

Article

Application of Some Modern Analytical Techniques for Characterization of Non-Metallic Inclusions in a Fe-10mass%Ni Alloy Deoxidized by Ti/Zr and Ti/Mg

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Abstract: In this study, a complete and comprehensive analysis of non-metallic inclusions (NMI) in an Fe-10%Ni alloy was done by using two modern analytical methods that complement each other: Electrolytic Extraction (EE) of inclusions from metal samples followed by investigations by using Scanning Electron Microscopy (SEM) and Fractional Gas Analysis (FGA). The composition, morphology, size and number of different NMIs and clusters were investigated in metal samples taken after deoxidation by additions of Ti, Ti/Zr and Ti/Mg. The obtained results were discussed with respect to formation, modification and removal of NMIs and clusters depending on the type of deoxidations and the holding time. It was found that the peaks of oxygen reduced from different oxide inclusions obtained by the FGA measurements corresponded well to the main types of inclusions and clusters observed by using the EE + SEM method. More specifically, the total O content in oxide inclusions (O_{NMI}) increases by 10% after a Zr addition and then decreases linearly by 40% during 5 min of holding due to flotation of NMIs and clusters. However, after a Mg addition in the melt deoxidized by Ti, the O_{NMI} content decreases drastically by 63% during 5 min of holding, due to a fast flotation of NMIs caused by bubbles of vaporized Mg.

Keywords: Fe-10%Ni alloy; complex deoxidation; oxide non-metallic inclusions; electrolytic extraction; fractional gas analysis



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1. Introduction

Quantitative and qualitative determinations of non-metallic inclusions (NMI) in steel are vital for quality assessments of clean steels and alloys. This is due to the fact that the total quantity, size distribution, morphology and chemical composition of NMI can significantly affect and reduce the consumer properties of steel as well as the processability of the steel production process due to possible clogging of nozzles during casting of steels. It is especially important to understand the formation, modification, growth and removal of NMI and clusters in liquid steel during steel production, to be able to predict, control and manage the refining of liquid steel from NMI during secondary metallurgy processes and casting [1,2].

The properties of metals and alloys, their quality and performance, largely depend on the presence of some harmful impurity elements (such as hydrogen, nitrogen, oxygen and sulfur) and carbon. These elements form interstitial inclusions and have significant solubilities in liquid metal, exceeding their solubility in solid metal. Table 1 listed upper concentration limits of some impurity elements in steels and alloys and critical sizes and types of NMIs. To reduce the harmful effect of impurities, especially oxides, complex deoxidation of metals is often used. Thermodynamic calculations show that an equilibrium

concentration of oxygen can significantly be reduced by using a complex deoxidation and results of laboratory and industrial experiments that are well aligned with calculations [3–6]. For instance, studies of the complex deoxidation of steel with titanium and aluminum are still relevant in order to study the formation and modification of non-metallic inclusions and determine their effect on the castability and quality of steels [7–9].

Table 1. Upper concentration limits of some elements in steels and alloys as well as critical sizes and types of non-metallic inclusions (NMIs).

Steels and Alloys	Impurity Content, (ppm)	Type and Critical Size of NMI	Ref.
Interstation free steels	H < 2; N < 15; C < 10, O < 15	Deformable, <100 μm	[10]
Cord steels	H < 1.5; N < 40; O < 30; S < 50	Deformable oxides, <30 μm ; Non-deformable, <10 μm	[11]
Pipeline steels	H < 1.5; O < 10; S < 8; P < 50	Deformable, <100 μm ; manganese sulfides	[12]
Rail steels	H < 2.0; O < 20	Non-deformable, <20 μm	[13]
Bearing steels	H < 2; N < 20; O < 15	Non-deformable, <15 μm ; Nitrides, oxide clusters	[14]
High strength microalloyed steels	H < 1; N < 30; O < 12; S < 10	Non-deformable, <20 μm ; Nitrides, carbides	[15]
Pure Aluminum Alloys	H < 0.5; C < 5, N < 40; O < 10	-	[16]
Stainless steels	H < 5; N < 10; O < 20; S < 30	Non-deformable, <15 μm	[17]
Ti micro-alloyed steels	H < 30; C < 200, N < 80; O < 200	-	[18]

On the other hand, it is well known that oxide and nitride particles can significantly affect the pinning of austenitic grain growth during heat treatments and welding as well as the nucleation of intragranular ferrite (IGF) during the formation of a fine microstructure. The pinning effect of NMIs depends on the number and size of inclusions present in the steel. However, the nitrides can partially or completely be dissolved at high working temperatures or/and in the heat affected zone (1300–1400 °C) near the welding zone in steel. In this case, the role of small size oxide inclusions (such as TiO_x , MgO , ZrO_2 and other) for grain growth control can significantly increase. Moreover, in a previous study [19], it was reported that the two stage deoxidation process of the metal melt by an initial addition of Ti (0.025%) followed by the addition of Zr or Mg can significantly increase the number and decrease the size of precipitated particles compared to when adding only pure Zr or Mg. Furthermore, this Ti/M (M = Mg, Zr or Al) complex deoxidation process can considerably decrease the amount of clusters being formed. However, during the initial moment after an addition of a small amount of Ti, some TiO_x -FeO inclusions are precipitated in the melt. Then, the FeO and TiO_x oxides, which are part of the complex oxide inclusions, are partially or completely reduced by the added Zr and Mg. As the concentrations of FeO and TiO_x in the inclusions decrease, the particles that have a higher concentration of ZrO_2 and MgO can form clusters again. Therefore, it is important to control the formation and modification of the TiO_x -FeO-containing inclusions during all stages of the Ti/M complex deoxidation process.

A number of different methods exist for the determination of NMI in steels and alloys. The analytical methods, which are most commonly used by metallurgical enterprises and research centers, can be classified as follows:

- Automated methods of quantitative metallographic studies are used for determination of the number, size and type of non-metallic inclusions;
- Methods based on local X-ray spectral analysis using microprobes or methods using electrolytic extraction followed by subsequent chemical analysis, petrography, and

X-ray diffraction are used for the evaluation of the morphology and composition of inclusions;

- Gas analysis methods are used to determine the amount of gas-forming elements in steels, including C, O, H, N and S.

Table 2 shows a comparison of various methods used for the evaluation of non-metallic inclusions in steels with respect to the time, reliability as well as advantages and disadvantages of using the methods. It can be seen that each analytical method has a set of advantages and limitations. Therefore, to receive reliable and objective information about the steel cleanliness and inclusion characteristics, it is required that we use several methods that complement each other.

