



# Non-metallic inclusions in high manganese austenitic alloys

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## ABSTRACT

**Purpose:** The aim of the paper is to identify the type, fraction and chemical composition of non-metallic inclusions modified by rare-earth elements in an advanced group of high-manganese austenitic C-Mn-Si-Al-type steels with Nb and Ti microadditions.

**Design/methodology/approach:** The heats of 3 high-Mn steels of a various content of Si, Al and Ti were melted in a vacuum induction furnace and a modification of non-metallic inclusions was carried out by the mischmetal in the amount of 0.87 g or 1.74 g per 1 kg of steel. Evaluation of the metallurgical purity of steels with non-metallic inclusions was done basing on determination their fraction, type, size and morphology. Stereological parameters of the inclusions were assessed by the use of automatic image analyzer cooperating with light microscope. EDS method was used to assess the chemical composition of non-metallic inclusions.

**Findings:** It was found that the steels are characterized by high metallurgical purity connected to low concentrations of phosphorus and gases at a slightly higher sulphur content, introduced to a melt together with electrolytic manganese. The steels contain fine sulfide inclusions with a mean size from 21 to 25  $\mu\text{m}^2$  in a majority and their fraction equals from 0.047 to 0.09%, depending on sulphur content. MnS, carbonitrides of the (Ti,Nb)(C,N) type and complex carbosulfides containing Mn, Ti and Nb were identified in steels. The beneficial influence in decreasing a fraction of non-metallic inclusions and their susceptibility to elongate in a rolling direction has a higher addition of mischmetal and titanium microaddition. A modification of the chemical composition of non-metallic inclusions by Ce, La and Nd proceeds in an external zone of inclusions.

**Research limitations/implications:** Further investigations relating the type and morphology of non-metallic inclusions to mechanical properties of sheets at various sections according to the rolling direction are needed.

**Practical implications:** The knowledge of the type and morphology of non-metallic inclusions forming in high-Mn alloys and the effectiveness of their modification has a significant meaning for metallurgical and steel making technologies.

**Originality/value:** A problem of the identification of non-metallic inclusions modified by REE and titanium is a new topic in studies on the metallurgical purity of advanced high-strength high-manganese steels.

**Keywords:** Metallic alloys; High-Mn steel; Non-metallic inclusions; Rare earth elements; Ti microalloying

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## MATERIALS

## 1. Introduction

The development of modern steel grades for the automotive industry, characterized by advantageous combination of high strength, ductility and formability, is focused on mastering the production of multiphase steels, containing a significant fraction of retained austenite [1-3]. High-manganese steels with homogeneous austenitic microstructure find their potential application for the most important elements of the support structure of the car. The parts made of these steels with adequately formed geometrical structure are characterized with the highest ability to absorb the energy during the collision among all modern AHSS steels (Advanced High Strength Steels) [4, 5].

Apart from 15-30%Mn, high manganese steels most often contain also 0.03-0.2%C, 1-3%Si and 1-3%Al. Mechanical properties of these steels depend on structural processes occurring during cold deformation, which in turn are the derivative of stacking fault energy of austenite (SFE). In case its value ranges from 12 to 20 mJm<sup>-2</sup>, partial transformation of austenite into martensite with the use of TRIP effect (TRansformation Induced Plasticity) occurs. The values of SFE ranging from 20 to 60 mJm<sup>-2</sup> determine an intense course of mechanical twinning connected to TWIP (TWinning Induced Plasticity) effect [4-6]. The use of these phenomena allows obtaining tensile strength ranging from 600 to 1000 MPa and total elongation reaching up to 80%.

The studies of high manganese steels are mainly focused on the determination of their behaviour during cold plastic deformation [4, 5] and their hot workability [6-10]. It is commonly known that mechanical properties and hot-working behaviour are determined to a large extent by metallurgical purity of steel, related to the presence of non-metallic inclusions, among other factors. Besides high concentration of sulphur-binding Mn, high-manganese steels contain Si and Al with high chemical affinity for oxygen and nitrogen. Therefore, the presence of various sulphide and oxide inclusions should be expected. Chain-like packed, crushed oxide inclusions and sulphide inclusions elongated in the rolling direction are the cause of anisotropy of plastic properties of sheets; their substantial participation and size can cause delaminations and cracks in welding. Moreover, non-metallic inclusions are often the cause of decrease of crack resistance, fatigue strength and corrosion resistance [11-13].

Manganese, silicon and aluminium alloying additions present in high manganese steels are strong deoxidants. Therefore, limited oxygen content in molten steel, particularly under conditions of vacuum melts or final degassing of steel in the ladle should be expected. Yet, the protection of the stream of liquid steel from secondary oxidizing during casting is particularly meaningful; it is prevented by the use of sealed casing pipes, submerged casing tubes and bellows. Properly conducted process of cleaning run-purge, with the use of inertial gas, favours elimination of unwanted inclusions, oxide inclusions in particular [13].

One of the few results on the type and distribution of non-metallic inclusions in 0.05C-15/20/25Mn-3Al-3Si type high-manganese steels containing 75 ppm of N and S and 5 ppm of O<sub>2</sub> was released by Gigacher et al. [12]. Laboratory ingots, molten in an induction furnace, were subjected to solidification in conditions simulating the rate of heat removal during continuous casting of steel. It was found that (MnO-Al<sub>2</sub>O<sub>3</sub>) type

spinel inclusions are initially formed in the liquid metal. Along with lowering the temperature in the liquid state, AlN nitrides are formed on the spinels. Manganese sulphides grow on formed spinels in the temperature range between liquidus and solidus. The formability of formed inclusions has not been analyzed in the work mentioned above.

