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MODIFICATION OF OXYGEN AND SULPHUR INCLUSIONS IN STEEL BY CALCIUM TREATMENT

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In the article, the results of examinations of changes in deformability of oxygen and sulphur inclusions in structural steel processed with calcium are discussed. The results obtained imply the positive influence of the calcium additives on the changes in geometry of oxygen and sulphur inclusions related to the modification of their chemical composition.

Key words: modification, oxygen and sulphur inclusions, calcium treatment, deformability

Modificiranje kisikovih i sulfidnih uključaka u čeliku obradbom kalcijem. U članku se raspravljaju rezultati istraživanja promjena deformabilnosti kisikovih i sulfidnih uključaka u strukturalnom čeliku obradbom kalcijem. Dobiveni rezultati ukazuju na pozitivan utjecaj dodataka kalcija na promjenu oblika kisikovih i sulfidnih uključaka sukladno njegovom kemijskom sastavu.

Ključne riječi: kisikovi i sulfidni uključci; modificiranje, obrada kalcijem; deformabilnost

INTRODUCTION

The non-metallic inclusions are inevitable consequence of metal elaboration processes and are foreign phases always present in solid and liquid metal. The inclusions have a different shape and a size from several to several hundred micrometers (in diameter). They are randomly distributed in the matrix of the base metal and form a dispersion phase in liquid and in solid metallic phase.

The non–metallic inclusions may directly affect the functional properties of metals, especially steel which is commonly used constructional material. The reducing the contents of non-metallic dispersion particles in the metal and the introducing of modification process are significant methods for their decreasing the unfavourable effects. The modification is a process of adding to a metal bath a small amount of substance (i.e. a modifier) which changes the physical-chemical properties of inclusions. The modifiers are metallic substances that change the solid oxide and sulphide particles steel bath to liquid inclusions in liquid metal.

In this paper the results of modifications of oxide and sulphide inclusions in steel with calcium, especially in respect of change in theirs shape and deformability are presented and discussed.

MODIFICATION OF OXIDE AND SULPHIDE INCLUSIONS

The chemical affinity of calcium to oxygen is higher than that to sulphur and at the temperature of 1873 K oxides are more stable than sulphides [1]. If calcium is to react with sulphur and not with oxygen then the oxygen activity in a liquid steel at the temperature of 1873 K should be about 19 times lower than sulphur activity [2], that is a very difficult condition to achieve.

Consequently, it is presumed that the first reaction after calcium is introduced in to the liquid steel is the calcium oxidation.

The $CaO-Al_2O_3$ system [3] shows the possibility of occurrence of calcium aluminates a series with different melting temperature and only one of them, i.e. $12CaO{\cdot}7Al_2O_3$ is in a liquid form at liquid steel temperature. The following oxides may be liquid also:

- $C_{12}A_7$ – melting point 1728 K
- $C_{12}A_7$-CA – melting point 1673 K
- C_3A- $C_{12}A_7$ – melting point 1663 K.

As well as the following ternary eutectics:

- 62 % SiO_2; 23,25 % CaO; 14,75 % Al_2O_3 – melting point 1438 K;
- 42 % SiO_2; 38 % CaO; 20 % Al_2O_3 – melting point 1538 K;
- 40 % SiO_2; 49 % CaO; 11 % Al_2O_3 – melting point 1538 K.

On the basis of our results it is concluded that the modification of Al_2O_3 particles with calcium is achieved only for the CaO content in these particles is in the range of 25 % to 60 %.

Sulphur belongs to a group of elements which exhibit almost unlimited solubility in a liquid iron [4]. During the solidifi-cation sulphur is selectively deposed at grain boundaries producing characteristic steel defects. Sulphur is found at grain boundaries in form of various

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sulphides or theirs solutions, depending on the chemical composition of steel. The sulphides which have the most negative influence on steel properties are the sulphides of type II and III. These sulphides grow in length at plastic working (particularly hot working) and cause a heterogeneity of mechanical properties of final products.