Table 2. Comparison of various methods for evaluation of non-metallic inclusions and clusters in metal samples.

Method	Subject of Analysis	Analysis Time	Analyzed Parameters. Advantages	Disadvantages and Limitations	Ref.
Microchemical	Precipitate	~1 day	Chemical composition	Labor intensity, complexity and low accuracy	[20]
Electrochemical or electrolytic extraction	Steel sample 0.1–30 g	3 h–3 days	Analysis of morphology, composition, size and number of NMIs.	Labor intensity, complexity	[21]
Metallographic	Thin section, 10 cm ²	~0.5 h	Analysis of morphology, size and number of NMIs. Rapidity	Influence of the capabilities of the microscope, the quality of thin sections, labor intensity and subjectivity of the assessment	[22,23]
Automatic image analyzers	Thin section, 10–200 mm ²	~2–3 h	Rapidity, representative data	Influence of the capabilities of the microscope, the quality of thin sections, and influence of settings and analyzer type	
Local petrographic	Thin section	~0.5 h	Structure and phase composition	Little informative when analyzing NMI	[24]
X-ray microanalysis	Thin section	~2–3 h	Analysis of composition and morphology of inclusions. Locality.	Influence of thin section quality, subjectivity of results	[25]
PDA/OES spectrometry	Thin section, 60 mm ²	~2–3 min	Analysis of Al, Ca in inclusions. Short analysis time.	Low precision, semi-quantitative results	[26]
Gas analysis (C, O, H, N, S)	Steel sample 1–3 g	~1–2 min	High accuracy, short analysis time.	Integral characteristics only	[27]

However, conventional two-dimensional (2D) analytical methods and the online PDA/OES method, which are used for analysis of NMIs on a surface of metal samples, cannot be used for precise determinations of the FeO content in complex oxide inclusions due to the high content of Fe in the steel matrix. Therefore, in this study, the analytical methods such as an electrolytic extraction of NMIs from the steel matrix and Fractional Gas Analysis were studied. Specifically, they were applied for the evaluation of complex TiO_x-FeO-containing inclusions and their modifications after additions of Zr or Mg.

The method of electrolytic extraction (EE) of non-metallic inclusions from steel samples with a following determination of the NMI using scanning electron microscopy (SEM) has successfully been used during the last 20 years to evaluate the morphology, size distribution and chemical composition of NMI in different steels and alloys [28–32]. A distinctive feature and advantage of this method is that it is a true three dimensional (3D) method of investigating NMI as 3D objects after their extraction from metal samples. This method makes it possible to extract NMI without changing their shapes and compositions. By using the EE method, researchers can analyze how inclusions are modified, change shape and determine the chemical composition during different stages of the steel production. However, this method is not useful to determine the mass fraction of NMI with a high accuracy in steel and alloys, due to the limited volume of the analyzed metal. Only a thin outer layer of the metal sample (~10–250 µm) is usually dissolved in the electrolyte. As a result, only few inclusions can be investigated. Moreover, the compositions of complex and heterogeneous inclusions in metal samples can be significantly varied, which leads

to additional errors by determination of mass fraction of different NMI based on results obtained by using only the EE method.

Fractional Gas Analysis (FGA) is a modified gas analysis method which allows for a determination of the mass fraction of different oxide inclusions in steel samples. During the reducing melting of steel specimens in a graphite crucible at controlled monotonic heating conditions (fractional gas analysis), the rate of CO gas formation in the melt can be measured. This, in turn, is directly related to the phase composition of the reduced oxide inclusions and the process temperature. The method is based on the fact that different oxides have different thermodynamic stabilities at high temperatures [33–36]. A significant advantage of this method is that it is possible to quickly determine the average phase composition and the amount of oxygen in the main groups of oxide inclusions. However, FGA analyses have their own limitations such as the inability to determine the size and shape of inclusions, the precise chemical composition of each inclusion, and the possibility of obtaining only the integral characteristics of NMI.

Based on possibilities and limitations of different methods, it was decided to select and evaluate the EE and FGA methods, which could provide the most complete information with respect to the characteristics of non-metallic inclusions in steel and alloys [37]. The aim of this study was to investigate a modification of NMIs and clusters in an Fe-10%Ni alloy after a complex deoxidation by Ti/Zr and Ti/Mg by using a combination of EE and FGA methods. The results obtained by these two different methods were compared and discussed with the aim to study the processes of formation, modification and removal of non-metallic inclusions in the melt depending on the added deoxidizers as well as holding time after their addition into the melt.

2. Materials and Methods

2.1. Sample Preparation

In this study, 70 g of a Fe-10%Ni alloy were melted in a high purity MgO crucible under an Ar atmosphere in a laboratory high-frequency induction furnace. A schematic illustration of experimental setup and the main operations during experiments are shown in Figure 1. After melting of Fe-10%Ni alloy, the melt was kept for 15 min at 1600 °C for homogenization of the composition and temperature. Thereafter, it was deoxidized by the addition of 0.03% Ti (of Fe-50%Ti alloy) following with mechanical stirring for 20 s for the homogenization of the melt composition. The stirring was done by hand using a pure MgO tube without opening the furnace. In the first reference experiment, referred to as Ti-1, the melt was deoxidized by using only a Ti addition. After a 1 min holding time in the furnace, the crucible containing the melt was rapidly withdrawn from the furnace and quenched in water (sample S1). In the other experiments, Ti was added and the melt was held for 1 min before 0.08%Zr (of Fe-10%Zr alloy) or 0.1%Mg (of Ni-12%Mg alloy) was added to the melt. After stirring for 20 s and holding the melt for 1, 3 or 5 min, the melt was rapidly withdrawn from the furnace and quenched in water (samples 2, 3 and 4). These experiments with the corresponding holding times are referred to as follows: Ti/Zr-1, Ti/Zr-3 and Ti/Zr-5 for the Ti/Zr addition experiments and Ti/Mg-1, Ti/Mg-3 and Ti/Mg-5 for the Ti/Mg addition experiments. A central vertical slice was cut from each experimental ingot and two identical samples were prepared for evaluation of NMI by using the EE and FGA methods.