In order to reduce the deformability of non-metallic inclusions during rolling, modification of chemical composition and morphology of non-metallic inclusions with Ca or CaSi is carried out [13-15]. Rare earth elements (REE), introduced into the metal bath in the form of mischmetal, i.e. mixture of Ce, La, Nd and Pr, have similar deoxidizing and desulphurization effect and the ability to modify non-metallic inclusions [16]. The result of their interaction is obtaining complex oxysulfides with low susceptibility to plastic deformation during hot-working of steel [13-16]. Taking into consideration high chemical affinity of REE for oxygen and sulphur and high melting point of their compounds, they are formed right after their introduction into the liquid steel. However, due to high density, their removal from the liquid metal is difficult [16]. Hence, it is essential to introduce those elements in a concentration necessary for deoxidation, desulphurization and modification of non-metallic inclusions. For example, the effectiveness of modification of chemical composition of non-metallic inclusions in C-Mn-Si-Al type multiphase steels using mischmetal in the amount of 0.77 g per 1 kg of steel is described in [17].

## 2. Experimental procedure

The investigated steel melts, weighing 23 kg, were done in Balzers VSG-50 type laboratory vacuum induction furnace, in the Institute for Ferrous Metallurgy in Gliwice. Different chemical composition of the A, B and C melts derives mainly from diversified concentration of Si, Al and Ti (Table 1). In order to enhance mechanical properties of steels in the result of grain refinement and precipitation hardening during thermomechanical treatment, Nb and Ti microadditions with high chemical affinity for C and N were introduced. The concentration of Nb in melts is similar, but it should be noticed that the concentration of Ti is 7-times higher in the B steel.

The ARMCO iron was the primary charge to the furnace; its chemical composition was as follows: 0.02%C, 0.009%P, 0.036%Al, 0.23%Mn, 0.006%S, 0.02%Ni, 0.02%Si, 0.02%Cu and 0.02%Cr. Required chemical composition was complemented with additions such as carbon (graphite), pure silicon, electrolytic manganese, ferroniobium, pure titanium and aluminium. 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 degassing, argon was introduced into the furnace chamber and final deoxidation was done with the use of aluminium, which was an alloying addition at the same time. Calculated mass of aluminium was introduced into the bath from the alloy hopper, and then the bath was stirred in order to facilitate formed Al<sub>2</sub>O<sub>3</sub> inclusions to come up to the surface. Next, the rest of alloy additions, silicon and manganese and subsequently ferroniobium, carbon and titanium were introduced in portions into the bath from the alloy hopper.

Table 1.  
Chemical composition and structure of the investigated steels

Element content, wt. %										Mischmetal addition	Structure
C	Mn	Si	Al	S	P	Nb	Ti	N	O		
Designation: 0.040C-27Mn-4Si-2Al-Nb-Ti (grade A)										0.87 g/ 1 kg of steel	$\gamma + \epsilon$
0.040	27.5	4.18	1.96	0.017	0.002	0.033	0.010	0.0028	0.0007		
Designation: 0.054C-25Mn-4Si-2Al-Nb-Ti (grade B)										0.87 g/ 1 kg of steel	$\gamma + \epsilon$
0.054	24.5	3.49	1.64	0.016	0.004	0.029	0.075	0.0039	0.0006		
Designation: 0.065C-26Mn-3Si-3Al-Nb-Ti (grade C)										1.74 g/ 1 kg of steel	$\gamma$
0.065	26.0	3.08	2.87	0.013	0.004	0.034	0.010	0.0028	0.0006		

The bath was stirred after every addition for their complete dissolution and homogenization of the bath. In order to modify non-metallic inclusions, mischmetal (~50%Ce, ~20%La, ~20%Nd), introduced as the last addition into the metal bath, was used. Addition of mischmetal in the A and B melts was equal 0.87 g/1 kg of steel; its portion in the C melt was double (Table 1). The necessity to add large amounts of manganese into the metal bath was the major obstacle in conducting the melts. Due to the limited number of compartments in the alloy hopper, portions of additives had to be relatively large, causing difficulties in their melting and causing local cooling of the bath. This led to formation of solidified layer of metal on the walls of crucible, difficult to be re-molten. Manganese is characterized by high vapour pressure and therefore it could not be introduced into the crucible earlier due to the possibility of large losses in the subsequent process of degassing.

Casting from the temperature of 30-50°C above liquidus temperature for molten steel grade was conducted in the argon atmosphere into a hot-topped, solid bottom, big-end-up round cast iron ingot mould with the following internal dimensions: bottom – Ø122 mm, top – Ø145 mm, h = 200 mm – without the hot top (with the hot top – 300 mm).

In order to obtain 20x220 mm flat bars, initial hot-working of ingots was performed in high-speed hydraulic press, produced by Kawazoe, applying 300MN of force. Heating of ingots to forging was conducted in a gas forging furnace. The range of forging temperature was equal 1200-900°C, with inter-operational reheating in order to prevent the temperature of the material to drop below 900°C. Subsequently, flat bars were rolled in four passes into 5 mm thick sheets, and then air cooled up to the room temperature. Rolling temperature range was equal from 1200 to 900°C and rolling was conducted in two-high reversing mill with 430 mm diameter roll mills and rolling peripheral velocity equal 0.65 ms<sup>-1</sup>.

Evaluation of the degree of metallurgical purity of steel with non-metallic inclusions was done basing on determination of their fraction, type, size and morphology. The examinations were performed on longitudinal metallographic specimens taken from 5 mm sheet sections. Determination of stereological parameters of the inclusions was conducted on non-etched metallographic specimens with average area of 100 mm<sup>2</sup>. For this purpose, LEICA

Qwin automatic image analyzer cooperating with OPTON AXIOVERT 405M light microscope was used. The analysis was performed basing on the measurement of average size and the surface fraction of non-metallic inclusions as well as the ratio of their length to their thickness.

The analysis of the chemical composition of non-metallic inclusions and the effectiveness of their modification with rare earth elements was done using JEOL JCSA 733 X-ray micro-analyser, implementing 1 µm diameter electron beam, the voltage accelerating the electron beam equal U=20 kV and the current I=10<sup>-8</sup> A.

