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THE USE OF BARIUM AND CALCIUM ALLOYS IN THE LADLE FURNACE TREATMENT OF SELECTED GRADES OF CONTINUOUSLY CAST STEELS

ZASTOSOWANIE STOPÓW BARU I WAPNIA W OBRÓBCE POZAPIECOWEJ WYBRANYCH GATUNKÓW STALI ODLEWANYCH W SPOSÓB CIĄGŁY

The subject of the paper are the results of laboratory and industrial investigations into the use of Si – Ca – Ba alloys for modifying non-metallic inclusions. Based on laboratory tests, the morphology and chemical composition of non-metallic inclusions in carbon steel were examined before and after refining with the use of the above-mentioned alloy as a refining addition. In particular tests, variable additions of the alloy were used at a constant refining time and temperature.

Comparison of the process of casting of a sequence of seven heats of the same steel grade using the stopper system in the tundish was made under industrial conditions. In these heats, additions of Si – Ca (three heats) and Si – Ca – Ba (four heats) were introduced as a non-metallic inclusion modifier in the form of core wires during the process in the ladle furnace. For the investigated heats, the contents of total oxygen and calcium were assayed in the finished steel. A significant effect of the simultaneous addition of barium and calcium on steel castability, and thus on the process of continuous casting of the investigated heats, was found.

Keywords: continuous casting of steel, non-metallic inclusion modification, calcium – barium alloy, steel castability

Przedmiotem opracowania są wyniki badań laboratoryjnych oraz przemysłowych, dotyczących zastosowania stopów Si – Ca – Ba do modyfikacji wtrąceń niemetalicznych. Na podstawie badań laboratoryjnych zbadano morfologię i skład chemiczny wtrąceń niemetalicznych w stali węglowej przed i po rafinacji przy zastosowaniu ww. stopu w charakterze dodatku rafinacyjnego. W poszczególnych próbach zastosowano zmienne dodatki stopu przy stałym czasie i temperaturze rafinacji.

W warunkach przemysłowych dokonano porównania przebiegu odlewania sekwencji siedmiu wytopów tego samego gatunku stali z zastosowaniem układu zatyczkowego w kadzi pośredniej. W wytopach tych podczas procesu w piecu kadziowym wprowadzono w charakterze modyfikatora wtrąceń niemetalicznych dodatki Si – Ca (trzy wytopy) oraz Si – Ca – Ba (cztery wytopy) w postaci drutów rdzeniowych. Dla badanych wytopów w gotowej stali oznaczono zawartości tlenu całkowitego oraz wapnia. Stwierdzono istotny wpływ jednoczesnego dodatku baru i wapnia na leżność stali, a tym samym na przebieg ciągłego odlewania badanych wytopów

1. Introduction

The contemporary technologies of ladle furnace treatment and continuous steel casting stay in a close relationship. On the one hand, refining processes are required to provide metallurgical purity adequate to meet the requirements for the manufactured grade and, on the other hand, the thermal condition of the liquid metal, as well as the form of non-metallic inclusions contained in it, should ensure the undisturbed process of continuous casting of a sequence of heats.

The research direction called "Non-metallic inclusion engineering", which has been developed for many years, and especially intensively in recent times, is currently geared to achieving two basic goals:

1. to minimize the quantity and optimize the shape and distribution in the metallic matrix of non-metallic inclusions

(NMIs) left after metallurgical processes with respect to steels of special plastic and mechanical properties,

2. to precisely control the chemical composition of NMIs to ensure the undisturbed continuous casting process with the use of the system of ceramic sheaths of streams and the stopper system in the tundish (to eliminate the clogging of submerged entry nozzles (SEN) in tundishes).

A justification for the above claims can be provided by the currently applicable standards for the purity of steels intended for rolling bearings of the highest quality demands, in which the total oxygen concentration shall be less than $T[O] \leq 10$ ppm, while the maximum size of non-metallic inclusions shall not be greater than $15 \mu\text{m}$. Similar demands are imposed on steels intended for the production of car tyre cords, for which the NMI size may not be greater than $10 \mu\text{m}$ [1].

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A measure of progress in the area of NMI engineering is the definition of the steel with "zero non-metallic inclusion contents", introduced by Fukumoto and Mitchell [2] as early as in 1991. In line with this definition, if the NMI size is smaller than $1\mu\text{m}$, and the distance between adjacent non-metallic inclusions is larger than $10\mu\text{m}$, then such non-metallic inclusions will not have any effect on the properties of the metallic matrix on a macro scale. Such a state can be called "zero non-metallic inclusion contents" [2]. Although no such metallurgical steel purity has been managed to achieve so far, even in laboratory conditions, yet this definition does indicate a direction for the development of special steel refining processes and technologies. Achieving the above-mentioned goals and, in actual steelmaking technologies, manufacturing steel with the complete control of the NMI morphology, requires the application of advanced refining processes and the knowledge of the thermodynamic and kinetic conditions of the course of chemical reactions, and the properties and conditions of flotation of (most often complex) chemical compounds making up non-metallic inclusions.