2.2. Investigation of Non-Metallic Inclusions and Clusters by Different Methods

2.2.1. Electrolytic Extraction Method (EE + SEM)

For 3D investigations of non-metallic inclusions in different deoxidation experiments, metal samples were extracted at KTH Royal Institute of Technology (Stockholm, Sweden) by using a 10%AA electrolyte (10 v/v% acetylacetone—1 w/v% tetramethylammonium chloride—methanol) for the Ti and Ti/Zr experiments and a 2%TEA electrolyte (2 v/v% triethanolamine—1 w/v% tetramethylammonium chloride—methanol) for the Ti/Mg experiments. According to results reported by Inoue et al. [38,39], the selected electrolytes did

not dissolve Ti, Ti/Zr and Ti/Mg oxide non-metallic inclusions. During the EE process, the metal matrix of steel samples has been dissolved by using the following electric parameters: a current of 50–70 mA, a voltage of 3.0–3.6 V, and an electric charge of 500 coulombs. The weight of the dissolved metal (W_{dis}) for extracted samples varied from 0.13 to 0.15 g. The depths of dissolved metal layer of steel samples were about 0.19–0.26 mm.

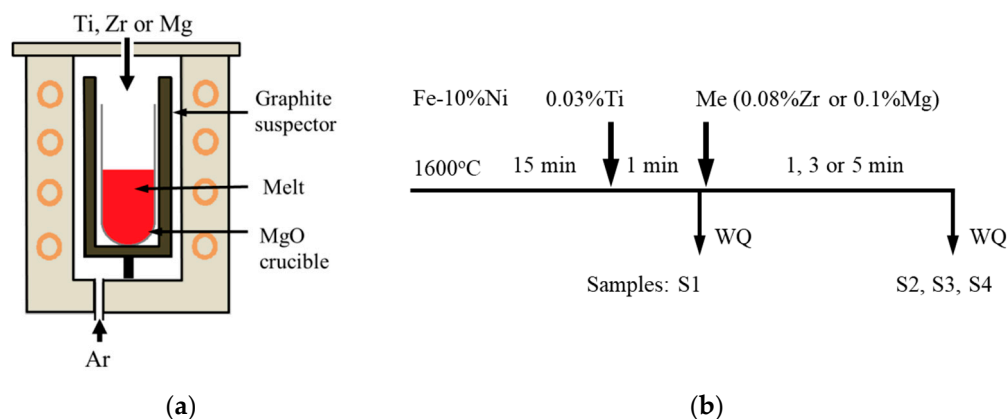


Figure 1. Schematic illustration of experimental setup (a) and main operations during experiments (b).

After electrolytic extraction and filtration, the undissolved NMIs were collected on polycarbonate membrane film filters with an open pore size of 0.4 μm . Thereafter, the morphology, size distribution and chemical composition of non-metallic inclusions were investigated on a surface of film filters by using a scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS). Typical NMIs and clusters observed on film filters after electrolytic extraction are shown in Figure 2.

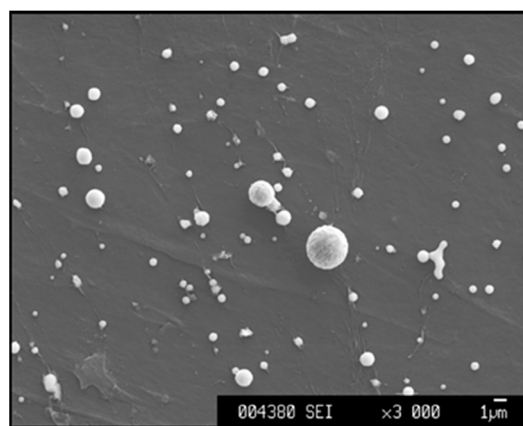


Figure 2. SEM images of inclusions and clusters observed on film filter after electrolytic extraction.

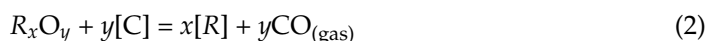
The diameter of spherical inclusions as well as the maximum length (l) and width (w) of non-spherical inclusions and clusters were measured on SEM images. The aspect ratio (AR) of inclusions and clusters was calculated as a ratio between their length and width ($AR = l/w$). Furthermore, the total number of clusters per unit volume (N_V) of metal sample was calculated by using the following equation:

$$N_V = (n \cdot A_f / A_{obs}) \cdot (\rho_m / W_{dis}) \quad (1)$$

where n is the number of observed clusters on SEM images, A_f is the total area of the film filter containing the collected inclusions and clusters ($\sim 1200 \text{ mm}^2$), A_{obs} is the observed area of SEM images on film filter which were used for investigation of NMIs, ρ_m is the metal density ($\sim 0.0078 \text{ g/mm}^3$), and W_{dis} is the total weight of dissolved metal sample after electrolytic extraction (g).

2.2.2. Fractional Gas Analysis (FGA)

Mass fractions of different oxide types in the experimental metal samples were determined at IMET RAS (Moscow, Russia) by using original fractional gas analysis (FGA) on modified gas analyzer LECO TC-600. In total, 3–5 specimens from each experimental ingot were prepared and analyzed. The weights of each specimen for the FGA measurement varied from 1.0 to 1.5 g. Each FGA measurement was carried out under the same conditions: (i) a sample preparation mode (which includes sample preheating during 1 min at temperature 1100 °C), (ii) a basic analyses temperature range from 1100 °C to 2300 °C with a heating speed of 2 °C/s, and (iii) an approximate helium flow 300 mL/min. During the FGA measurement, each specimen was melted and heated in a double graphite crucible (with a replaceable inner crucible). These double graphite crucibles were calibrated preliminary by using the same heating process without metal samples. After the melting of the metal specimen, various oxides in the melt have been reduced by graphite from the crucible due to the chemical reaction according to the following Equation:



Each oxide (such as FeO, TiO_x , ZrO_2 and MgO or their complex oxides) has its own start and end reduction temperature. According to the results of the FGA determinations, the mass fraction of oxygen in different oxides having certain chemical compositions is determined through the area of the peak on the CO_2 evolution curve (Evalogram), which corresponds to the reduction of the given type of oxide inclusions in a certain temperature interval:

$$O_{oxide} = \frac{F}{W} \int_{t_s}^{t_e} I_{CO_2}(t) dt \quad (3)$$

where F is the calibration factor, W is the metal specimen weight, $I_{CO_2}(t)$ is the rate of CO_2 entry into the gas analyzer cell (expressed in the own analyzer units) and t_s and t_e are the time of the starting and the end of the gas release peak, respectively.

By the peak of gas evolution, it is possible to determine the volume fraction of CO_2 (which is formed during the afterburning of CO during the FGA measurement according to reaction (2)). Then, by using the original software OxSep (oxides separation), it is possible to recalculate the evolution curve and mass fraction of oxygen in each type of reduced oxides. The average value for characterization of NMI in each reference and experimental ingot was obtained based on 3–5 measurements per specimen. The time of one FGA measurement was about 10 min. The total time for one analysis including preliminary preparation of metal specimen was 12–15 min.