### 3. Results

Developed steels are characterized with high metallurgical purity, connected with low concentration of phosphorus, sulphur and gasses in particular (Table 1). Low concentration of total oxygen, at the level of 6 and 7 ppm is especially noteworthy. Increased concentration of nitrogen in the B steel with the highest content of titanium is probably the result of high participation of this element in TiN nitride, formed already in the interdendritic spaces during steel solidification [14]. The content of phosphorus is smaller than it is in Armco iron, used as a charge. The concentration of sulphur is more than double comparing to the charge and is ranging from 0.013 to 0.017 wt.% (Table 1). It should be noted that sulphur concentration is the lowest (0.013 wt.%) in the C melt, where double addition of mischmetal was introduced, comparing to A and B melts.

The microstructure of investigated steels after casting and hot forging is mostly austenitic matrix. For example, the microstructure of austenite with numerous annealing twins and non-deformed non-metallic inclusions with diversified size in the C steel is presented in Fig. 1. Because of the heterogeneous chemical composition, affecting the reduction of stacking fault energy, the remaining steels apart from austenite also contain a certain fraction of lamellar precipitations of  $\epsilon$  martensite. The fraction of martensitic phase is the largest in the B steel and is equal about 30%. The results of detailed microstructural and X-ray research of studied steels in the initial state together with the evolution of austenite microstructure during hot-working is presented in [6, 7].

Table 2.

Quantitative analysis of non-metallic inclusions carried out by the use of the LEICA Qwin image analyze

Parameters of non-metallic inclusions	Minimum value			Maximum value			Average value			Standard deviation		
	Steel A	Steel B	Steel C	Steel A	Steel B	Steel C	Steel A	Steel B	Steel C	Steel A	Steel B	Steel C
Number of inclusions, mm <sup>2</sup>	13.6	5.5	9.0	127.5	74.3	90.6	64.3	32.1	40.6	19.5	11.9	18.2
Surface fraction, %	0.04	0.01	0.02	0.25	0.11	0.15	0.090	0.047	0.061	0.043	0.020	0.028
Surface area of inclusion, μm <sup>2</sup>	2.6	2.5	2.6	150.7	161.8	159.4	21.5	25.1	22.3	11.8	10.2	10.5
Aspect ratio, l/t*	1.23	1.12	1.16	7.50	6.47	6.74	2.32	1.90	1.96	0.73	0.70	0.77

\*l/t – the ratio of the length of the inclusion to its thickness

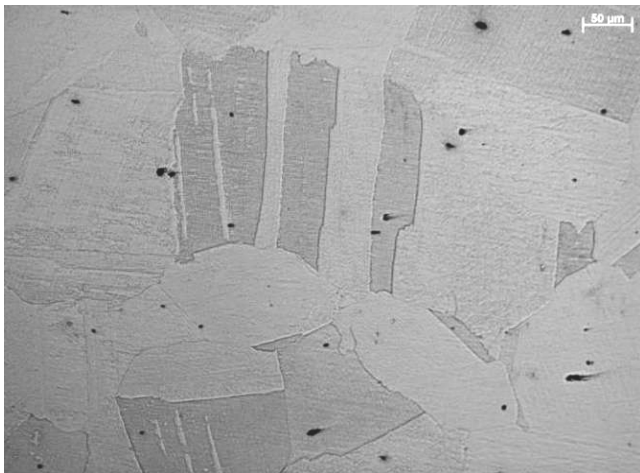


Fig. 1. Austenitic microstructure with annealing twins and non-metallic inclusions of the steel C at an initial state after forging

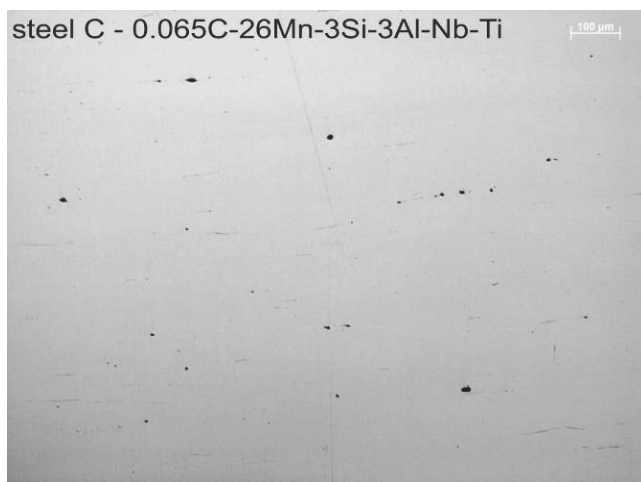


Fig. 2. Elongated non-metallic inclusions of various morphology in a longitudinal section of the steel C

Morphology of non-metallic inclusions changes after reducing flat bars into 5 mm thick test samples. Diversified concentration of sulphur in steels influences participation of non-metallic inclusions observed in longitudinal section of specimens cut in the direction of rolling (Fig. 2). Sulphide inclusions elongated in the rolling direction are a definite majority in case of the A steel with the highest sulphur content (0.017%S). The fraction of non-metallic inclusions in the B and C steel is lower (Fig. 2). Part of the inclusions is elongated in the rolling direction and the rest is composed of chain-like packed point wise inclusions.