2. Theoretical fundamentals

The use of alkaline earth metals, mainly calcium, in the processes of iron metallurgy has been known for many years, but still research is continued to more fully understand their interactions with harmful elements in iron alloys, and especially in advanced steel refining processes. Many of those interactions are more extensively studied, in particular using modern research techniques and apparatus [3-5]. The use of the metals of group IIA of the periodic system, i.e. strontium and barium, as refining materials is much less investigated and understood. An example can be the lack of data on the thermodynamic behaviour concerning the interaction of these elements with harmful components, as well as with NMIs existing in iron alloys.

With respect to barium, this information provided in available databases is very scanty. It is therefore justifiable to provide information comparing selected physicochemical properties of alkaline metals, based on which it would be possible to determine their behaviour at the temperatures of steelmaking processes and during adding them to liquid iron alloys. Selected data is presented in Table 1.

TABLE 1
Selected properties of alkaline earth metals [6, 7]

Property	Element			
	Mg	Ca	Sr	Ba
Density, $\text{kg}\cdot\text{m}^{-3}$	1740	1540	2630	3750
Atomic radius, nm	0.172	0.197	0.215	0.278
Melting point, K	923	1112	1041	1002
Boiling point, K	1363	1757	1640	1910
Vapour partial pressure of 1873 K, MPa	2.038	0.184	0.462	0.0303
Maximum solubility in iron (1873 K, 0.1 MPa), ppm	6900	170÷340	36	4 ^[7] , 43 ^[6]

By examining the data in Table 1, it can be found that the alkaline metals are characterized by a relatively low melting point, and the boiling point is only for barium higher than the melting point of pure iron. An equally important property decisive to the losses of an element taking part in reactions with harmful admixtures, as well as the method of its introduction to the liquid metal, is the vapour pressure at steelmaking process temperatures. Only barium does exhibit a vapour pressure lower than 0.1 MPa at a temperature of 1873 K. A characteristic feature of all alkaline metals is low solubility in liquid iron and its alloys; for barium, it is only trace, though there is no definite data available.

The solubility of alkaline metals in liquid iron increases with the increase in temperature, and this relationship is described by Equation (1), [6]:

$$\lg [\% Ba] = 6.86 - \frac{18100}{T} \quad (1)$$

Equation (1) shows that the solubility of barium in pure liquid iron at a temperature of 1773 K is 0.00044%, while at 1873 it increases to 0.00157%. Alkaline earth metals exhibit also another common feature: their solubility in liquid iron increases with increasing nickel concentration, and decreases with the increase in chromium concentration [8]. It should be emphasized, however, that this increase due to nickel is much greater than the decrease with increasing chromium content. It is essential to note that, in the binary system, calcium and barium exhibit unlimited mutual solubility in the temperature range above 1115 K [6].

Alkaline earth metals are characterized by high chemical affinity with many harmful elements removed in a majority during refining processes, and the products of occurring reactions – chiefly with oxygen and sulphur, constitute components of non-metallic inclusions. Equally important is the modifying interaction of alkaline metal additions with previously formed aluminium or silicon oxides. Comparison of the values of the standard Gibbs free energy of formation of calcium and barium oxides and sulphides is presented in Table 2.

The relationships and the values of the energy of formation ΔG° for selected chemical compounds, being potential NMI components, provided in Table 2, suggest that their formation in the temperature range of steel refining processes is possible from the thermodynamic point of view. The contribution of individual reactions to the development of the composition of forming NMIs is dependent on a number of factors of a thermodynamic and kinetic nature; indeed, it should be noted that the change in the chemical composition of the NMIs results not only from the occurring reactions, but also from coagulation and coalescence processes that take place as the NMIs move within the bulk of liquid metal.

The quantity of the addition of calcium or calcium and barium designed for modifying the non-metallic inclusions should be selected so that the reactions proceeding with the participation of aluminium oxides will result in the formation of chemical compounds with the lowest possible melting point, according to Fig. 1.

As follows from Fig. 1, only the compounds $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ and $3\text{CaO}\cdot \text{Al}_2\text{O}_3$ do exhibit a melting point lower than the temperature of refining of continuous steel casting, thus, in the majority of steelmaking technology stages,

TABLE 2

Dependence of standard Gibbs free energy of formation of calcium and barium oxides and sulphides vs. temperature [9÷11]