3. Results and Discussion

3.1. Evaluation of NMIs in Ti and Ti/Zr Experiments

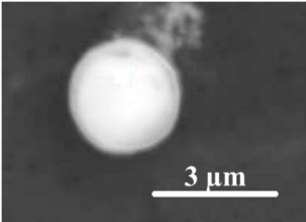
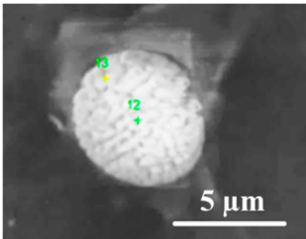
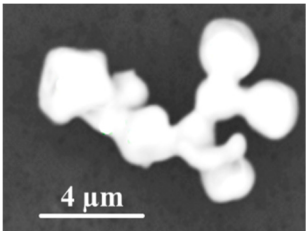
According to results obtained from 3D investigations of NMIs on surface of film filters after electrolytic extraction, the observed inclusions were classified based on their morphologies and compositions. SEM images and main parameters of typical NMIs and clusters are given for the Ti/Zr experiments in Table 3.

It can be seen that the following three types of typical inclusions and clusters were observed in the samples from the Ti/Zr experiments: (i) Type I inclusions which are relative small spherical inclusions (0.5–5.2 μm) having very high FeO contents (~49–100%), (ii) inclusions of Type II which are mostly larger spherical inclusions (2.5–13.5 μm) with high contents of FeO (~18–94%) and rough surface layers containing ZrO_2 (up to 78%) and TiO_x (up to 33%) and (iii) Type III clusters which have larger sizes (up to 26 μm) and consist of irregular or spherical shape inclusions containing 64–100% of ZrO_2 and small contents of TiO_x and FeO.

Most (~80–95%) of the NMIs observed on the film filters in the Ti/Zr experiments were spherical inclusions of Type I, which were liquid in the melt at 1600 °C. Only 2–6% of

the total numbers of inclusions in the metal samples from the Ti/Zr-1, Ti/Zr-3 and Ti/Zr-5 experiments were classified as clusters (Type III). A small amount of Al_2O_3 , which was observed in some inclusions, can be caused by the presence of this oxide or Al in raw materials (Fe, Ni, Fe-50%Ti and Fe-10%Zr alloys) and in the MgO crucible material.

Table 3. Classification of different NMIs observed in Ti/Zr experiments after EE.

Type of NMI	SEM Image of NMI	Composition (Mass%)	Size Range (μm)	AR
Type I		49–100% FeO, 0–39% ZrO_2 , 0–36% TiO_x , 0–11% Al_2O_3	0.5–5.2	1–1.2
Type II		18–94% FeO, 0–78% ZrO_2 , 4–33% TiO_x , 0–7% Al_2O_3	2.5–13.5	1–2.7
Type III		0–24% FeO, 64–100% ZrO_2 , 0–36% TiO_x , 0–1% Al_2O_3	2.8–26.1	1.1–3.8

One of the goals of the experiment was to determine how fast the initial oxide inclusions in the melt can be modified after Zr additions carried out in stages by using a complex Ti/Zr deoxidation. For that purpose, the experiments were conducted with holding times of 1, 3 and 5 min after a Zr addition. Furthermore, triple FeO– TiO_2 – ZrO_2 diagrams were constructed to show how compositions of different types of inclusions were changed depending on the holding time, as shown in Figure 3.

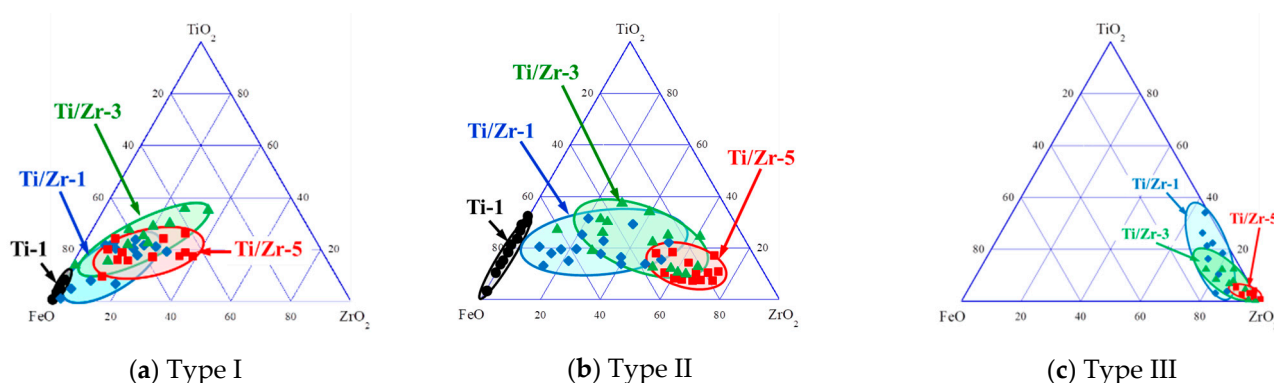


Figure 3. Changes of compositions of inclusions (Types I and II) and clusters (Type III) depending on holding time in the Ti/Zr experiments.

It can be seen that the contents of FeO in inclusions of Types I and II decreased significantly with an increased holding time. More specifically, the FeO content decreased from 85–100% (Ti-1) to 41–77% (Ti/Zr-5) in Type I inclusions and from 65–97% (Ti-1) to 13–32% (Ti/Zr-5) in Type II inclusions. However, the content of ZrO₂ in all oxide inclusions increased with an increased holding time (up to 64–100% in Type III inclusions in sample Ti/Zr-5). This can be explained by the reduction of FeO and TiO_x oxides by the added Zr. The solid inclusions with high concentrations of ZrO₂ can be agglomerated into clusters, as shown in Table 3. As a result, the frequency of harmful clusters in metal samples increased from 2% in the Ti/Zr-1 sample up to 6% in the Ti/Zr-5 sample. However, the total number of these clusters per unit volume of metal sample (N_V) was drastically reduced from $25.6 \times 10^5 \text{ mm}^{-3}$ (Ti/Zr-1) up to $0.9 \times 10^5 \text{ mm}^{-3}$ (Ti/Zr-5).