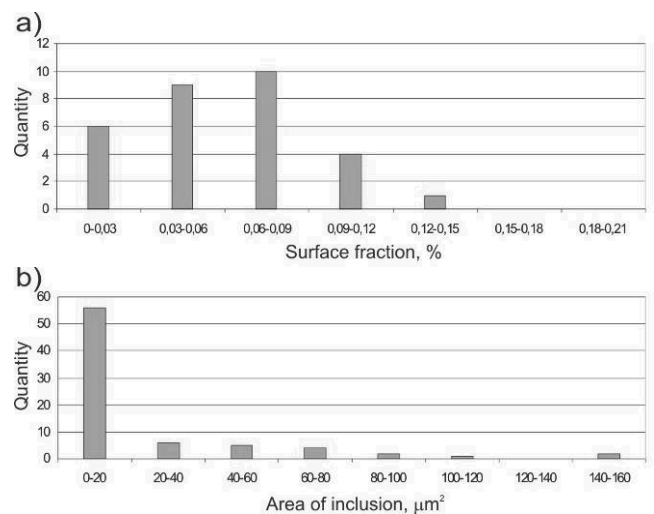


Fig. 3. Surface area fraction distribution of non-metallic inclusions (a) and their area (b) in the steel C; the surface area fraction was determined on a basis of the analysis of 30 regions of the specimen and the surface area distribution was given for a selected region

Quantitative analysis of non-metallic inclusions made it possible to determine the quantity of inclusions per 1 mm<sup>2</sup>, their fraction, the average surface area and aspect ratio, characterized by susceptibility of the inclusions to elongate in the direction of hot-working. As shown in Table 2, the average quantity of

inclusions per 1 mm<sup>2</sup> of the surface of the A steel metallographic specimen is equal about 64, and their average fraction of 0.09%. The steel contains mostly fine inclusions, elongated in the direction of rolling, with an average surface area of 21 μm<sup>2</sup>.

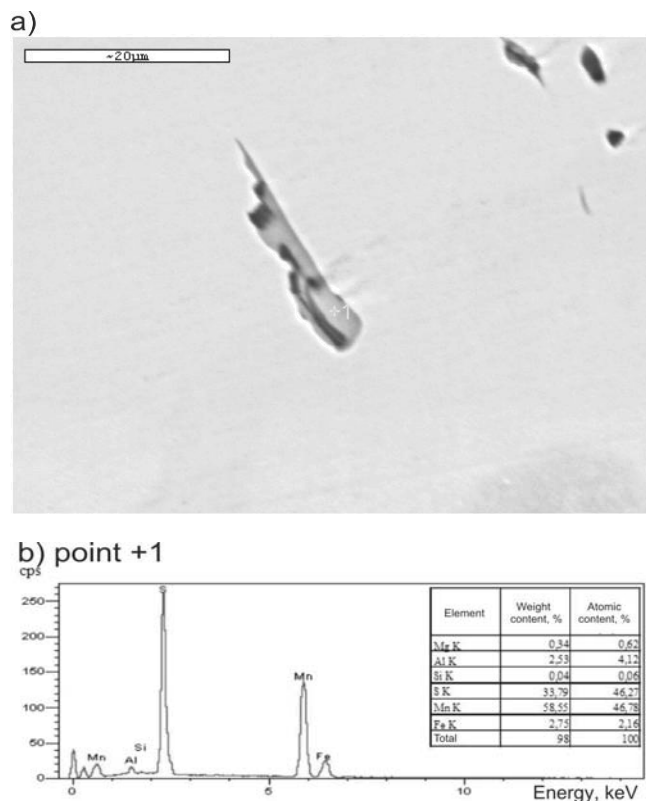


Fig. 4. The elongated in a rolling direction manganese sulfide, growing at a particle of TiN; a – view of the inclusion, b – spectrum of the inclusion from the point 1 (steel A)

The fraction of non-metallic inclusions in the B steel is about two times smaller, at comparable size of inclusions (Table 2). Higher addition of mischmetal into the C melt results in participation of non-metallic inclusions at the level of about 0.06% (Table 2), much higher than in the A steel, with comparable concentration of titanium. Small fraction of non-metallic inclusions and the prevalence of fine inclusions are confirmed in histograms presented in Fig. 3. Values of the aspect ratio are equal from 1.9 to 2.32 (Table 2). Inclusions present in the A steel, with higher concentration of sulphur, are characterized with the highest susceptibility to elongate in the rolling direction. Relatively high value of the aspect ratio, i.e. ratio of length to thickness of non-metallic inclusions equal 2.32, indicates that modification implementing rare earth metal elements was only partially effective. Positive effects of reducing the shape ratio below 2 occur in the B and C steel, containing increased concentration of titanium or bigger addition of mischmetal, respectively.

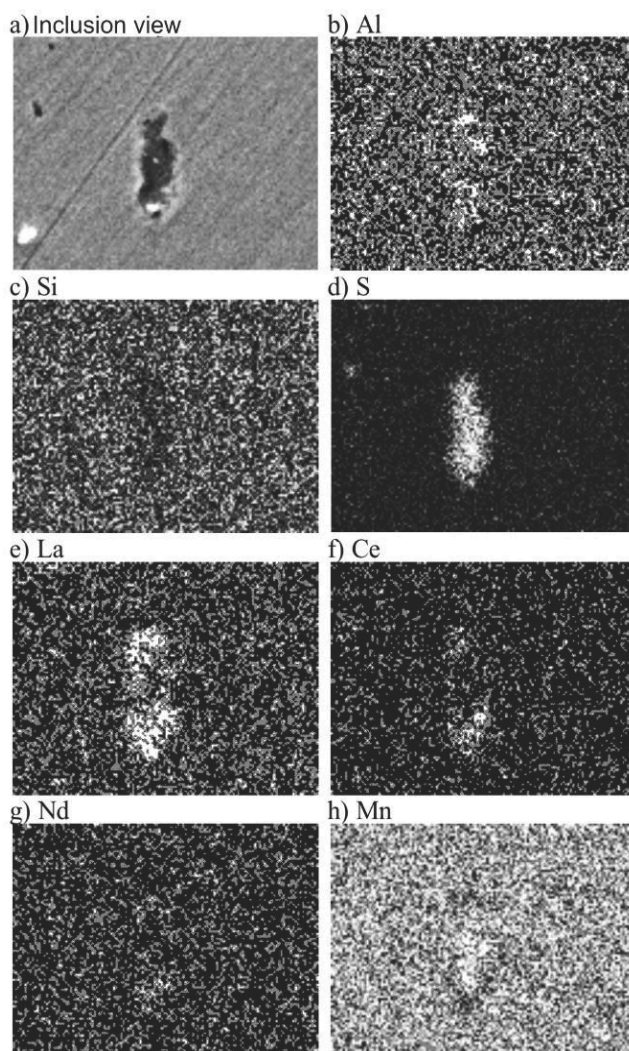


Fig. 5. The complex, sulfide-type non-metallic inclusion partially modified by La, Ce and Nd; view of the inclusion (a) and the element distribution maps (b-h)

