Modification of Non-Metallic Inclusions by Rare-Earth Elements in Microalloyed Steels

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Abstract

The modification of the chemical composition of non-metallic inclusions by rare-earth elements in the new-developed microalloyed steels was discussed in the paper. The investigated steels are assigned to production of forged elements by thermo-mechanical treatment. The steels were melted in a vaccum induction furnace and modification of non-metallic inclusions was carried out by the michmetal in the amount of 2.0 g per 1 kg of steel. It was found that using material charge of high purity and a realization of metallurgical process in vacuous conditions result in a low concentration of sulfur (0.004%), phosphorus (from 0.006 to 0.008%) and oxygen (6 ppm). The high metallurgical purity is confirmed by a small fraction of non-metallic inclusions averaging 0.075%. A large majority of non-metallic inclusions are fine, globular oxide-sulfide or sulfide particles with a mean size 17 μm^2. The chemical composition and morphology of non-metallic inclusions was modified by Ce, La and Nd, what results a small deformability of non-metallic inclusions during hot-working.

Keywords: Rare-earth Elements, Modification of Non-metallic Inclusions, Microalloyed Steels

1. Introduction

In the last 15 years, the issues concerning non-metallic inclusions in steels have become one of the leading subjects of research in the field of metallurgy due to significant impact on the quality of steel. In the earlier period, non-metallic inclusions were treated as a dangerous but indispensible product of deoxidation and desulphurization of steel, which should be removed or modified as much as possible so it did not decrease mechanical properties. In the result of performed research of the behavior of non-metallic inclusions during solidification of steel, it was found that depending on the chemical composition and their size, they can have varied impact on properties of steel, starting from strongly negative to almost conditioning obtaining desired mechanical properties [1-3].

Products of deoxidation and desulphurization in the form of oxides and sulfides flow out from liquid metal to slag only partially. The remaining part of the product of these reactions is retained in steel after solidification in the form of non-metallic inclusions, often decreasing mechanical properties of products. MnS sulfide inclusions are usually located on grain boundaries, while Al_2O_3 oxide inclusions are present in a dendritic form. Sulfide inclusions are ductile and elongate in the direction of metal flow, whereas dendritic oxides crumble and take the chain-like form during hot plastic working. It causes anisotropy of plastic properties of metallurgical products, sheets and pipes in particular [4, 5].

In order to reduce the anisotropy of plastic properties, modification of chemical composition and morphology of non-metallic inclusions with calcium compounds introduced into the metal bath is carried out. Treatment of liquid steel consists in shooting Ca-Si or Ca-Fe flux-core wires into the bath up to the depth of 1.5 to 2 m below the surface of liquid metal without the contact with the bottom of the ladle or injection of these substances into the bath at the said depth [5]. Calcium is more active towards oxygen than Al and Si and its chemical affinity for

sulfur is higher than for Mn, thus it leads to displacement of Al from oxide inclusions and displacement of Mn from sulfide inclusions, which go into the bath. Formed calcium aluminates as well as globular CaS and (Ca,Mn)S inclusions are hardly deformable during hot plastic working. Detailed description of modification of non-metallic inclusions with calcium compounds can be found in [4-7].

Rare earth metals introduced into the metal bath in the form of mischmetal, i.e. mixture of Ce, La, Nd and Pr and trace amounts of Fe and Si, have similar deoxidation and desulphurization effect as well as the ability to modify non-metallic inclusions as alkali metals [4, 8]. The result of their interaction is obtaining complex, often dispersive, oxysulfide inclusions with low susceptibility to plastic deformation during hot plastic working. Taking into consideration high chemical affinity of rare earth metals for oxygen and sulphur and high melting points of their compounds, they are formed right after introduction of these elements into the liquid steel. However, due to high density, their removal from the liquid metal is difficult [9, 10]. Table 1 presents properties of selected compounds of rare earth metals with oxygen and sulphur. For comparison, the melting point of MnS is equal 1539°C, Al_2O_3 - 2030°C and CaO - 2600°C. Therefore it's important to introduce these elements in concentration necessary only for deoxidation, desulphurization and for modification of non-metallic inclusions. The ratio of rare earth elements to sulphur required for complete modification of the shape of inclusions must be slightly higher than 4:1, i.e. higher from the value derived from stoichiometric ratio of (Ca, La) S [4].