The purpose of introducing calcium to a metal bath is a change of the sulphur release mechanism in such a way that the sulphur is bound to oxide or aluminate particles and not deposed as sulphide inclusions at grain boundaries during the steel solidification.

EXAMINATIONS

The previous researches reveal that constructional steels are very sensitive to non-metallic inclusions. Currently, it the application of such steel for the production of elements which feature uniaxial symmetry e.g. bolts and shafts is investigated. A very important issue is the machining, especially the process of tool wear and the mechanism of chip formation [5, 6]. New technological solutions are being searched with the aim to change the chemical composition, deformability of non-metallic particles and achieve their a more advantageous distribution in steel.

Thermodynamic analysis [7, 8] shows that in aluminium-killed steels, the solid particles of alumina or hercenite are formed that form clusters. After the calcium is introduced, heterogenic reactions of calcium aluminates formation take place on the surface of the oxide particles previously formed. The small activity of oxygen and sulphur enables the modification of oxide inclusions to calcium aluminates. For increasing sulphur contents, the range in which oxides are modified by calcium is narrowing as result of the increased formation of calcium sulphide [8].

In the investigation a carbon construc-tional steel was used. The modification was peformed with the calcium alloy CaSi (30 % Ca) that was introduced into steel in form of core wire into the ladle of volume of 20 Mg. The samples of metal were examined 20 minutes after the addition of calcium. Ten test melts were treated: two without calcium treatment and the remaining ones with diverse calcium addition.

The aim of experiments was to evaluate the modification with calcium of non-metallic dispersion phase in steels of various aluminium, calcium and sulphur contents - represented as Ca/Al and Ca/S. The melts without calcium additives were marked as O1 and O2. The melts in which Ca/Al lower than 0,09 were marked as A1÷A3; the melts in which Ca/Al is within the range 0,09÷0,14 were marked as B1÷B3, whereas the melts of Ca/Al > 0,14 were marked as C1 and C2.

The assessment of non-metallic particles, their chemical composition, distribution, size and shape was carried out with using the following metallographic methods:

- number of particles per 1mm^2 (N_A),

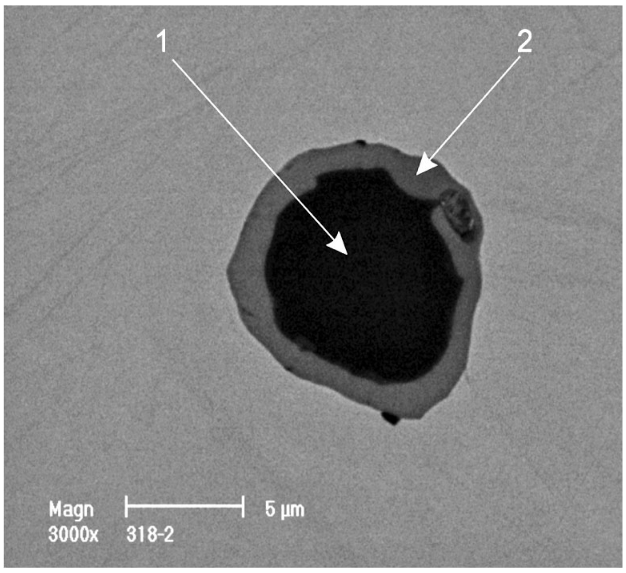

Figure 1. The sulpho-oxide inclusion; 1 – calcium aluminate, 2 – sulphide (Ca,Mn)S