Reaction	$\Delta G^\circ = f(T)$	ΔG_{1873} , kJ/mol	Temperature range
$\text{Ca}_{(l)} + [\text{O}]_{1\%, \text{Fe}} \rightarrow (\text{CaO})_{(s)}$	$\Delta G^\circ = -482920 + 108 \cdot T$	-280,6	$T < 3200 \text{ K}$
$\text{Ca}_{(l)} + [\text{S}]_{1\%, \text{Fe}} \rightarrow (\text{CaS})_{(s)}$	$\Delta G^\circ = -419900 + 101 \cdot T$	230,7	$T < 2798 \text{ K}$
$\text{Ba}_{(l)} + [\text{O}]_{1\%, \text{Fe}} \rightarrow (\text{BaO})_{(s)}$	$\Delta G^\circ = -492850 + 140 \cdot T$	-229,9	$T < 1895 \text{ K}$
$\text{Ba}_{(l)} + [\text{S}]_{1\%, \text{Fe}} \rightarrow (\text{BaS})_{(s)}$	$\Delta G^\circ = -409120 + 221 \cdot T$	-221,6	$T < 1895 \text{ K}$
$12\text{CaO}_{(s)} + 7\text{Al}_2\text{O}_3_{(s)} \rightarrow 12\text{CaO} \cdot 7\text{Al}_2\text{O}_3_{(l)}$	$\Delta G^\circ = 617977 - 612 \cdot T$	-528,3	$T < 1728 \text{ K}$
$3\text{CaO}_{(s)} + \text{Al}_2\text{O}_3_{(s)} \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3_{(l)}$	$\Delta G^\circ = -12558 - 24,7 \cdot T$	-58,8	$T > 1808 \text{ K}$
$3\text{BaO}_{(s)} + \text{Al}_2\text{O}_3_{(s)} \rightarrow 3\text{BaO} \cdot \text{Al}_2\text{O}_3_{(s)}$	$\Delta G^\circ = -212230 - 18,8 \cdot T$	-247,5	$T < 2023 \text{ K}$
$\text{BaO}_{(s)} + \text{Al}_2\text{O}_3_{(s)} \rightarrow \text{BaO} \cdot \text{Al}_2\text{O}_3_{(s)}$	$\Delta G^\circ = -124324 - 6,69 \cdot T$	-224,7	$T < 2103 \text{ K}$

TABLE 3

Chemical composition of steel used in the laboratory investigations

Element content, wt. %											
C	Mn	Si	P	S	Cr	Ni	Cu	Al	Sn	Ca	N
0,19	0,79	0,20	0,009	0,014	0,03	0,05	0,15	0,024	0,011	0,0012	0,0095

they remain in a liquid state. This observation is essential when determining the optimal addition of calcium (or Ca + Ba) that will ensure the liquid state of calcium – alumina inclusions, that is maintaining the proportion: 51% Al_2O_3 and 49% CaO.

Equally important it is to allow for the possibility of formation of calcium sulphide (CaS) during the processes of NMI refining and modifying using calcium, whose melting point is about 2773 K, which means that it is a solid phase in the steel casting temperature range.

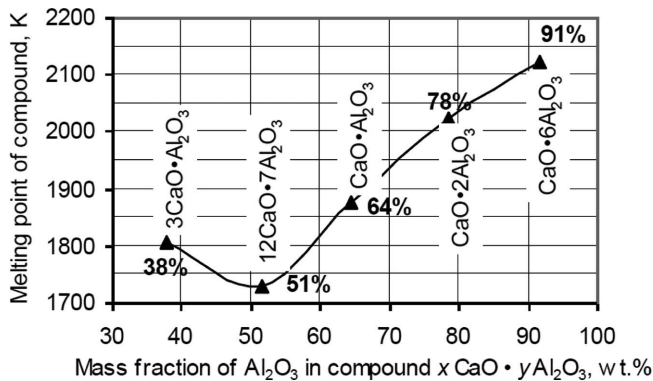


Fig. 1. Dependence of melting point of calcium aluminates on their chemical composition

The ability of NMIs to floating from the liquid metal is determined not only by their state of aggregation, but also their density, size and shape, as well as the interface tension at the „metal – NMI” phase boundary ($\sigma_{\text{Fe-Al}_2\text{O}_3} \approx 1.0 \text{ J} \cdot \text{m}^{-2}$, while for iron silicates, $\sigma_{\text{Fe-SiO}_2-\text{FeO}} \approx 0.4 \text{ J} \cdot \text{m}^{-2}$). The value of interface tension determines, e.g., the wettability of NMIs by the liquid metal (a high value of $\sigma_{\text{Fe-WN}}$ – low wettability), as well as the intensity of nucleation of a new phase (at lower interface tensions and high supersaturation values, the nucleation intensity increases). Pure aluminium oxide (Al_2O_3) has a density of $3960 \text{ kg} \cdot \text{m}^{-3}$, while the density of the compound $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ is $2830 \text{ kg} \cdot \text{m}^{-3}$, whereby the greater difference in density between liquid steel and $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ will favour the flotation of the latter.

3. The investigation methodology

The subject of investigation was commercial low-carbon steel with chemical composition, as shown in Table 3, smelted in the electric arc furnace, subjected to secondary metallurgical treatment in the ladle furnace, and continuously cast into square cross-section billets that were subsequently rolled into $\text{Ø}30 \text{ mm}$ round bars.