Table 1.
Properties of compounds of O and S with rare-earth elements [8]

Compound	Melting point, °C	Density, kg/m³
Ce_2O_3	~2177	6200
La_2O_3	~2249	6500
Nd_2O_3	~2271	7300
Ce_2S_3	~2150	5020
La_2S_3	~2099	5000
Nd_2S_3	~2199	5400

In addition to the positive impact of modified non-metallic inclusions on a decrease of anisotropy of plastic properties of metallurgical products, it was found [11-13] that inclusions characterized by increased dispersion – particularly in microalloyed steels – can positively influence formation of steel microstructure. For instance, positive impact of MnS, CuS dispersive particles and Mn-Cu-S complex sulphides with size ranging from 30 to 100 nm on inhibition of grain growth of austenite in low carbon steels with Ti and V microadditions has been revealed in [11, 14]. In steels with microaddition of titanium, $MnO-SiO_2-TiO_2$ type fine precipitations or TiN are sometimes used as places of nucleation of acicular ferrite inside austenite grains [1, 15, 16]. Issues concerning the influence of non-metallic inclusions on microstructure and properties of steel have been described in detail in [4, 6, 17-19].

The goal of the work is to determine the effectiveness of modification of non-metallic inclusions with rare earth elements in newly elaborated micro-alloyed steels.

2. Experimental procedure

The research consisted in designing chemical composition of steels assigned for production of forged elements with the method of thermo-mechanical processing. Investigated steel melts, weighing 100 kg, were done in PVA TePla VSG-100S type laboratory vacuum induction furnace, in the Institute for Ferrous Metallurgy in Gliwice. Molten steels are characterized with high metallurgical purity, i.e. they have limited concentration of P and S impurities and gases. Studied steels slightly differ in concentration of C and Mn. Significant differences concern the content of metallic microadditions. The A steel consists of 0.033%Ti and 0.008%V, while the B steel - in addition to Ti and V in the amount of 0.028 and 0.019%, respectively – contains also microaddition of Nb in the concentration of 0.027% (Table 2). The aim of introduction of metallic microadditions into both steels is to increase mechanical properties as a result of grain refinement and precipitation hardening during thermo-mechanical treatment.

Table 2.
Chemical composition of the investigated steels

Alloying	Mass contents, (%)	
	Steel A	Steel B
C	0.31	0.28
Mn	1.45	1.41
Si	0.30	0.29
P	0.006	0.008
S	0.004	0.004
Cr	0.26	0.26
Ni	0.11	0.11
Mo	0.22	0.22
Nb	—	0.027
Ti	0.033	0.028
V	0.008	0.019
B	0.003	0.003
Cu	0.20	0.20
Al	0.040	0.025
N	0.0043	0.0039
O	0.0006	0.0006

The charge to the furnace was set from materials with known chemical composition. Basic chemical composition consisted of ARMCO 04JA grade iron and alloy additions, mainly in the form of pure metals and ferroalloys (FeV, FeNb and FeB), as well as non-metallic additions (C and Si). In order to modify non-metallic inclusions, mischmetal (~50% Ce, ~20% La, ~20% Nd) was used. ARMCO iron was loaded into the crucible while the alloying additions and mischmetal were distributed into individual compartments of the alloy hopper, in the sequence complying with their subsequent introduction into the bath. After the charge was loaded, furnace was closed and vacuum pumps, creating vacuum in the furnace chamber, were turned on. Once the pressure in furnace reached 10÷20 Pa, heating of charge was initiated. Subsequently to the beginning of charge melting, further process was carried out under argon, with vacuum pumps turned off. Degassing of metal bath was performed after the charge was completely molten down and adequate temperature of liquid steel

was obtained. After degassing was finished, argon at the pressure of ~30 kPa was introduced into the furnace chamber and final deoxidation of bath was carried out with the use of Al. Then, the rest of alloy additions was introduced into the bath while stirring. Modification of non-metallic inclusions was performed using mischmetal in the amount of 2.0 g per 1 kg of steel, which was made as the last addition. Casting was carried out in atmosphere of argon through heated intermediate ladle into cast iron hot-topped mould with the following dimensions: top – 160 mm, bottom – 140 mm, h = 640 mm.