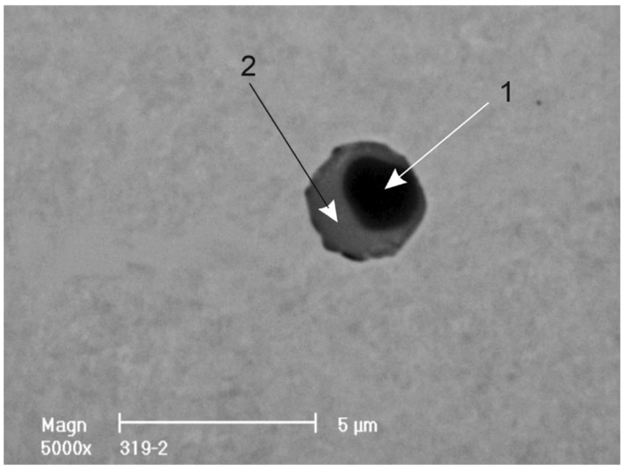

Figure 2. The sulpho-oxide inclusion; 1 – Al_2O_3, 2 – MnS

- area fraction of particles (A_A),
- distribution of number and area fraction of non-metallic particles,
- shape coefficient value of non-metallic particles.

The microscopic examinations proved that in steel samples treated with calcium, the most numerous inclusions are oxide-sulphides with an oxide core of the Al_2O_3-MgO-CaO system. The calcium aluminates are of different shape and have a lower content of calcium. Most of aluminates had a sulphidic ring of type (Ca,Mn)S – Figure 1.

The form of sulphides forming the inclusions case and their chemical compositions depend on the content of sulphur and calcium in steel. By low calcium content, the main coating component is MnS – Figure 2.

With the increase of the content of calcium in steel also its content in the surface ring increases up to the point of formation of CaS (Figure 3).

The quantitative evaluation has been performed with Morphopericolor picture analyser and the evaluation of inclusions on 50 field of view of each separate microsection has been made. The analysed area was of 2,349 mm^2.

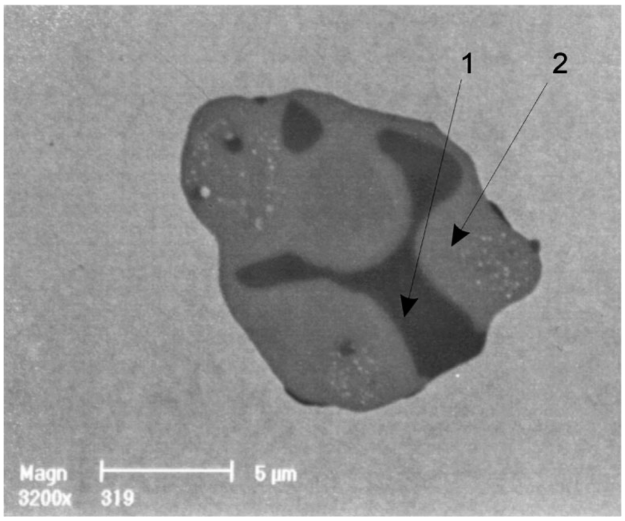

Figure 3. The sulpho-oxide inclusion; 1 – oxide like $2Al_2O_3$-MgO, 2 – CaS

The shape coefficient of particles in non-metallic dispersion phase was calculated using to the dependence:

$$\xi = \frac{4 \cdot \pi \cdot a}{l^2}$$

where: a - the area of measured particle in mm^2 and l - perimeter of a measured particle in mm.

The examinations based on quantitative metallography have been conducted on crosswise microsections of samples taken from rolled ingots.

The non-metallic particles in the tested steel have been divided into two groups. According to the results of analyses (electron microprobe) it has been decided that the oxide and oxide sulphides particles achieve the maximal value of elongation (the value of Feret's diameters ration F_x /F_y) of 2 these particles were considered as non-plastic; sulphides the elongation was higher than 2 therefore, they have been considered as plastic particles.

Table 1 and Table 2 presents the results of quantitative assessment of non-metallic inclusions (Table 1 – non-plastic particles, Table 2 – plastic particles).