Sulphide inclusions are a definite majority in all investigated steels. For example, Fig. 4 presents manganese sulphide elongated in the direction of rolling in the steel with higher sulphur content (steel A). It is characteristic that the growth of the inclusion occurred on the particle of titanium nitride, with typical regular shape, formed at higher temperature (upper part of the inclusion in Fig. 4a). The second group of sulphides in the studied steel is composed of inclusions with different grade of modification of chemical composition, what confirms partial effectiveness of modification of inclusions with rare earth elements applied in the melting process. Spectrograms of analyzed non-metallic inclusions apart from spectral lines deriving from S, Mn, Al, Si and Fe contain also spectral lines coming from Ce, La and Nd (Figs. 5, 9). Figure 5 presents elongated, fine non-metallic inclusions with 25 μm<sup>2</sup> of surface area, typical for investigated steels.

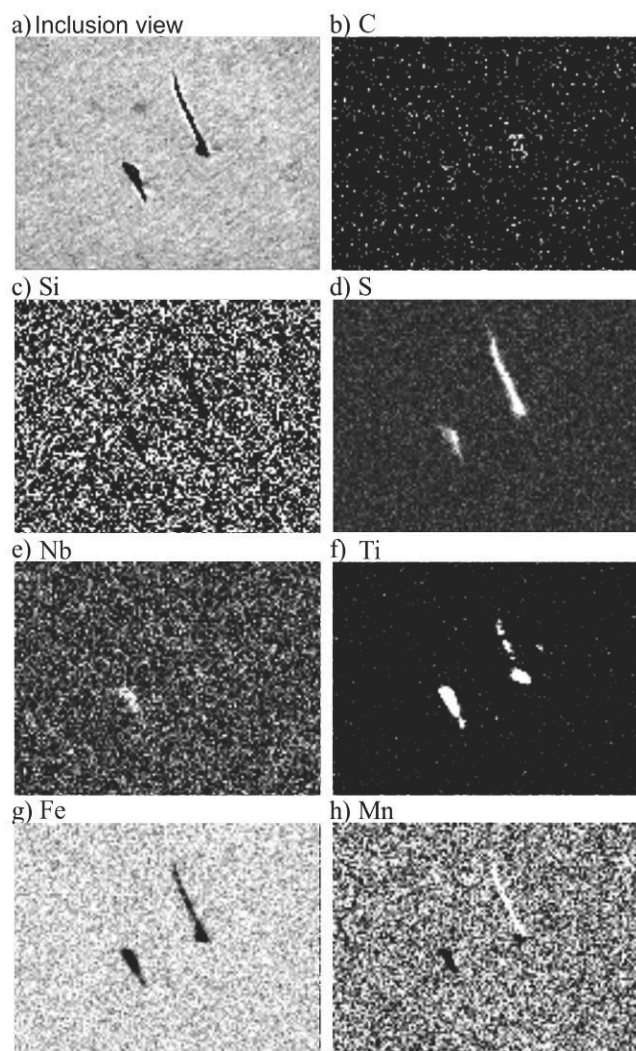


Fig. 6. The complex inclusions of sulfides and carbosulfides containing Mn, Ti and Nb; view of the inclusions (a) and the element distribution maps (b-h) in the steel B

Manganese sulphide is the central part of the inclusion while rare earth elements, which partially displaced manganese, locate themselves on the periphery. Analyzed inclusion contains minimal share of Al and does not contain Si. Partial modification of chemical composition prevents further elongation of the inclusion in the direction of rolling and influences obtaining the average value of the aspect ratio at the level of about 2.3, while its value for non-modified MnS reaches up to 7.5 (Table 2). Considerable higher fraction of particles with titanium was observed in the B steel, containing 0.075%Ti. In this steel, in addition to the nucleating impact of TiN particles on the growth of non-metallic inclusions, titanium partially displaces manganese from sulphide inclusions. The presence of this element is a result of higher chemical affinity of Ti for sulphur than for Mn [13-15].