In order to obtain 32x160 mm flat bars, initial hot plastic working of ingots was performed implementing the method of open die forging in Kawazoe high-speed hydraulic press, applying 300 MN of force. Heating of ingots to forging was conducted in a gas forging furnace. Temperature range of forging was equal 1200÷900°C, with interoperational reheating in order to avoid decrease of the temperature of material below 900°C. The process of forging was performed on ingot bodies without hot-tops, which were cut off during forging.

Evaluation of the degree of metallurgical purity of steel with non-metallic inclusions was done basing on determination of their participation, type, size and morphology. The examinations were performed on longitudinal metallographic specimens taken from cogged flat bars. Analysis of chemical composition of non-metallic inclusions and effectiveness of their modification using rare earth elements was executed with the use of JOEL JCXA 733 X-ray microanalyzer. Local analyses and observations of distribution of individual elements, forming investigated non-metallic inclusions, were carried out. Determination of metallurgical purity of studied steels with non-metallic inclusions and evaluation of stereological parameters of inclusions were conducted on non-etched metallographic specimens with average area of 220 mm^2. For this purpose, LEICA Qwin automatic image analyzer cooperating with OPTON AXIOVERT 405M light microscope was used. The analysis of the grade of contamination of steel with non-metallic inclusions was performed basing on the measurement of surface area and superficial participation of non-metallic inclusions as well as the anisotropy ratio, calculated as the ratio of their length to their thickness.

3. Results and discussion

The application of charge materials with high purity and realization of melts under vacuum conditions decide that elaborated steels are characterized with high metallurgical purity connected with low concentration of sulfur and phosphorus. Low concentration of oxygen, equal 6 ppm, is particularly noteworthy.

Quantitative analysis of non-metallic inclusions after cogging into 32 mm thick flat bars allowed determining the quantity of non-metallic inclusions per 1mm^2, their fraction, average surface area and the ratio, characterizing susceptibility of inclusions to elongate in the direction of hot plastic working. Conducted analysis revealed, that investigated steels consist of small fraction of fine non-metallic inclusions, mainly in globular form (Fig. 1,2).

As shown in data set together in Table 3, the quantity of non-metallic inclusions per 1 mm^2 of the A steel is equal about 22, and their average surface fraction of only 0.085%. This steel contains very fine, globular or weakly elongated in the direction of plastic

working non-metallic inclusions with average surface area of approximately 17 μm^2. Low value of the elongation factor, i.e. ratio of length to thickness of the inclusion equal 1.40 indicates, that modification of non-metallic inclusions with rare earth metals reduces their susceptibility to elongate in the direction of hot plastic working, similarly as in case of modification with the use of calcium compounds in the ladle process.

Analysis performed on longitudinal section of the B steel revealed that values of parameters of non-metallic inclusions are comparable to the A steel. On the basis of quantitative analysis it was found that the B steel contains an average of about 16 non-metallic inclusions per 1 mm^2 of metallurgical specimen with the average surface area of about 16 μm^2, while the surface participation of the inclusions is equal only 0.07%. Similarly as in the A steel, low value of elongation factor 1/s equal 1.33 decides about low susceptibility of non-metallic inclusions to elongate in the direction of plastic working.
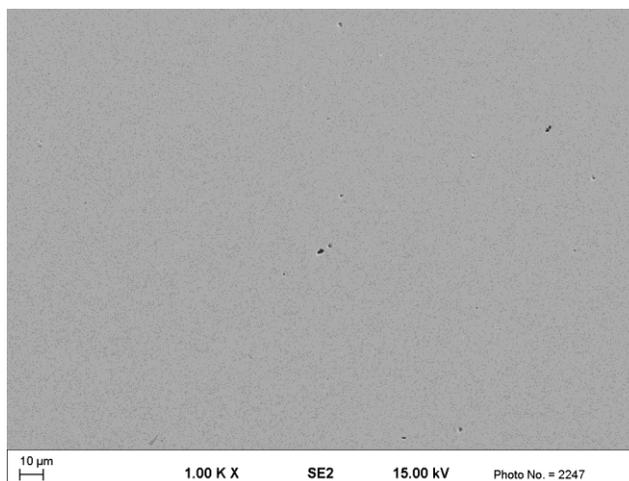