Table 1. **Results of quantitative assessment of non-plastic of non-metallic inclusions.**

Melt	Number of non-metallic particles (N_A) / mm^{-2}	Area fraction of non-metallic particles, (A_A) / %	Mean area of particles / μm^2	Shape coefficient / ξ	Ca/Al
O1	1265	0,226	1,09	0,74	-
O2	861	0,175	0,98	0,73	-
A1	614	0,086	1,05	0,81	0,089
A2	1184	0,231	1,01	0,79	0,039
A3	490	0,074	0,85	0,78	0,027
B1	905	0,149	0,94	0,78	0,100
B2	1439	0,174	0,68	0,85	0,112
B3	586	0,077	0,73	0,79	0,095
C1	543	0,098	0,94	0,81	0,165
C2	820	0,127	0,87	0,81	0,350

The analysis of a number and the area fraction of non-metallic particles indicate
a positive influence of the treatment of steel with calcium. In all of the tested samples after the CaSi treatment the number and area fraction of plastic and non-plastic particles were lower.

The results of examination, i.e. number, area fraction and shape coefficient of non-plastic particles show that the calcium treatment effects do not depend on the volume of the Ca addition within the range analysed of Ca/Al = 0,0247÷0,0350 (Table 1).

Table 2. **The results of quantitative evaluation of plastic of non-metallic inclusions.**

Melt	Number of non-metallic particles, (N_A) / mm^{-2}	Area fraction of non-metallic particles, (A_A) / %	Mean area of particles / μm^2	Shape coefficient / ξ	Ca/S
O1	109	0,071	9,80	0,37	-
O2	270	0,085	4,42	0,42	-
A1	156	0,050	5,25	0,39	0,262
A2	127	0,027	5,36	0,44	0,300
A3	78	0,021	2,87	0,53	0,087
B1	222	0,038	2,54	0,49	0,250
B2	120	0,012	1,04	0,63	0,350
B3	161	0,026	1,09	0,54	0,550
C1	76	0,007	0,72	0,58	0,757
C2	89	0,008	0,42	0,63	1,167

Comparing the results obtained with the melts without calcium treatment, it is worth to mention that the area fraction of non-plastic particles decreases within the range of 0÷66 %, the mean area decreases only slightly (4÷33 %) while the increase of the shape coefficient values is in the range of 0,73 to 0,85. The addition calcium for aluminium-killed stells causes globularisa-tion of particles as well as their inconside-rable breaking up. The best result were obtained for melt B2 with Ca/Al = 0,112.

In comparison with steels without the calcium treatment the addition of calcium for aluminium-killed steels in the amount which enables obtaining Ca/S < 0,7 leads to. The decrease of the area fraction, mean area and increase of shape coefficient of plastic particles. For Ca/S > 0,7 the number of plastic particles is decreased by ca. 55 %, the area fraction by ca. 90 %, the mean area by more than that and value of shape coefficient is increased by ca. 50 % are found. Such a decrease of the number, the area fraction and the mean area of plastic particles proves the positive influence of calcium treatment on the steel cleannes, whereas the increase of the shape coefficient proves the globularisation of other particles remaining in the steel.

In the following figures, the distributions of the area fraction and number of non-metallic inclusions with regard to their shape coefficient (Figure 4), elongation F_x/F_y (Figure 5) and length (Figure 6) is shown.

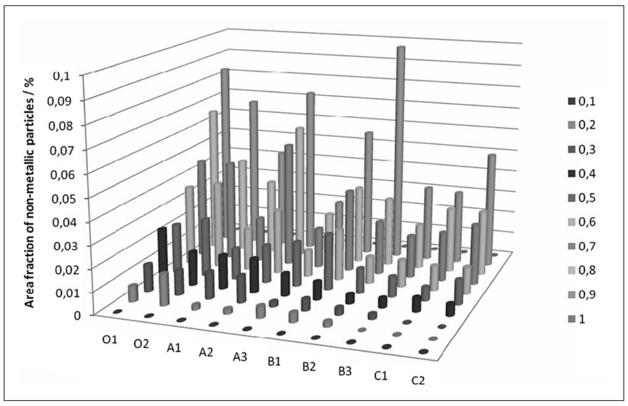

Figure 4. Distributions of the area fraction of non-metallic inclusions with regard to their shape coefficient.