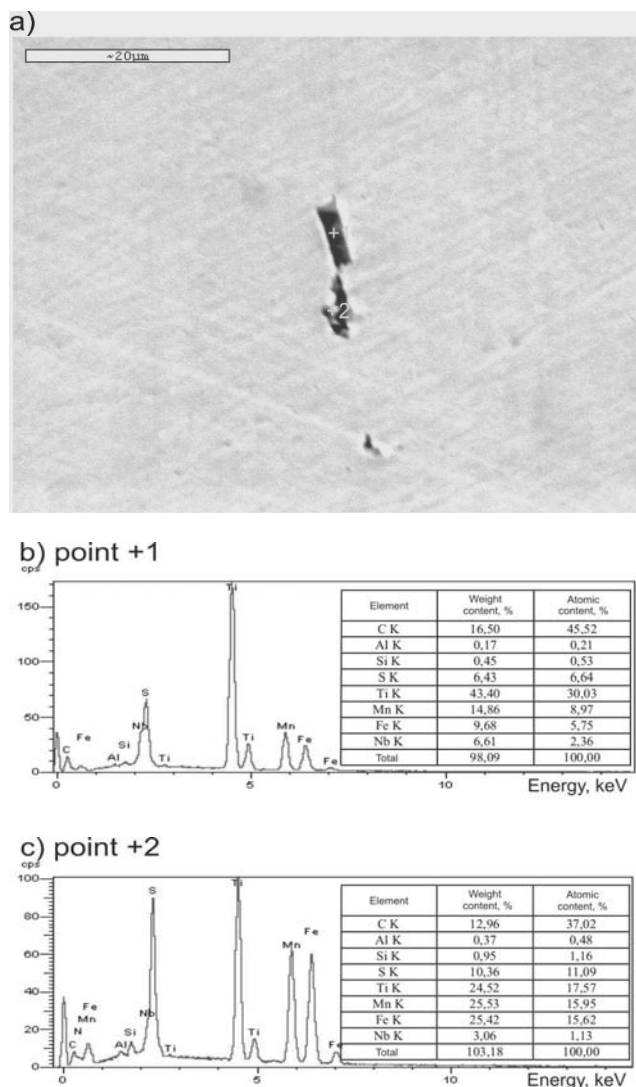


Fig. 7. Fine particles of carbosulfides with a various content of Ti, Mn and Nb in the steel B; a – view of the inclusions, b – spectrum of the particle from the point 1, c – spectrum of the particle from the point 2

Basing on the maps of chemical distribution of individual elements (Fig. 6) it can be found that partially elongated inclusions correspond to complex sulphides and carbosulphides, containing Mn, Ti and Nb. Figure 6 shows that inclusions containing Mn elongate in the direction of rolling more than carbonitrides containing only Ti and Nb.

Titanium microaddition, apart from high chemical affinity for sulphur, visible in its presence in sulphide-type inclusions, has a particularly high chemical affinity for N and C [13, 14]. For this reason, also (Ti,Nb)(C,N)-type complex carbonitrides with slight portion of MnS were identified in the investigated steels apart from sulphide inclusions (Fig. 7).

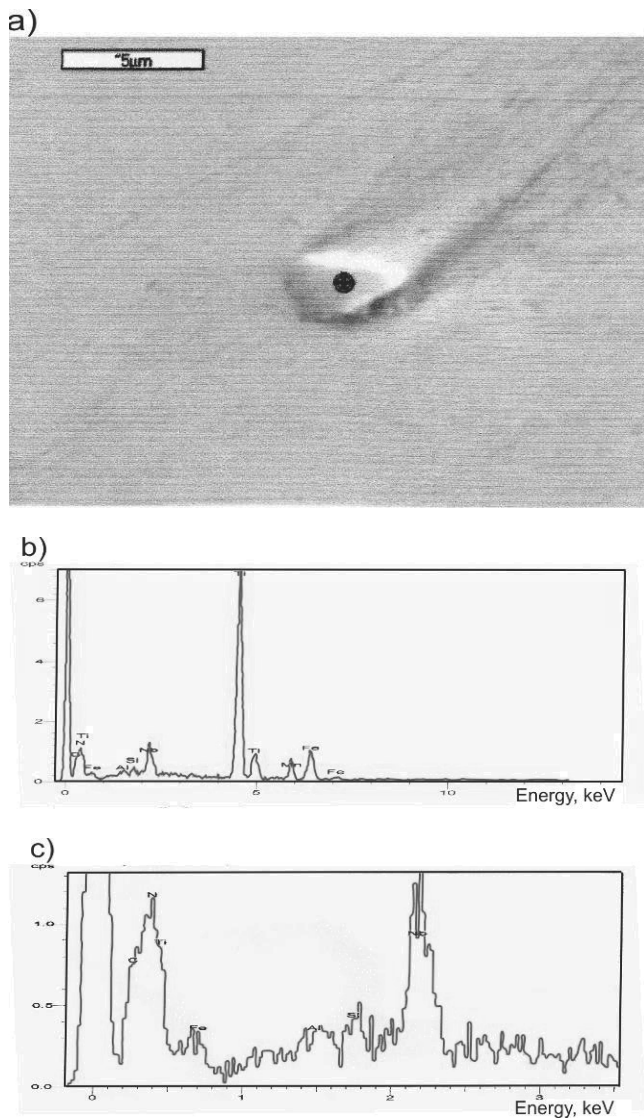


Fig. 8. Complex carbonitride of the (Ti,Nb)(C,N) type in a steel C; a – view of the particle, b – spectrum of the particle, c – a fragment of the particle spectrum indicating the presence of nitrogen

The size of these particles ranges from 2 to 5 µm. Chemical composition of regular inclusions approximately corresponds with (Ti,Nb)(C,N)-type inclusions (Fig. 7b), while particles with developed area are a (Ti,Nb)(C,N) + (Mn,Ti)S type complex conglomerate (Fig. 7c). Fine precipitations of carbonitrides were identified also in the C steel. For example, Fig. 8 presents (Ti,Nb)(C,N)-type particle with the size of about 3 µm. In this case, spectral lines (Fig. 8b, c) do not exhibit increased concentration of Mn and S, while detailed analysis of spectrum for the low energy range (Fig. 8c) allowed distinguishing spectral lines deriving from N and C, what confirms that it is a carbonitride.