This steel was deoxidized during tapping from the furnace with the addition of aluminium in the amount of about 1.0 kg/t of steel, with supplementing this element during the ladle furnace process, where the Si – Ca alloy was also added in the form of core wire to modify the NMIs. From the round bars rolled out of the steel with composition as given in Table 3, $\text{Ø}30 \text{ mm}$ -diameter cylindrical specimens were made with a special chamber in the lower part, in which the addition of

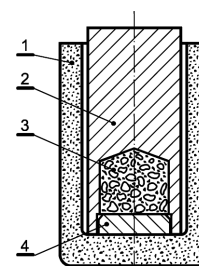


Fig. 2. The shape of a metal specimen before remelting, 1 – magnesia crucible, 2 – steel specimen, 3 – refining agent, 4 – steel plug

the refining agent was put, and then it was closed with a steel plug (made of the same steel grade) and placed in an technical purity magnesia crucible (Fig. 2).

In laboratory tests, the Si – Ca – Ba alloy of the following chemical composition was used as a refining agent:

TABLE 4
Chemical composition of the Si – Ca – Ba alloy

Element content, wt. %					
Si	Ca	Ba	Al	C	Fe
56,47	15,82	15,48	1,47	0,26	10,50

A variable addition of the refining agent mass was used in individual refining tests; the duration of refining was 15 and 30 minutes, respectively, at a temperature of 1823K (1550°C). The liquidus temperature of the investigated steel is about 1793K (1520°C. Conditions in which particular refining tests were carried out are specified in Table 5.

TABLE 5
The mass of the refining agent addition and the refining duration in particular tests

Probe №	Refining agent addition, wt. %	Refining time, min.
1	0,05	15
2	0,1	15
3	0,5	15
4	1	15
5	0,1	30
6	0,25	30
7	0,5	30

After remelting and refining, while maintaining the conditions specified in Table 5, steel specimens of a diameter of approx. Ø32 mm and a height of 50 mm had the upper and lower surfaces ground, and then they were cut in the middle into two parts, as per Fig. 3. On the indicated surfaces, the quantitative and qualitative analysis of NMIs was made, including the so called "0" specimen, which was made up of steel after remelting and with no refining agent addition.

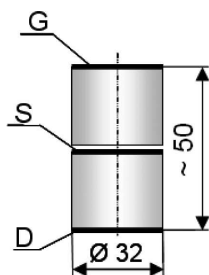


Fig. 3. A schematic diagram illustrating the arrangement of the planes in the metal specimen after refining, on which the analysis of NMIs was made; G – specimen top, S – specimen centre, D – specimen bottom

The quantitative analysis was made using optical microscopy with the following parameters:

- Magnification, 500x;
- Number of analyzed fields, 30 (10 on each surface i.e. G S, D)
- Specimen surface area covered by measurement: (3×0.221mm² /surface ≈ 0,7 mm²)
- Minimum NMI size for: the equivalent diameter, length, and the maximum Feret diameter, 0,4÷1,4µm.

The following NMI parameters were determined: the number of inclusions on the analyzed surface, the inclusion surface area fraction, the equivalent inclusion diameter, the Feret diameter and the shape factor. The qualitative analysis of NMIs was made with an Inspect F scanning microscope equipped with EDS (Energy Dispersion Spectrometer) detectors.

4. Investigation results and their analysis

4.1. Laboratory tests

Out of numerous relationships that were determined as a result of the tests carried out, the effect of the refining agent mass on the quantity of NMIs identified on the analyzed surface in three steel specimen planes: the top, central and bottom planes, as per the schematic diagram shown in Fig. 3, is illustrated in Figures 4, 5 and 6. When comparing these quantities with the quantity of NMIs in the unrefined steel it can be noticed that as a result of refining lasting for 15 minutes the quantity of NMIs left in the metal has been reduced by approx. 2÷3 times. A regularity has been found that the largest quantity of NMIs after 15 minutes of refining occurs in the top plane of the specimen, as it is in this plane that the floating inclusions concentrate. A Si – Ca – Ba alloy addition greater than 0.05 wt.% of metal mass is not justifiable in respect of the quantity of removed NMIs. Extending the refining duration to 30 minutes increases the quantity of removed NMIs; however, this increase is not very large. The qualitative NMI analysis was started with the identification of typical NMIs in the "raw" material, i.e. in the commercial steel used in the tests without refining with the Ca – Ba alloy.

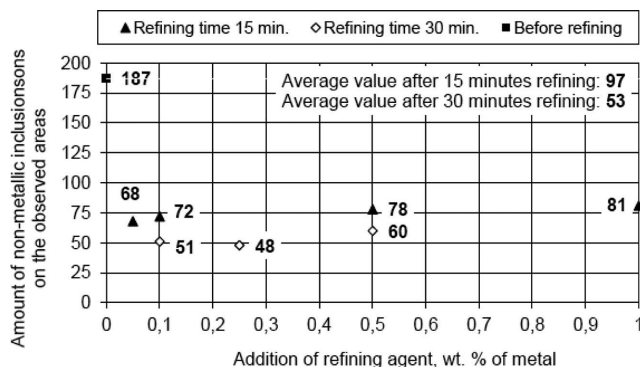


Fig. 4. The effect of the refining agent addition amount on the quantity of non-metallic inclusions in the top specimen plane after low-carbon steel refining

