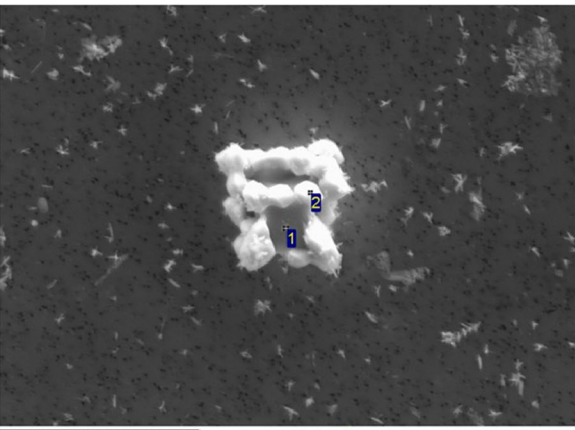| Spectrum	Ti	Cr	Fe	Nb
1	44	0,7	1	24
2	13	-	-	72
3	11	1,4	5,6	66

(a)

w-%
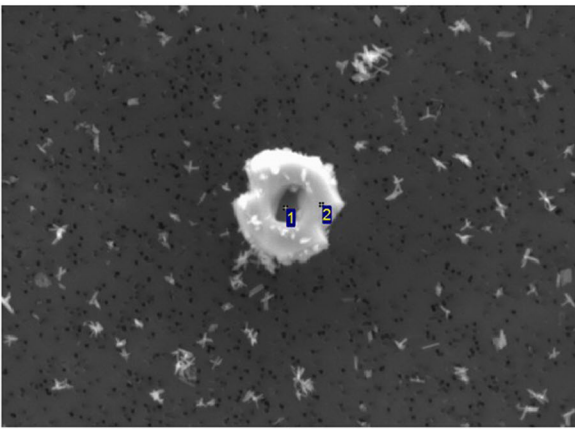
Spectrum	Ti	Cr	Fe	Nb
1	53	0,9	-	13
2	16	-	-	69

(b)

w-%

Spectrum	Ti	Cr	Fe	Nb
1	61	1,5	2,5	12
2	16	-	-	66

(c)

Fig. 3—(*a*) through (*c*): Titanium- and niobium-containing inclusions and their corresponding EDS analysis of main elements.

sions. Also niobium- and iron-containing inclusions were detected. Typical inclusions are presented in Figures 3(a) through (c) with the corresponding EDS analyses of the main elements. The signal due to carbon was subtracted from the analyses.

The nucleus of presented inclusions is most likely titanium oxide, surrounded with Ti- and Nb-rich nitrides.[19] An analysis of oxygen, nitrogen, or carbon using FESEM was not possible due to the carbon signal from the sample base and coating.

Thousands of titanium- and niobium-containing inclusions were analyzed for particle size and chemical composition. Approximately 50 pct of the observed particles were dismissed from chemical composition analysis due to their small size (<1 μm). Simultaneous particle size analysis of particles between 0.1 and 1 μm and over 1 μm is very time consuming, because they have to be determined with different microscope settings. In this study, the focus was on particles between 1 and 6 μm, because their elemental amount is more significant in solubility studies and also their EDS analysis is more reliable than for smaller particles. In addition to that, the inclusions smaller than 1 μm are not assumed to have a remarkable effect on steel physical properties. Figure 4 shows the particle size distribution of inclusions between 1 and 6 μm. The titanium content varied between 5 and 56 wt pct and niobium content between 6 and 67 wt pct. The size of the particles is presented by ECD. ECD depicts the diameter of a particle as a circle with the same observed area.

C. Elemental Analysis of Alloying Elements

Results from electrolytic extraction and both inclusion dissolution experiments are presented in Table VI. The dissolved mass was calculated according to formula [1]:

$$\frac{\text{wt pct}_{\text{alloying element}}}{100 \text{ pct}} * m_{\text{dissolved sample}} = m_{\text{alloying element}}. \quad [1]$$

Approximately 50 pct of total alloyed titanium and niobium was measured from the dissolved steel matrix. The total yield of manganese, nickel, and chromium was nearly 100 pct from the steel matrix. Nickel, manganese, and chromium are in a soluble form in a steel matrix, and therefore their amount in the inclusions is nonexistent. This was an expected result, because there were no Ni-, Mn-, or Cr-containing inclusions detected on the film filter after the electrolytic extraction. Alternatively, their amount compared to Ti- and Nb-containing inclusions was insignificant.