Detailed information about morphology, chemical composition, size distribution or different types of NMIs was obtained by 3D investigations of inclusions and clusters after electrolytic extraction. However, this EE + SEM method has a significant limitation to obtain accurate and fast determination of total contents (mass fraction) of different oxide phases in metal samples. This accuracy limitation is caused by the fact that only 0.13–0.15 g of a metal sample was dissolved during the electrolytic extraction. A second reason is that wide ranges of contents of main oxide components were observed in each type of inclusion and cluster. In addition, as was reported in some previous studies [40–42], the distribution of NMIs and clusters in metal samples taken from liquid steel cannot be homogeneous. As a result, an investigation of inclusions in only small volumes of metal samples cannot provide accurate results.

Therefore, a fractional gas analysis (FGA) was also used to determine the mass fraction of each type of oxide. This method provides a much faster analysis of larger volumes of metal samples compared to the EE + SEM method. As mentioned above, the FGA method is based on the fact that each oxide has its own temperature of reduction by carbon, which can be determined at the peak of the gas evolution during the test. Typical time charts for relative concentrations of reduced oxygen from oxide inclusions in metal specimens from the Ti and Ti/Zr experiments obtained by FGA analysis are shown in Figure 4. Data are presented as a function of the process temperature and holding time after a Zr addition. It can be seen that the peaks of oxygen reduced from different oxide inclusions and clusters shifted to the right side of diagrams (zone of higher reduction temperatures) with an increased holding time. This is due to the reduction of FeO and TiO_x oxides by Zr and due to an increase of the ZrO₂ concentrations in the inclusions, which have significantly higher reduction temperatures compared to FeO and TiO_x.

Based on a superimposition analysis of pictures of gas evolution curves obtained by FGA measurements of 3–5 metal specimens for each experiment, three groups of oxides were determined. It should be pointed out that some time charts of the reduced oxygen obtained by FGA measurements can have more than three peaks, as can be seen in Figure 4c,d. It means that some oxide phases have transitional complex compositions, which can be reduced at the respective temperature during the FGA measurement. However, to enable a comparison of results obtained from the EE + SEM method and from the FGA method, classification temperature intervals were selected corresponding to the liquid, semi-liquid and solid states of inclusions at 1600 °C. These correspond well to the classification of NMIs depending on morphology (Table 3) after electrolytic extraction of metal samples. The classification of the main oxide inclusions found in the Ti/Zr experiments depending on the temperature ranges corresponding to the maximum peaks of gas evolution (T_m) is given in Table 4. It should be pointed out that some types of complex oxides (such as TiO_x-ZrO₂ and ZrO₂-TiO_x in Groups 2 and 3) were placed in different groups, depending on the proportion of oxide components in these complex inclusions and locations of the corresponding peaks on FGA time charts. On the another hand, the Group 3 oxides can contain clusters (Type III, Table 3) as well as separate oxide inclusions with high concentrations of ZrO₂ (Type II and III), which did not agglomerate into clusters.

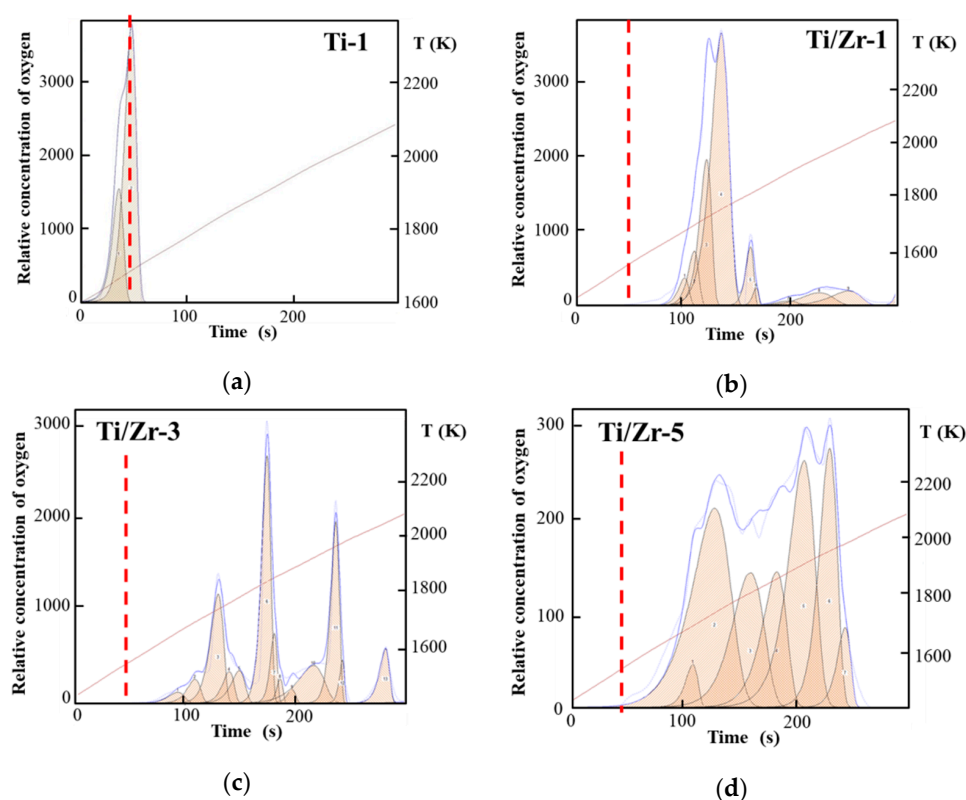


Figure 4. Typical time charts obtained by fractional gas analysis (FGA) measurements of oxide inclusions in metal specimens from the Ti and Ti/Zr experiments: (a) Ti-1, (b) Ti/Zr-1, (c) Ti/Zr-3 and (d) Ti/Zr-5.

Table 4. Classification of main oxide inclusions in the Ti/Zr experiments by using FGA measurements.