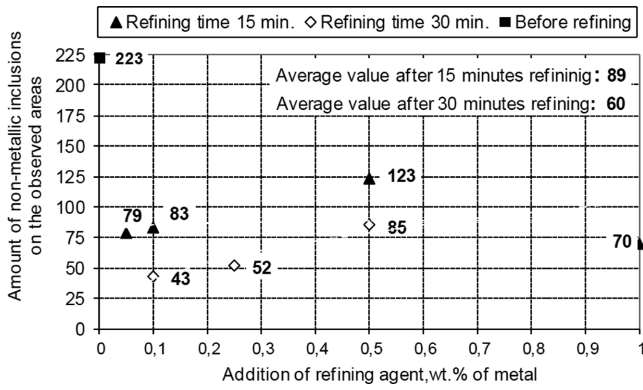


Fig. 5. The effect of the refining agent addition amount on the quantity of non-metallic inclusions in the central specimen plane after low-carbon steel refining

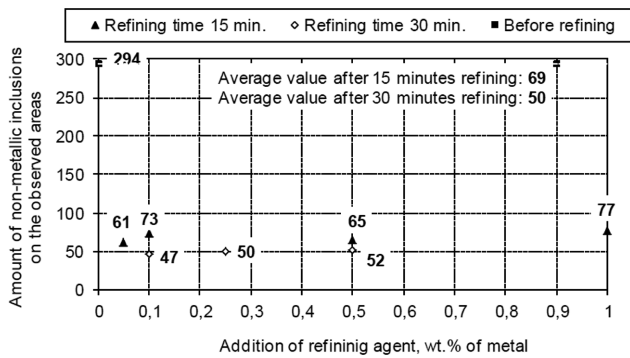


Fig. 6. The effect of the refining agent addition amount on the quantity of non-metallic inclusions in the bottom specimen plane after low-carbon steel refining

It should be noted that the observation of non-metallic inclusions in the rolled bar material before refining found a considerable quantity of inclusions that, as could be judged by their shape and chemical composition, had undergone modification with the participation of calcium. The characteristic and unmodified NMIs occurring in this material, though not in a very large numbers, are illustrated in Fig. 7a, while Fig. 7b shows the EDS spectrum of this inclusion, along with chemical composition of the phase denoted as "1" in Fig. 7a (the table on the figure 7b).

This inclusion is not very large – with a size of approx. 16 μm; however, it forms an irregular body with sharp corners, and the floating of this type of inclusions from the liquid metal is considerably more difficult compared to globular inclusions. It is made up primarily of a mixture of aluminium and silicon oxides with a slight amount of calcium oxide (16.02 wt%). If the Al₂O₃ : CaO fraction 37.97 wt.% : 16.02 wt.% (convert Ca wt.% and Al wt.% in Table 7b to the wt.% of their oxides, respectively) determined in this inclusion is related to the proportion of these components in low-melting, properly modified NMIs (Fig. 1), it will be justifiable to conclude that the inclusions occurring in the investigated material are unmodified inclusions.

Similar conclusions can be drawn from the EDS spectrum displayed in Fig. 8 and the chemical composition given in the table for the second phase dominant in the inclusion shown in Fig. 7, denoted with the number "2". The Al₂O₃ : CaO concentration ratio, being even smaller than in phase "1", indicates the lack of the desirable chemical composition of this NMI.

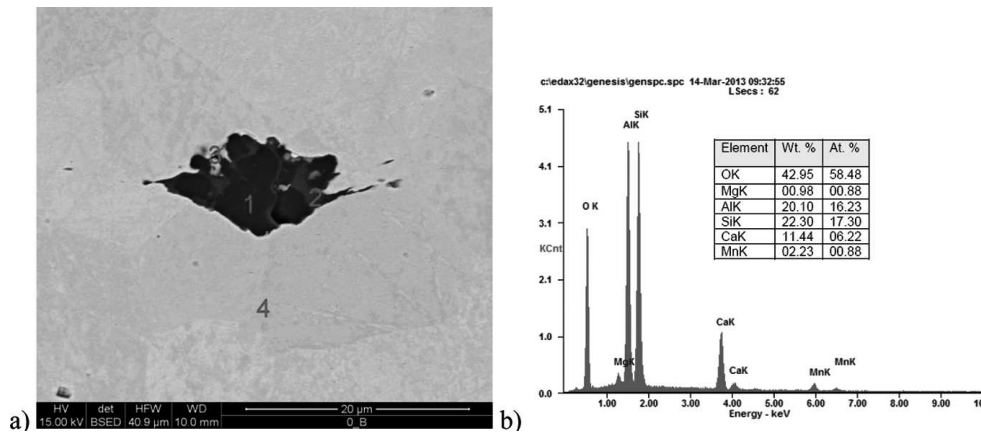


Fig. 7. a. An example of NMIs identified in steel specimen "0" prior to refining with Ca – Ba alloy; Fig. 7b. The EDS spectrum of phase "1" of the non-metallic inclusion visible in Fig. 7a