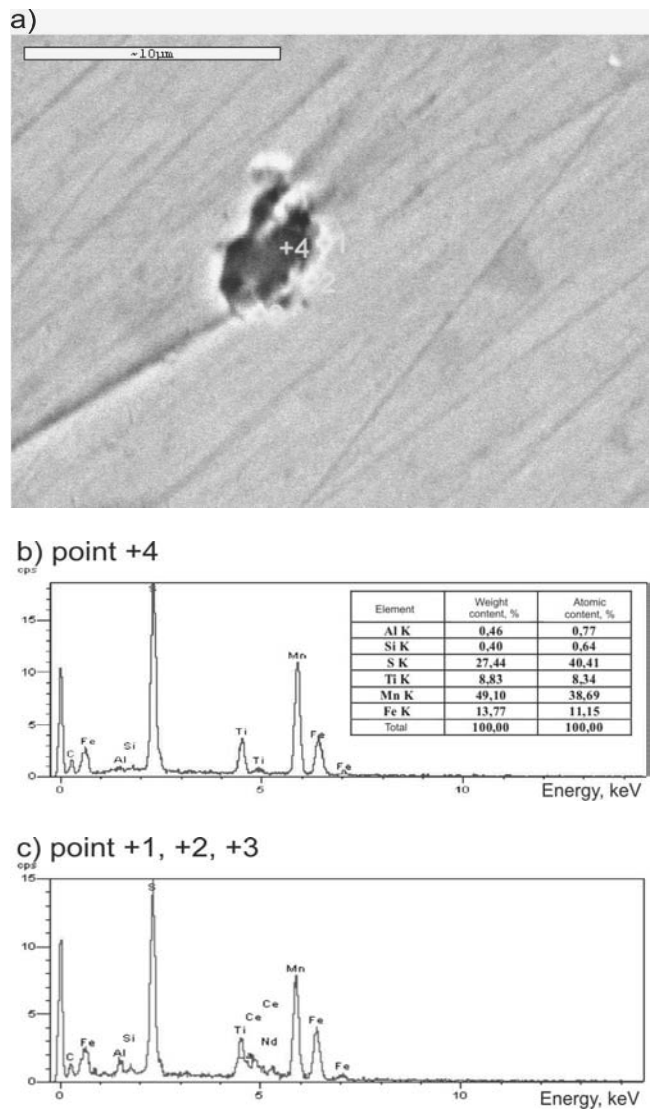


Fig. 9. The globular sulfide of (Mn,Ti)S modified in an external part by Ce, La and Nd; a – view of the inclusion, b – spectrum of the non-metallic inclusion from the point 4, c – spectrum of the non-metallic inclusion from the points 1, 2, 3; steel C

Increased addition of mischmetal in this steel causes a decrease of susceptibility of inclusions to elongate in the rolling direction, when comparing to the A steel (Table 2). Fine, globular, complex sulphide inclusions are the largest group (Fig. 9a).

The central part of inclusions is usually (Mn,Ti)S type sulphide (Fig. 9b), while modification of chemical composition with Ce, La and Nb occurs in the outer zone of inclusions, effectively preventing their elongation in the direction of rolling. Partial displacement of Mn from sulphide inclusions caused by rare earth elements is because they form sulphides, which are more stable than MnS [13, 16].

## 4. Discussion

The microstructure of elaborated high-manganese steels is austenitic (Fig. 1) or austenitic with minor participation of  $\epsilon$  type martensitic phase, as a consequence of decreased stability of  $\gamma$  phase caused by Ti and Nb microadditions (in the B steel) [6, 11] or the impact of increased concentration of Si and reduced content of Al on a decrease of stacking fault energy of austenite (in the A steel) [6, 7]. The use of charge materials with high purity and realization of melts under vacuum conditions decide that developed steels are characterized by high metallurgical purity (Table 1). No oxide inclusions were observed in the investigated steels due to particularly low concentration of oxygen. Taking into consideration low content of sulphur in the Armco iron charge (0.006 wt.%), slightly overestimated concentration of the element in steels univocally results from high concentration of sulphur brought to the metal bath by electrolytic manganese (concentration of S in electrolytic manganese was equal 0.06 wt.%). There is no possibility to remove it later due to lack of slag in the vacuum induction furnace. The technology of desulphurization with the use of slag-forming mixtures, also in this type of industrial furnaces, is not used on a large scale due to the presence of scorification of crucible walls, decrease of its durability and complex removal of slag. This indicates the essence of application of pure charges in induction furnaces, particularly in the range of Fe and Mn. In ongoing studies, meeting these requirements with the use of washing melts after two consecutive melts led to a decrease of S below 0.005 wt.%.

The addition of mischmetal has a significant impact on the concentration of sulphur and fraction of non-metallic inclusions. Obtained results show that twice as higher addition of rare earth elements determines the lowest concentration of sulphur in the C steel (Table 1) and minor participation of non-metallic inclusions (Table 2, Fig. 2). Similarly, the advantageous impact on a decrease of fraction of non-metallic inclusions is caused by increased by approximately 7 times concentration of Ti in the B steel (compared to the A and C melts). Obtained fraction of non-metallic inclusions and particle size (Table 2) in investigated high-manganese steels are comparable to those present in C-Mn-Si-Al type multiphase low-alloy steels, containing similar concentration of O and N, modified with rare earth elements [17]. However, values of the aspect ratio – equal from 1.9 to 2.32 (Table 2) – are higher, what mainly results from higher concentration of sulphur in the studied high-manganese steels.

Qualitative and quantitative analysis of chemical composition of non-metallic inclusions in the studied steels confirmed partial effectiveness of applied modification of the inclusions with rare earth elements during the melting process. Microaddition of titanium is also very important, especially in the B steel, containing 0.075%Ti. The smallest identified regularly shaped precipitations approximately correspond to (Ti,Nb)(C,N) type particles (Figs. 7, 8). The particles of carbonitrides, formed in the interdendritic spaces, often play a role of nucleus for the growth of sulphide inclusions (Figs. 4, 7). Moreover, due to higher chemical affinity of titanium for S than manganese, this element partially displaces manganese from sulphide inclusions. This results in formation of complex (Mn,Ti)S type sulphides and

carbosulphides containing Mn, Ti and Nb (Figs. 6, 7). In turn, the participation of Ti in the inclusions determines their susceptibility to elongate in the direction of rolling. The particles with higher concentration of titanium possess lower deformability than the inclusions with prevalence of Mn (Fig. 6), what results from increased hardness of Ti modified inclusions [13].

Presented analysis univocally indicates strong sulphur removal effect of titanium microaddition, particularly in the B steel with highest concentration of Ti at decreased influence of rare earth elements on modification of chemical composition of non-metallic inclusions. Modification of chemical composition of sulphides with titanium causes advantageous reduction of susceptibility of inclusions to elongate in the rolling direction, as indicated by the lowest value of shape factor of inclusions, equal 1.9 (Table 2). However, high concentration of titanium in steel causes that formed carbonitrides and carbosulphides are relatively big, which is a result of their precipitation already in the liquid state. This can cause a danger of cracking of particles during hot plastic working, leading to the reduction of ductility. Moreover, the lack of dispersive precipitations can cause partial or even total elimination of titanium microaddition from its share in formation of fine-grained microstructure of products during hot-working [13, 14].