The niobium yield is poor even with HNO_3–HF treatment. Approximately 30 pct of the total Nb was not detected with these dissolution techniques. This could be due to the presence of carbides, which are poorly soluble in most acids. Preparation of samples with alkali fusion might be necessary to totally dissolve niobium. It is also possible that some of the Nb-containing inclusions are not dissolved evenly during the
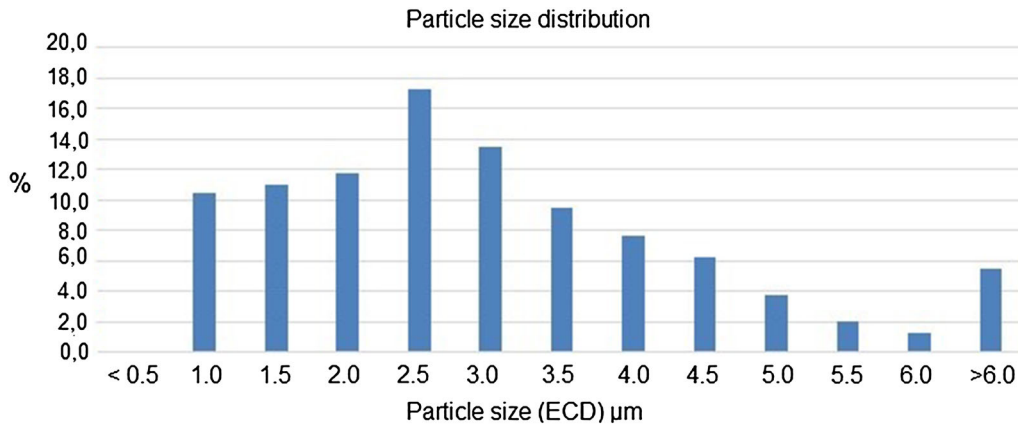
Fig. 4—Particle size distribution of Ti-Nb-containing inclusions between ECD 1 through 6 μm.

Table VI. Dissolved Mass of Alloying Elements (mg) and Measured Masses of Alloying Elements in Electrolyte and in Inclusions (mg)

Alloying Element	Soluble Alloying Element Mass (mg)	Alloying Elements in Inclusions Mass (mg)	Total Mass (Soluble + Inclusions) (mg)	Dissolved Mass (mg)
Electrolytic extraction + inclusion dissolution in *aqua regia*				
Ti	0.67	0.28	0.95	1.4
Nb	2.3	0.41	2.7	3.8
Mn	3.3	<0.01	3.3	3.4
Ni	1.4	<0.01	1.4	1.5
Cr	164	0.92	165	165
Electrolytic extraction + inclusion dissolution in HNO_3–HF				
Ti	0.69	0.66	1.4	1.5
Nb	2.1	1.0	3.1	4.1
Mn	3.2	<0.01	3.2	3.7
Ni	1.5	<0.01	1.5	1.6
Cr	188	0.07	188	177

extraction process. More studies are required in the determination of niobium.

VI. DISCUSSION

Separate dissolution of steel and inclusions followed by an elemental analysis of alloying elements gives reliable results of the steel composition. This experimental design is planned specially for those steel types that contain micro-inclusions. The method is suitable for estimating the success of the alloying practice used for steel grades. The yield of specific alloying element in the steel matrix is important to know if alterations in the manufacturing process are planned. Alterations could be, *e.g.*, testing new alloying materials, manufacturing new steel grades, or testing a new process stage. This type of study is also applicable as a tool for evaluating other methods that are used or under development in the determination of steel purity (*e.g.*, OES-PDA).

The major inconvenience of this method is that it is time consuming for the routine analysis of steel. The greatest benefit is the detailed analysis of the steel matrix and the inclusions. The advantages and disadvantages of OES and the presented method are listed in Table VII.

HNO_3–HF treatment may be sufficient when determination of alloying elements from oxide and nitride inclusions is performed. An alkali fusion technique might be necessary in the dissolution of inclusions when carbide-forming elements are determined.[5,9,20] Kinoshiro et al.[4] obtained good results in the determination of microalloying elements Ti, Nb, V, and Mo from reference materials. Depending on the reference materials, microalloying elements were present in the sample in soluble form or insoluble form. In their study, insoluble particles were dissolved with a strong acid mixture and heat.

The amount of alloying element from the steel lattice and the inclusions should be measured simultaneously to ensure the correctness of the result. Sakata et al.[9] reported errors in chemical analysis in which the amount of the insoluble alloying element was greater than the total amount of the alloying element. These types of errors in analysis can be avoided with the presented measurement method.

Table VII. Advantages and Disadvantages of Spark-OES and Electrolytic Extraction Method Combined with the Dissolution of Inclusions

	Spark-OES	Electrolytic Extraction + Inclusion Dissolution
Analysis speed	fast	slow
Suitable for routine analysis of steel	yes	no
Accuracy	good for the total amount of alloying element in steel	good for the amount of alloying element in the steel matrix and inclusions
Analysis of inclusions in the steel matrix	no	yes (after etching)
Separate analysis of inclusions	no	yes (on filter)
Elemental analysis of inclusions	no	yes

VII. CONCLUSIONS

An electrolytic extraction method connected to an elemental analysis is one way to perform steel analysis. The separate analysis of steel and inclusions offers accurate information about the steel matrix. The amount of the alloying elements in the steel lattice and in the inclusions can be determined. Therefore, when it comes to method accuracy and trueness of the results, elemental analysis of a dissolved sample is superior to solid sample analysis. The presented method can also be used in the determination of other alloying elements than the ones in this study, such as aluminum and molybdenum.

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