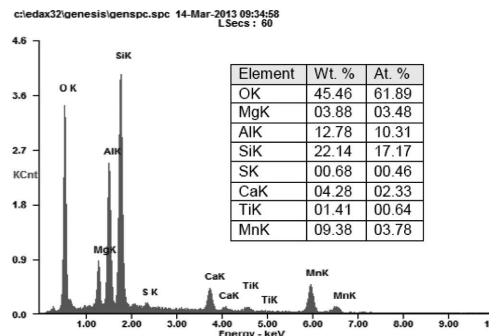


Fig. 8. The EDS spectrum of phase "2" of the non-metallic inclusion visible in Fig. 7a

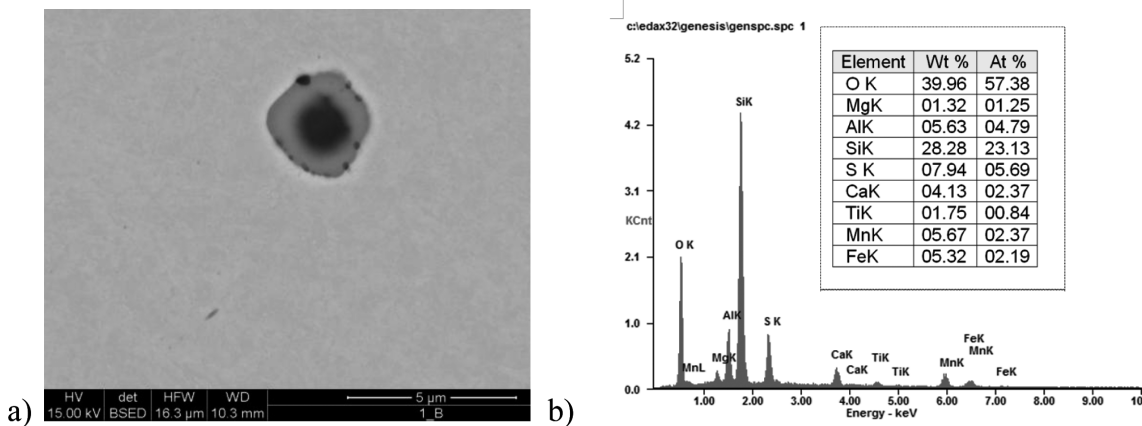


Fig. 9. a). Shape of the NMI after refining of steel with using of Si – Ca – Ba alloy (0.1 wt.% of metal), refining time 15 min; top specimen plane, b) EDS – spectrum and chemical composition of NMI visible in Fig. 9a (grey, outer region)

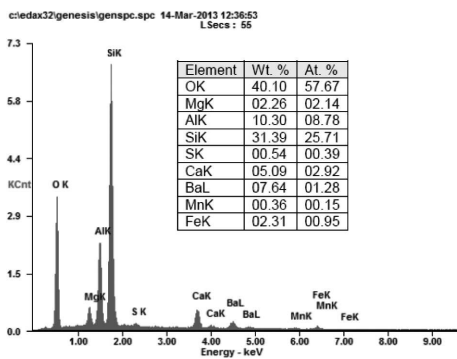


Fig. 10. EDS – spectrum and chemical composition of NMI visible in Fig. 9a (dark, internal region)

As a result of the refining of the investigated steel performed with the Si – Ca – Ba alloy for a duration of 15 and 30 minutes, practically a complete NMI modification was achieved. On the examined surfaces, NMIs were dominant, whose most characteristic form is represented in Fig. 9 and their chemical composition in Figs 9b and 10.

A definite majority of the observed NMIs were inclusions of a globular type, with diameters of approx. 1 ÷ 3 μm. Chemical composition of these inclusions indicates that the sum of their CaO + BaO contents (16.88 wt.%) is approximately equal to the content of Al₂O₃ (19.45 wt.%), which, if related to Fig. 1, suggests that at the refining temperature, i.e. 1823K, these were liquid inclusions. This is also indicative of the coupled effect of calcium and barium in the modification of NMIs. At the same time, the extremely small sizes of these inclusions and their shape very approximate to the spherical one, provide evidence for meeting the main objective of NMI modification, with a favourable effect on the steel properties.

The qualitative analysis of NMIs in the test specimens, regardless of the position of the plane in the metal specimen (*G, S, D* Fig. 3) showed that barium compounds occurred only occasionally in the examined inclusions, in spite of the fact that they had a globular shape, which suggest a modifying effect of both elements contained in the refining agent material.

This regularity can be explained by the easier flotation from the liquid metal of complex inclusions containing, e.g., barium oxide (BaO), due to their much larger size compared to inclusions composed of CaO, which results from the mag-

nitudes of the atomic radii of barium and calcium (Table 1) [6, 12]. In spite of the fact that calcium is characterized by higher NMI modification capabilities compared to barium, the strong effect of barium on the activity of calcium in liquid iron solutions containing oxygen clearly enhanced this capability of calcium in interactions with NMIs, among other things, as a result of reducing the calcium vapour pressure due to the presence of barium.