Group	T _m (K)	T _m (°C)	Oxides
1	1670–1800	1397–1527	FeO, FeO-TiO _x , FeO-TiO _x -ZrO ₂
2	1800–1930	1527–1657	TiO _x , TiO _x -ZrO ₂
3	1930–2150	1657–1877	ZrO ₂ -TiO _x , ZrO ₂

Based on this classification, it was found that the composition ranges of oxide inclusions obtained from the FGA method in the three main groups correspond well to the compositions obtained using 3D investigations of NMIs after electrolytic extraction, as is given in Table 3. Moreover, the frequencies of the main types of oxide inclusions in the Ti and Ti/Zr experimental samples obtained by the EE + SEM and FGA methods showed similar tendencies with an increased holding time. Figure 5 shows the average frequencies and contents of oxygen reduced from different oxide components of non-metallic inclusions in metal specimens from the Ti and Ti/Zr deoxidation experiments during the FGA measurements. It can be seen that the frequency of inclusions containing larger amounts of ZrO₂ in Groups 2 and 3 increased significantly (up to 50% in Ti/Zr-5 sample) with an increased holding time. The total O content in all oxide inclusions (O_{NMI}) in the metal sample of the Ti/Zr-1 experiment at 1 min of holding after a Zr addition is slightly larger compared to that in the Ti-1 experiment. It can be explained by some reoxidation of the surface of the added FeZr alloy and oxide inclusions contained inside the FeZr piece. Then, the O_{NMI} value decreased significantly (on ~40% in Ti/Zr-5 sample) due to a floatation of oxide inclusions from the melt during holding. However, it should be pointed out that though the amount of NMIs in Group 2 increased by about 2 times, the number of inclusions and clusters with higher concentrations of ZrO₂ (Group 3) decreased during the holding period.

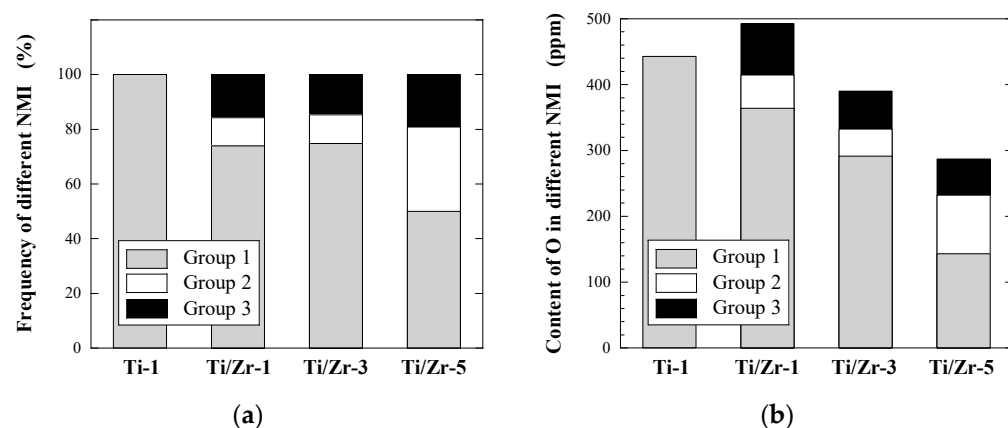
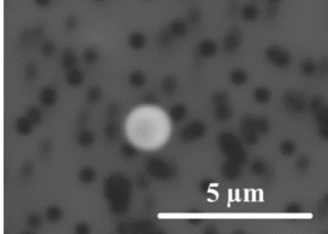
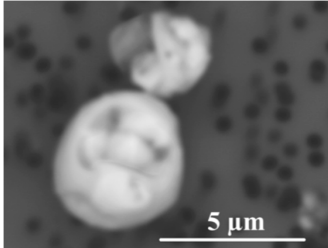
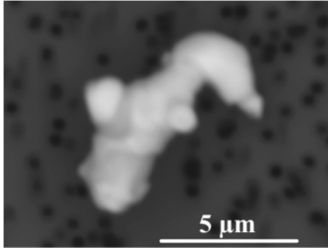


Figure 5. Average frequencies (a) and contents of oxygen (b) in different NMIs determined by using the FGA method in the Ti and Ti/Zr deoxidation experiments.

3.2. Evaluation of NMIs in Ti/Mg Experiments

Different inclusions observed after electrolytic extraction of Ti/Mg samples were divided into the following three types depending on their morphologies and sizes (Table 5): (i) Type IV—small size globular oxides (<2.5 μm), (ii) Type V—large size inclusions (up to 6 μm) contained different phases and (iii) Type VI—clusters (up to 13 μm).

Table 5. Classification of different inclusions observed in the Ti/Mg experiments after electrolytic extraction.

Type of NMI	Composition (Mass%)	Size Range (μm)	AR
Type IV			
	21–58% FeO, 6–42% MgO, 0–45% TiO _x , 0–5% Al ₂ O ₃ , 0–21% SiO ₂	0.5–2.5	1–1.5
Type V			
	22–60% FeO, 8–56% MgO, 11–37% TiO _x , 0–18% Al ₂ O ₃ , 1–13% SiO ₂	2.6–6.1	1–1.6
Type VI			
	11–44% FeO, 16–83% MgO, 3–54% TiO _x , 0–4% Al ₂ O ₃ , 0–2% SiO ₂	4.1–13.3	1.2–2.5

The contents of the main oxide components (such as MgO, FeO, TiO_x and SiO_2) obtained by using the EDS method to study various NMIs are shown as a function of their type and size in Figure 6. It can be seen that the content of these oxides in inclusions can vary in the wide ranges. This can be explained by the presence of different phases with different ratios of these oxides in one heterogeneous inclusion. Therefore, it is difficult to quantify the mass fraction of each oxide in the observed inclusions in the given experimental samples investigated by using only the EE + SEM method.