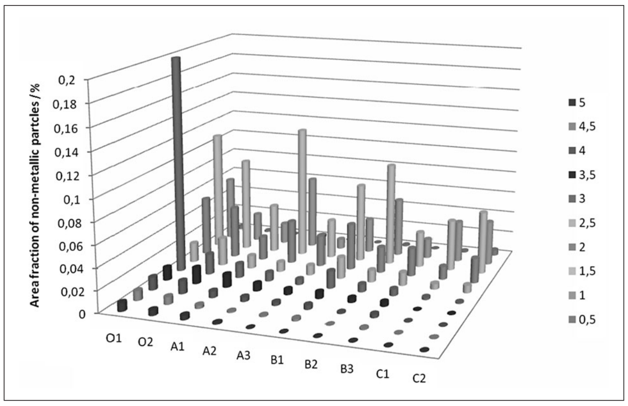

Figure 5. Distributions of the area fraction of non-metallic inclusions with regard to their elongation F_x/F_y.

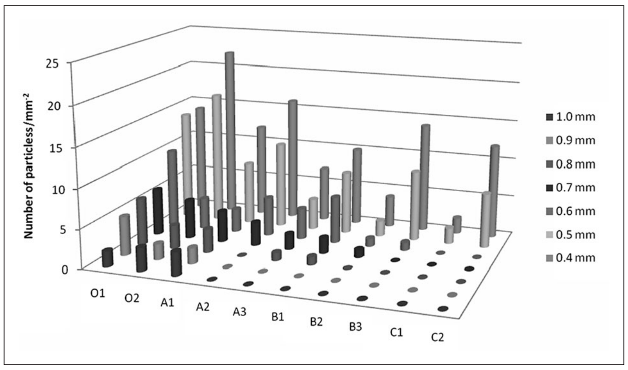

Figure 6. Distributions of the number of non-metallic inclusions regard to their length in the tested constructional steel.

The results provided indicate that the calcium treatment of aluminium-killed steels leads to:

- a decrease of area fraction of particles characterised by the lowest values of the shape coefficient (Figure 4). The best results were obtained for melts C1 and C2 (Ca/Al>0,14 and Ca/S>0,7); below the level of 0,4 of shape coefficient no inclusions have been found;
- a decrease of area fraction of particles of the largest elongation of F_x/F_y (Figure 5). The best results have been obtained for melts C1 and C2 (Ca/Al>0.14 and Ca/S>0,7), where inclusions of elongation exceeding 3,0 have not been found;
- a decrease of the number of long non-metallic particles (Figure 6). A considerable decrease of the number of inclusions of the length below 0,7 mm has been attained for melts A3, B1÷B3 and C1, C2, and the largest one for melts C1 and C2, where no inclusions longer than 0,5 mm have been found.

One of the two steps could be the rate-controlling for the interaction between the liquid calcium aluminate and solid alumina: (1) calcium diffusion in the liquid calcium aluminate layer, or (2) the chemi-cal reaction at the alumina/calcium alumi-nate interface. If the rate is controlled by the calcium diffusion in the liquid product layer there should be a significant calcium concentration gradient in the liquid product layer [9, 10].

CONCLUSIONS

The calcium treatment of aluminium-killed steels leads to the modification of non-metallic inclusions and the change of their chemical composition and plastic deformability. Based on the results of the examinations presented, the following conclusions are drawn:

1. In aluminium-killed steel treated with calcium, the most numerous inclusions are oxide-sulphides with an oxide core and a sulphide surface layer.
2. The addition of calcium to the steel has a positive influence on the steel cleannes by decreasing the number and area fraction of non-metallic inclusions.
3. The addition of calcium to the steel in an amount ensuring that Ca/Al>0,14 and Ca/S>0,7 leads to considerable decrease of the number and area fraction of long inclusions as well as their high plastic deformability.
4. The addition of calcium to the aluminium-killed steel has a positive influence on globularisation of other inclusions remaining in steel.

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Note: The responsible translator for English language is the author T. Lis.