4.2. Tests out under industrial conditions

To verify the usefulness of the Si – Ca – Ba alloy for NMI modification under industrial conditions, comparison of the process of casting a sequence of seven heats of the same steel grade C45E using the tundish stopper system was made. In those heats, additions of Si – Ca (three heats) and Si – Ca (15 wt.%) – Ba (15 wt.%) (four heats) were introduced as a non-metallic inclusion modifier in the form of core wires during the process in the ladle furnace. Chemical composition of the steel from the seven heats examined and the ladle furnace treatment duration are given in Table 6.

TABLE 6
Chemical composition of C45E steel grade from the industrial heats refined with using of Si – Ca and Si – Ca – Ba alloys

Heat №	Element content, wt. %							
	C	Mn	Si	S	Al _{ca}	Al _{met}	Ca, ppm	O _{ca} , ppm
1	0.44	0.72	0.23	0.013	0.011	0.010	23	25
2	0.44	0.75	0.19	0.014	0.011	0.009	22	18
3	0.43	0.71	0.21	0.014	0.010	0.008	9	16
4	0.46	0.70	0.20	0.008	0.010	0.008	20	16
5	0.46	0.70	0.20	0.011	0.010	0.008	10	24
6	0.46	0.71	0.21	0.016	0.012	0.010	9	30
7	0.43	0.71	0.23	0.013	0.011	0.010	10	22

Note: Heats no. 3, 5, 6, 7 – addition of Si – Ca – Ba alloy, heats no. 1, 2 and 4 – addition of Si – Ca alloy

The examination of the chemical composition of steel C45E, provided in Table 6, shows a very high level of its met-

allurgical purity, relatively low sulphur contents and very low total oxygen contents. In heats nos. 1, 2, 4 (Table 6), to which the Si – Ca alloy was introduced as a NMI modifier, higher calcium contents, on average by about 22 ppm, were found, whereas in the heats with the Si – Ca – Ba alloy addition, by half less, that is 9.5 ppm on average. At the same time, difficulties were found during continuous casting of the heats with the Si – Ca alloy addition, which involved the consistent deposition of NMIs in the tundish nozzles, as indicated by the tendency to the increasing opening of the stoppers in the tundish system during the course of casting (Figs. 11 and 12).

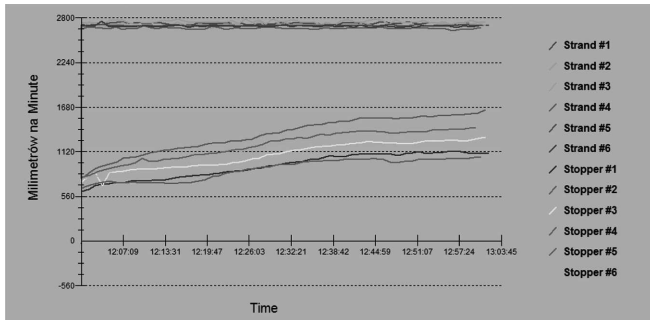


Fig. 11. Change in the position of the tundish stoppers in real time during continuous casting of heat no. 1 with the addition of the Si – Ca alloy

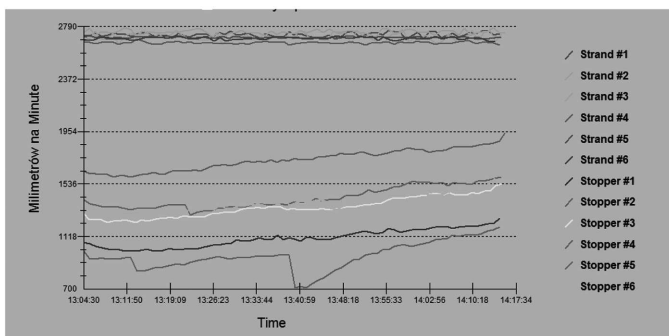


Fig. 12. Change in the position of the tundish stoppers in real time during continuous casting of heat no. 2 with the addition of the Si – Ca alloy

A quite opposite tendency was observed during continuous casting of the heats, for which the Si – Ca – Ba alloy was used as a NMI modifying material in the amount identical as for the heats with the use of the Si – Ca alloy (Figs. 13, 14, 15).

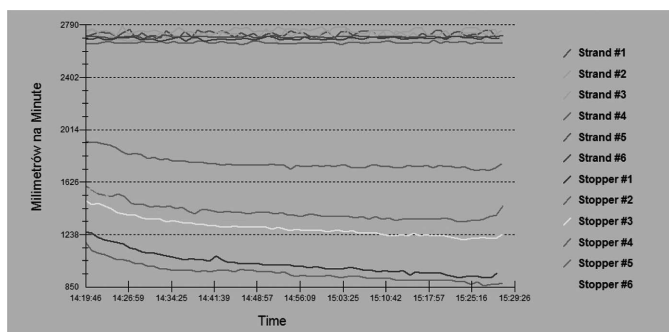


Fig. 13. Change in the position of the tundish stoppers in real time during continuous casting of heat no. 3 with the addition of the Si – Ca – Ba alloy

The automatic stopper position regulation system controlled towards the lowering of the stoppers, as indicated by the complete absence of NMI deposition in the tundish nozzles, and the effect of partial flushing of the discharge nozzles (heat no. 3), and in the subsequent heats of the sequence, the complete stabilization of the stoppers' position followed (Figs. 14, 15).