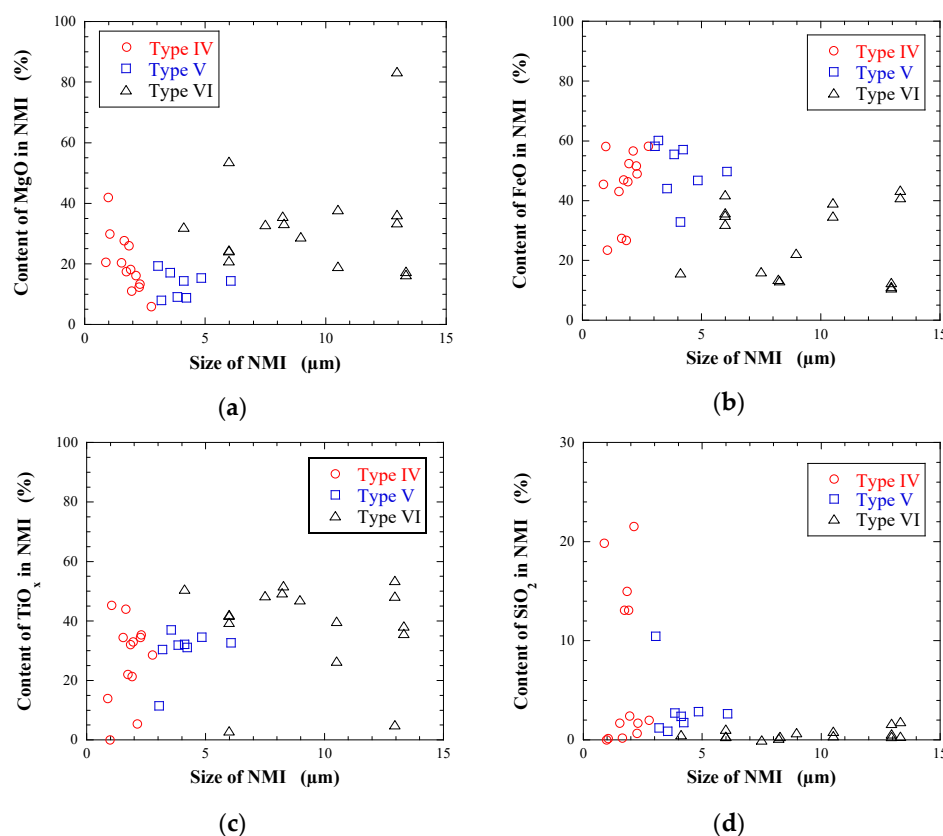


Figure 6. Contents of MgO (a), FeO (b), TiO_x (c) and SiO_2 (d) in different inclusion types observed after electrolytic extraction of the Ti/Mg-5 sample.

For that purpose, the FGA method was also used for determination of the mass fraction for each type of oxide in the observed NMIs. Typical time charts of reduced oxygen from different oxides in metal specimens of Ti and Ti/Mg experiments are shown in Figure 7. It can be seen that the peaks of oxygen corresponding to different oxide inclusions and clusters shifted to higher reduction temperatures with an increased holding time. This is due to the reduction of FeO and TiO_x oxides by Mg and due to increased MgO concentrations in inclusions, which have significantly higher reduction temperatures compared to the FeO and TiO inclusions.

As was described above, a superimposition analysis of pictures of gas evolution curves obtained by FGA measurements was used for classification of the main oxide inclusions in the Ti/Mg experiments as a function of the reduction temperatures and maximum peaks of gas evolution. However, some types of complex oxides in Table 6 (such as TiO_x -MgO and MgO- TiO_x) were placed in Groups 5 and 6. Depending on proportion of oxide components in these inclusions, their reduction temperature and, as a result, locations of the corresponding peaks, were plotted on FGA time charts. Moreover, Group 6 can contain the clusters (Type VI, Table 5) as well as separate oxide inclusions with high concentrations of MgO, which did not yet agglomerate into clusters.

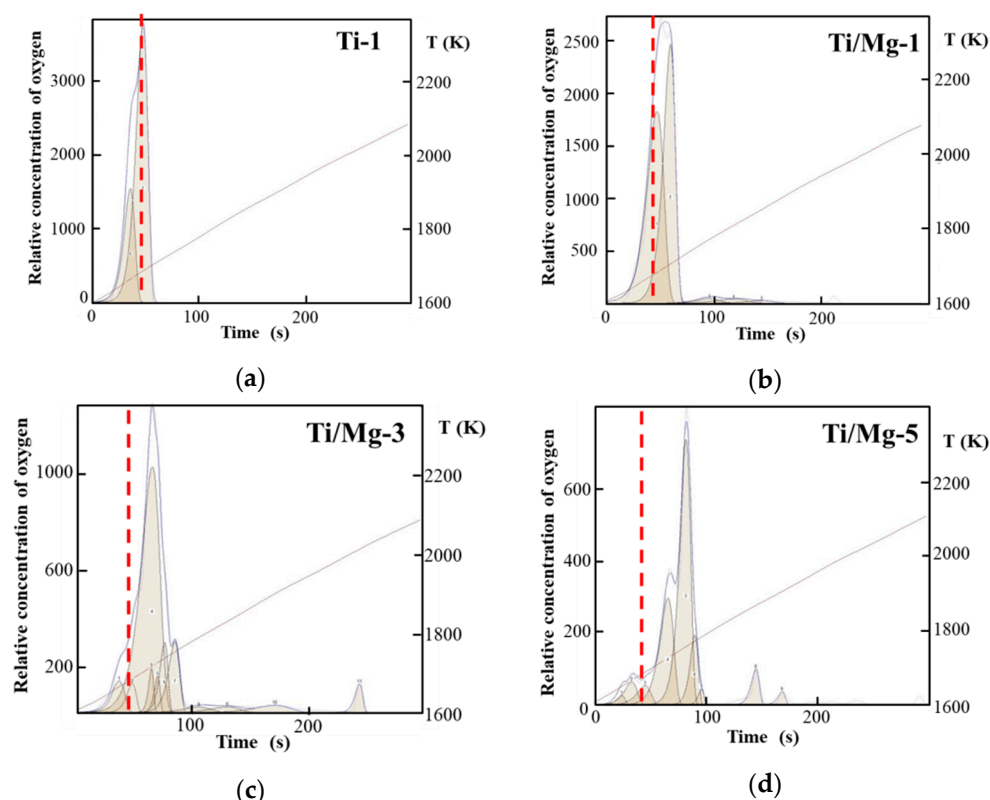


Figure 7. Typical time charts obtained by FGA measurements of oxide inclusions in metal specimens from the Ti and Ti/Mg experiments: (a) Ti-1, (b) Ti/Mg-1, (c) Ti/Mg-3 and (d) Ti/Mg-5.

Table 6. Classification of main oxide inclusions in the Ti/Mg experiments by using FGA measurements.

Group	T_m (K)	T_m ($^{\circ}$ C)	Oxides
4	1670–1770	1397–1497	FeO, FeO-TiO _x , Fe-TiO _x -MgO
5	1770–1900	1497–1627	TiO _x , TiO _x -MgO
6	1900–2150	1627–1877	MgO-TiO _x , MgO

According to the given classification, the frequency and amount of oxygen reduced from different oxide inclusions determined by the FGA method in the Ti and Ti/Mg deoxidation experiments are compared in Figure 8. It was found that the frequency of inclusions containing larger amounts of MgO (Groups 5 and 6) increases drastically up to ~69% in the Ti/Mg-3 sample and then decreases up to 26% in the Ti/Mg-5 sample (Figure 8a). This can be explained by a partial vaporization of the added Mg from the melt at 1600 $^{\circ}$ C and the decrease of the Mg content in the melt after holding during 5 min. As a result, the concentration of MgO in most oxide inclusions decreased significantly due to the dissociation of MgO and precipitation of TiO_x and FeO. As shown in Figure 8b, the total O content was reduced for all oxide inclusions (O_{NMI}) in the metal samples after addition of Mg decreased drastically on 49% in the Ti/Mg-1 sample and on 63% in the Ti/Mg-5 sample compared to that in the Ti-1 deoxidation experiment. This may be explained by the fast removal of the present oxide inclusions due to the influence of rising bubbles of vaporized Mg and due to the additional stirring of the melt. However, it should be pointed out that the amount of oxide inclusions having larger contents of MgO (Groups 5 and 6) decreased drastically from 65% in the Ti/Mg-3 sample up to 24% in the Ti/Mg-5 sample, due to the decrease of the Mg content in the melt, as was explained above.