Fig. 1. Very fine non-metallic inclusions on the longitudinal section of the A steel sample
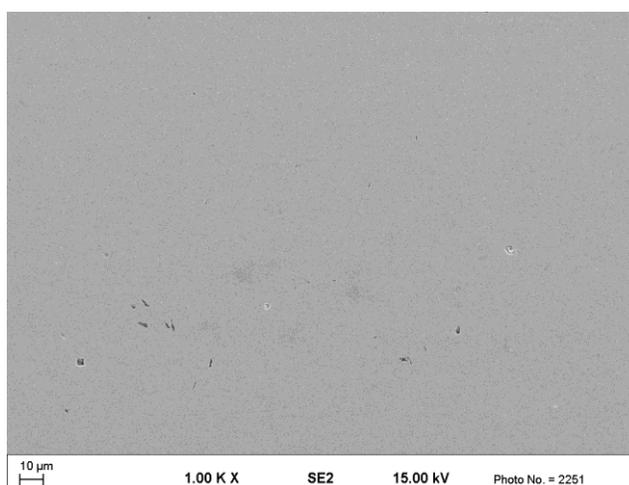

Fig. 2. Very fine non-metallic inclusions on the longitudinal section of the B steel sample

Table 3.
Quantitative analysis of non-metallic inclusions of investigated steels

Parameters of the non-metallic inclusions	Minimum value		Maximum value		Average value		Standard deviation	
	Steel A	Steel B	Steel A	Steel B	Steel A	Steel B	Steel A	Steel B
Number of inclusions, mm^{-2}	6.00	8.00	39.00	43.00	22.00	16.31	13.11	11.08
Surface fraction, %	0.02	0.01	0.280	0.200	0.085	0.069	0.055	0.056
Inclusions surface, μm^2	3.58	4.00	62.27	58.15	17.38	16.57	13.64	14.14
Elongation coefficient l/s[*]	1.17	1.14	1.670	1.500	1.400	1.330	0.160	0.140

[*]l – length, s – inclusion thickness

Qualitative and quantitative analysis of chemical composition of non-metallic inclusions confirmed effectiveness of applied modification of the inclusions with rare earth elements, i.e. Ce, La and Nd, during the melting process. It's confirmed in spectrograms of analysed non-metallic inclusions, where in addition to spectral lines deriving from S, O, Al, Fe and Mn, there are also spectral lines coming from Ce, La, Nd and Pr. Taking into consideration that rare earth metals are more active towards oxygen than Al and also its higher chemical affinity for sulphur than it's noted for Mn, rare earth elements lead to displacement of Al from oxide inclusions and displacement of Mn from sulphide inclusions. The presence of spectral lines deriving from Fe in spectrograms is because also a certain part of the matrix surrounding non-metallic inclusion was analysed. After cogging of ingots of the A steel into 32 mm thick flat bars, practically no non-metallic inclusions elongated in the direction of plastic flow were observed.