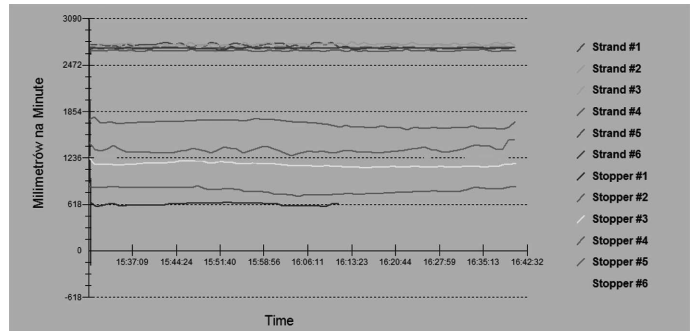


Fig. 14. Change in the position of the tundish stoppers in real time during continuous casting of heat no. 5 with the addition of the Si – Ca – Ba alloy

As indicated by the tundish stopper opening records shown in Figs. 13÷15, in the real time of heat casting, the state of modification of NMIs and thus the castability of the steel by using the Ca – Ba alloy added in the form of core wire in the ladle furnace was correct, since no phenomenon of NMI deposition in the nozzles occurred.

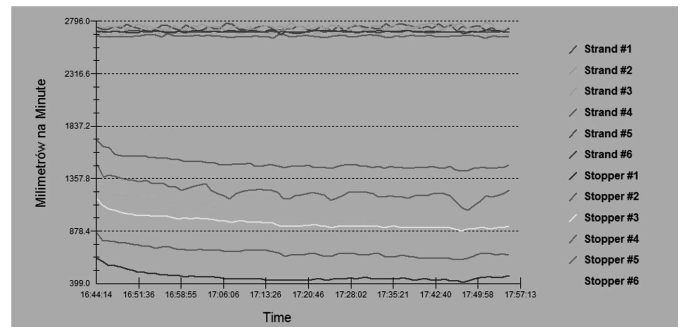


Fig. 15. Change in the position of the tundish stoppers in real time during continuous casting of heat no. 6 with the addition of the Si – Ca – Ba alloy

5. Summary

The use of the Si – Ca – Ba alloys in the processes of steel refining geared towards the modification of non-metallic inclusions (NMIs) is more advantageous than the modification with the Si – Ca alloys. By influencing the solubility of calcium in the liquid iron solution and reducing its vapour pressure, barium develops favourable conditions for the modification of non-metallic inclusions, especially aluminium oxides. The coupled effect of calcium and barium markedly reduces the number of NMIs by changing their physical properties, shape (globularization), and thus improving the floating conditions.

In the own laboratory tests, the Si – Ca – Ba alloy addition increasing above 0.05 wt.% had no significant effect on the overall number of NMIs in the refined steel. The addition of

the Si – Ca (15 wt.%) – Ba(15 wt.%) alloy considerably improves the castability of steel during continuous casting, which allows the undisturbed casting of the sequence of heats.

REFERENCES

- [1] L. Zhang, B.G. Thomas, 85th Steelmaking Conference Proceedings, ISS-AIME, Warrendale, PA, 431 (2002).
- [2] Z. Xue, Y. Weng, Z. Li, Steel Research International **76**, 10, 735 (2005).
- [3] W. Tiekink, B. Santillana, R. Kooter, F. Mensonides, B. Deo, R. Boom, AISTech Conference Proceedings **2**, May 1-4, Cleveland, Ohio, USA, 395 (2006).
- [4] P. Migas, M. Karbowniczek, Archives of Metallurgy and Materials **55**, 1147 (2010).
- [5] M. Karbowniczek, E. Kawecka-Cebula, K. Pytel, Steel Research International **74**, 10, 610 (2003).
- [6] K. Mukai, O. Han, ISIJ International **39**, 7, 625 (1999).
- [7] M. Breitzmann, H.J. Engell, D. Janke, Steel Research **59**, 7, 289 (1988).
- [8] M. Karbowniczek, E. Kawecka-Cebula, J. Reichel, Metallurgical Transactions B **43B**, June, 554 (2012).
- [9] H. Ono, Metallurgical Transactions B, **24B**, June, 487 (1993).
- [10] E.T. Turkdogan, Physical Chemistry of High Temperature Technology, New York, Academic Press (1980).
- [11] Y. Mioneura, ISIJ International **30**, 3, 192 (1990).
- [12] Y. Li, Z.-H. Jiang, Y. Liu, Chem. Eng. Mineral Process **14** (3/4), 439 (2006).