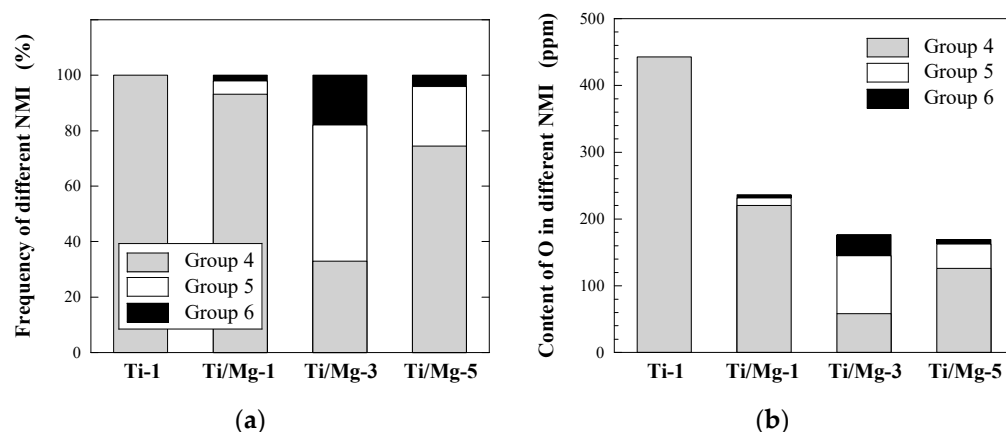


Figure 8. Average frequencies (a) and contents of oxygen (b) in different NMIs determined by the FGA method in the Ti and Ti/Mg deoxidation experiments.

Thus, the results obtained by using a combination of two modern analytical techniques for qualitative and quantitative characterization of non-metallic inclusions and clusters in Fe-10%Ni alloy deoxidized by Ti, Ti/Zr and Ti/Mg at 1600 °C are well correlated and complement each other. The electrolytic extraction (EE) of inclusions and clusters from metal samples was used to enable 3D investigations to determine their real morphology, size distribution and composition by using scanning electron microscopy (SEM). The Fractional Gas Analysis (FGA) method was applied to enable a fast quantitative determination of the total amounts and compositions of different main oxide phases in typical inclusions and clusters, as a function of the type of deoxidations and the holding time after the introduction of deoxidizers into the melt. Important advantages of the FGA technique by quantitative volumetric evaluation of NMI in steel samples are a fast analysis result (about 10–15 min per sample) and a significantly larger mass of analyzed metal (about 1.0–1.5 g per an analysis). Therefore, a combination of these modern analytical techniques can successfully be applied for more complete investigation of non-metallic inclusions and clusters in a wide range of steels and alloys.

4. Conclusions

In this study, oxide non-metallic inclusions and clusters were evaluated in the Fe-10%Ni alloy deoxidized by the addition of Ti, Ti/Zr and Ti/Mg as a function of holding time at 1600 °C after deoxidation. Inclusion characteristics were investigated by using the electrolytic extraction (EE) and Fractional Gas Analysis (FGA) methods. The obtained results can be summarized as follows:

1. Depending on morphology, size and composition, the following three main types of oxide inclusions and clusters were observed after electrolytic extraction of metal samples in all Ti/Zr and Ti/Mg deoxidation experiments: (i) small spherical inclusions (0.5–5 µm) having large contents of FeO and TiO_x and low contents of ZrO_2 (Type I) or MgO (Type IV); (ii) inclusions consisting of a FeO- TiO_x core and a rough outer solid layer or precipitated solid oxide phase containing larger amounts of ZrO_2 (Type II) or MgO (Type V); (iii) large size clusters (up to 26 and 13 µm in Ti/Zr and Ti/Mg experiments, respectively) containing higher concentrations of ZrO_2 (Type III) or MgO (Type VI).
2. The peaks of oxygen reduced from different oxides obtained by the FGA measurements correspond well to the main types of inclusions and clusters observed in the investigated metal samples observed in 3D by using the EE + SEM method. The frequencies of the main types of oxide inclusions and clusters in the Ti, Ti/Zr and Ti/Mg deoxidation experiments obtained by using the EE + SEM and FGA methods showed similar tendencies with an increased holding time of the melt after an addition of Zr or Mg.

3. After an addition of Zr in the melt deoxidized by Ti, the total O content, reduced from all oxide inclusions (O_{NMI}) during the FGA measurement, increased slightly in the Ti/Zr-1 sample. Thereafter, it decreased linearly by ~40% in the Ti/Zr-5 sample due to floatation of oxide inclusions from the melt during the holding period. At that time, the amount of NMIs with higher concentrations of ZrO_2 (Group 2) increased by approximately 2 times, despite that the number of almost pure ZrO_2 inclusions and clusters (Group 3) decreased during the holding period.
4. After an addition of Mg in the melt deoxidized by Ti, the O_{NMI} content decreased drastically by 49% in the Ti/Mg-1 sample and by 63% in the Ti/Mg-5 sample compared to that in the Ti-1 deoxidation experiment. This is due to a fast removal of oxide inclusions due to the floatation caused by rising bubbles containing vaporized Mg. However, the amount of NMIs at larger MgO contents (Groups 5 and 6) decreased significantly from 65% in the Ti/Mg-3 sample up to 24% in the Ti/Mg-5 sample. This is due to a fast decrease of the Mg content in the melt.
5. A combination of the given modern analytical techniques can be successfully applied for complete quantitative and qualitative evaluations of oxide non-metallic inclusions and clusters in a wide range of steels and alloys. More specifically, the EE method was used to enable 3D investigations of real characteristics of NMIs (such as morphology, size distribution, number and composition) by using a scanning electron microscopy (SEM). The FGA method was applied to enable a fast (about 10–15 min per analysis including sample preparation) and more representative (~1.0–1.5 g of metal specimen per an analysis) quantitative determination of the total amount and compositions of main oxide phases in typical inclusions and clusters. It was found that these two analytical techniques are well correlated and that the results from each method provided complementary information.

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