A better solution to modify chemical composition of non-metallic inclusions is to increase the addition of mischmetal, which was implemented in case of the C melt. Although the addition of 1.74 g of mischmetal per 1 kg of steel (Table 1) did not cause total modification of sulphide inclusions, but the aspect ratio of inclusions is equal 1.96 (Table 2) and is comparable to the value obtained for the B melt, where the decisive role belonged to microaddition of titanium. Modification of chemical composition of the inclusions occurs mainly in their external zone, where Ce, La and Nb are located (Figs. 5, 9), simultaneously hardening the inclusion which decreases their susceptibility to elongate in the direction of rolling. Partial replacement of Mn in sulphide inclusions caused by rare earth elements is because they form sulphides, which are more stable than MnS. High stability of rare earth elements compounds is reflected by their high melting point, which for selected sulphides and oxides is presented in Table 3.

Table 3.  
Melting point of selected rare-earth elements compounds and for MnS and  $Al_2O_3$  [13, 16]

Sulfide inclusions		Oxide inclusions	
Type	$T_m, ^\circ C$	Type	$T_m, ^\circ C$
LaS <sub>2</sub>	1970	La <sub>2</sub> O <sub>3</sub>	2249
La <sub>2</sub> S <sub>3</sub>	2100	Nd <sub>2</sub> O <sub>3</sub>	2271
CeS	2100	Al <sub>2</sub> O <sub>3</sub>	2030
Ce <sub>2</sub> S <sub>3</sub>	2150		
Ce <sub>3</sub> S <sub>4</sub>	2050	Complex inclusions	
NdS	2150	Type	$T_m, ^\circ C$
Nd <sub>2</sub> S <sub>3</sub>	2200	La <sub>2</sub> O <sub>2</sub> S	1993
MnS	1539	Nd <sub>2</sub> O <sub>2</sub> S	1988



For example, the melting point of  $Ce_2S_3$ ,  $CeS$  and  $LaS_2$  sulphides is equal 2150, 2100 and 1970°C, respectively. It is substantially higher than the melting point of  $MnS$  equal 1539°C, similarly as the melting point of rare earth elements oxides is higher than the melting point of  $Al_2O_3$  (Table 3) [13, 16].

Total modification of sulphide inclusions with sulphur concentration equal from 0.013 to 0.017 wt.% in the studied steels is impossible, because the ratio of rare earth elements concentration to the concentration of sulphur, required for total modification of the shape of inclusions, must be equal approximately 4:1, i.e. the value derived from the stoichiometric ratio of  $(Ce,La)S$  [13]. This criterion would be fulfilled when addition of mischmetal was higher than 1.74 g per 1 kg of steel used. However, addition of rare earth elements in large amounts creates a danger that low-melting eutectic mixtures will be formed, what is connected to red brittleness during rolling. Moreover, increased density of sulphides and oxysulphides of rare earth elements makes it difficult to remove them from the liquid metal [16]. For this reason, the best solution is to reduce the concentration of sulphur in high-manganese steels due to the use of pure charge of iron and electrolytic manganese. This is confirmed in test results performed by Gigacher et al. [12], where in 0.05C-15/20/25Mn-3Al-3Si type high-manganese steels containing sulphur content limited to 0.007%S, the portion of pure  $MnS$  sulphides was equal only 3% and the fraction of complex  $MnS$  compounds was equal about 40% of all inclusions. Spinel ( $MnO-Al_2O_3$ ) type inclusions with high concentration of  $AlN$  were the majority [12]. Low concentration of oxygen in the investigated steels results in the lack of oxide inclusions. The use of Ti microaddition with higher chemical affinity for N than Al also causes bonding of the whole nitrogen into  $Ti(C,N)$  and assures lack of aluminium nitrides. Sulphide inclusions with partially modified chemical composition by rare earth elements and titanium, nucleating on  $Ti(C,N)$  type carbonitrides formed at higher temperature represent a decisive majority in the elaborated steels.

## 5. Conclusions

Developed C-Mn-Si-Al type high-manganese steels with Nb and Ti microadditions are characterized by high metallurgical purity, connected with reduced content of gasses and phosphorus. The concentration of sulphur equal from 0.013 to 0.017 wt.% is satisfying and depends mainly upon the purity of electrolytic manganese and the addition of mischmetal applied as the charge. Basing on the qualitative and quantitative analysis of non-metallic inclusions it was found that:

- the steels contain small fraction of fine non-metallic inclusions, with the factor of elongation in the direction of rolling equal from 1.9 to 2.3;
- no oxide inclusions were observed due to reduce to 7 ppm concentration of total oxygen in the steel;
- concentration of sulphur, which determines the presence of sulphide inclusions and carbo-sulphides in the investigated steels has a decisive meaning for the type and the fraction of non-metallic inclusions in the investigated steels;
- the largest fraction in the investigated steels are  $MnS$  inclusions, partially modified in external zone by Ce, La and Nb and complex  $(Mn,Ti)S$  type sulphides and carbo-sulphides containing Mn, Ti and Nb. The particles of the  $(Ti,Nb)(C,N)$  type, being often the nucleus for the growth of sulphide inclusions, were also identified;
- the smallest fraction of inclusions was obtained for the steel with higher content of mischmetal and for the steel with increased microaddition of Ti. Modification of chemical composition of sulphide inclusions by rare earth elements and by titanium causes the improvement of their hardness and decides about their reduced deformability during hot plastic working;
- the best way to further reduce the participation of non-metallic inclusions and their susceptibility to elongate in the direction of rolling – implementing addition of mischmetal – is to reduce the concentration of sulphur in the steel.

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