Very fine, globular, complex oxysulfide inclusions, in which Mn and Al were completely displaced by rare earth elements, were mostly revealed in this steel (Fig. 3). The darker area of the inclusion presented in Fig. 3a corresponds probably to MnS sulphide, while bright area reflects only non-deformed oxysulfide type inclusion. Basing on the analysis of spectrum of a part of inclusion modified with the use of rare earth metals (Fig. 2b), no spectral lines coming from Mn were noted. It speaks about complete modification of this part of the inclusion with Ce, La and Nd. Modified part of the inclusion forms a halo around MnS, preventing its deformation. For the majority of analyzed inclusions, the ratio of concentration of rare earth elements to concentration of sulfur resolutely exceeded the value required for total modification of the shape of inclusions, i.e. 4:1. Average surface area of revealed non-metallic inclusions did not exceed 18 μm^2; most often they were inclusions with the length limited to 3 μm.
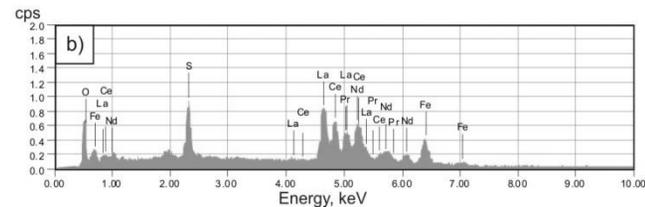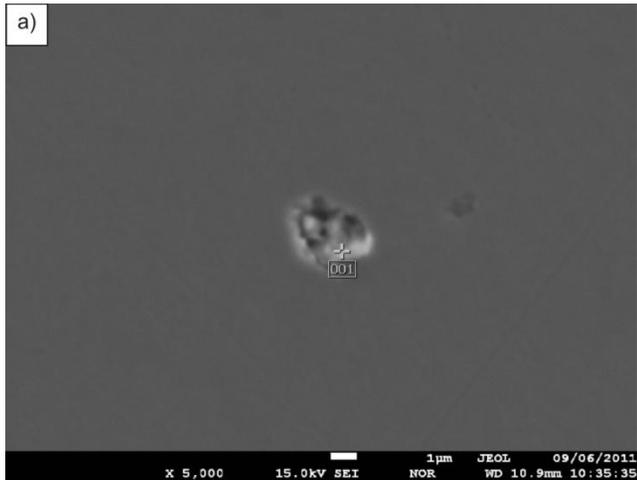

Fig. 3. Oxysulfide type non-metallic inclusion modified with rare earth elements: a – view of the inclusion, b – spectrum of the inclusion (steel A after forging)
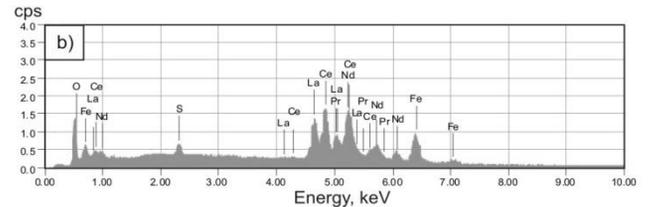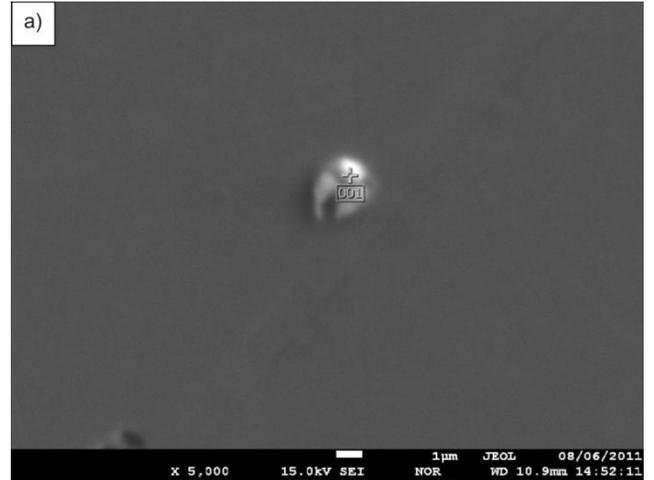

Fig. 4. Oxysulfide type non-metallic inclusion modified with rare earth elements: a – view of the inclusion, b – spectrum of the inclusion (steel B after forging)

The presence of (Ce,La,Nd,Mn,Fe)S complex sulfides, slightly modified with rare earth elements, was revealed in the A steel only incidentally.

Non-metallic inclusions with similar chemical composition and morphology as in case of the A steel were revealed in samples taken from ingots of the B steel, subjected to cogging. Globular oxysulfide type non-metallic inclusions modified with rare earth elements were identified in a decisive majority (Fig. 4). In these inclusions, Mn and Al were practically completely displaced by Ce, La and Nd, which speaks for correct modification of chemical composition of these non-metallic inclusions. Precise location of individual elements can be determined on the basis of the map of distribution of elements included in the composition of analyzed inclusion (Fig. 5). It confirms the presence of S in the central part of the inclusion and presence of Ce, La and Nd which are located in the outer zone of this inclusion.
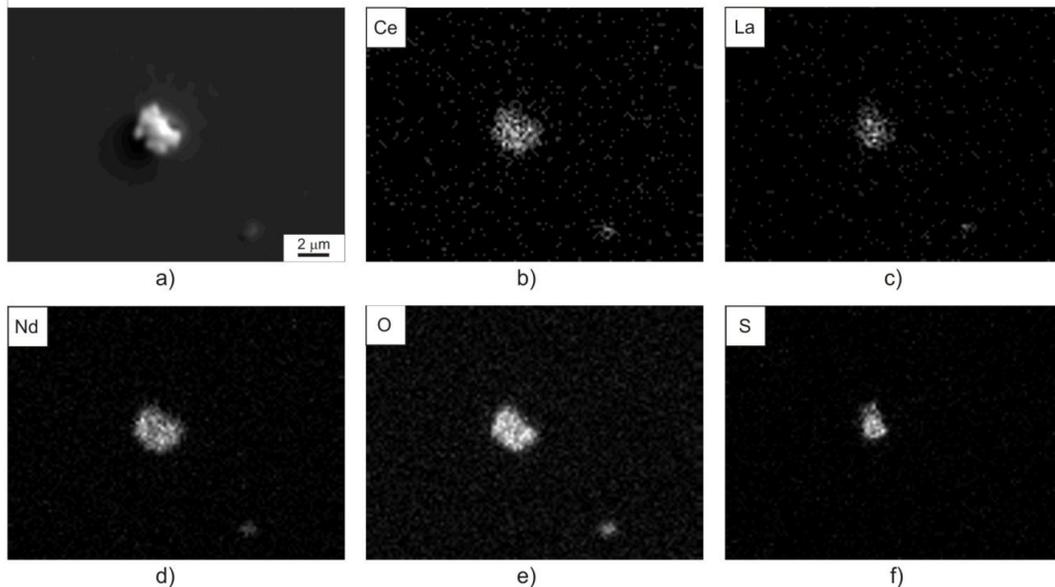

Fig. 5. Oxysulfide type non-metallic inclusion modified with rare earth elements: a – view of the inclusion, (b-f) – distribution maps of elements (steel B after forging)

4. Summary

Evaluation of the grade of metallurgical purity of newly elaborated steels with non-metallic inclusions indicates the correctness of conducted process of melting along with modification of non-metallic inclusions with rare earth metals. Application of charge materials with high metallurgical purity and realization of melts under vacuum conditions result in obtaining low concentration of sulfur equal 0.004% and particularly low concentration of oxygen equal 6 ppm. High metallurgical purity corresponds to low fraction of non-metallic inclusions equal 0.085% and 0.070% - for the A and B steel, respectively. Fine, globular oxysulfide inclusions are in decisive majority, rarely sulfide inclusions with average surface area of approximately 17 μm^2. Introduction of mischmetal in the amount of 2 g per 1 kg of steel causes total modification of chemical composition of non-metallic inclusions, connected with displacement of Mn from sulfide inclusions and Al from oxide inclusions by Ce, La and Nd, forming with oxygen and sulfur compounds with higher temperature stability when comparing to Mn and Al. Low value of elongation factor in the range from 1.33 to 1.40 decides about low susceptibility of non-metallic inclusions to elongate in the direction of conducted plastic working. The presence of dispersive, complex modified oxysulfide type non-metallic inclusions can have advantageous influence on a decrease of grain growth of austenite during hot plastic working similarly as MX interstitial phases. The factors mentioned above should favor the production of forgings with high strength and ductility.

Acknowledgements

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