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The Analysis of the Effect of Mischmetal Addition on the Formation of Non-Metallic Inclusions in Liquid Steel

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Abstract

The study focuses on the effect of rare earth elements (REM) in mischmetal on the morphology and chemical composition of non-metallic inclusions in pre-oxidised steel. Calculations were carried out using the WYK_STAL computer program according to two calculation models, considering/ignoring the sulphur partition coefficient at the liquid steel-liquid slag interfacial boundary. It was found that the chemical composition of the resulting precipitates is a consequence of the order in which deoxidising additives were admixed. Simulations confirmed the presence of Ce oxides and sulphides. This was also confirmed by the analysis of samples taken from the steel ingot after laboratory melting. Non-metallic inclusions Ce_2O_3 and CeS, and the complex of precipitates: La_2O_3-Ce_2O_3 was also identified in the steel. Introduction of mischmetal in the final stage refining is the most effective method. Therefore, the oxygen content is reduced below 0.001%, and the sulphfur content can be reduced to 0.004%.

Key words: Mischmetal, Steel, Non-metallic inclusions, Deoxidation

1. Introduction

Rare-earth metals are known as lanthanides. The International Union of Pure and Applied Chemistry (IUPAC) defines REM as the lanthanide series (15 elements): La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu with atomic numbers from 57 to 71 and two elements with REM-like properties: Sc, Y. The behavioral mechanism of rare-earth elements (REM) differs depending on the steel grade. Compared to alkaline earth metals (AEMs), REMs react with elements dissolved in liquid iron and during crystallization. REMs have a z-diameter in the range of 1.641A to 2.042A and are more electronegative than AEMs, so they lose electrons more easily and convert to positive ions and are therefore very chemically active in liquid steel. REMs show limited solubility in the Feα phase (0.1-0.5%) and low solubility in Feγ ≈0.04%. [1-3] The introduction of REM into steel results in deoxidation and desulphurization, the formation of non-metallic inclusions and the modification of pre-existing precipitates. Small additions (up to 0.10 per cent) of REM are consumed by reaction involving both oxygen and sulphur, as well as selenium, and at increased REM concentrations in steel they may form compounds with phosphorus, arsenic, antimony, lead, bismuth, tin, copper, nickel, and iron [1,4–6].

One of the most key features related to the presence of REM in steel is their modifying effect, which involves controlling the phenomenon of primary crystallization and changing the degree of fragmentation of the crystallizing phase. The introduction of REM micro-additives results in an improvement in the mechanical properties of the steel through a strengthening phenomenon, due to the formation of phases with limited solubility in the α-γ phase. Rare-earth elements have been found to increase the tensile strength of steel by inducing the crystallization of γ-Fe eutectics during the solidification process, which in turn increases the solidification temperature [4]. REM's modifying effect extends to altering the chemical composition, morphology and consequently the properties of non-metallic inclusions. Non-metallic inclusions modified with REM are like the steel matrix in terms of hardness, strength, brittleness, and thermal expansion. Consequently, they deform more easily with the steel matrix during rolling than other non-metallic inclusions present in the steel [6]. The modifying effect of REM is to transform detrimental inclusions, e.g., Al_2O_3, MnS by changing their morphology and composition, resulting in the formation of spherical REM oxysulphide inclusions, thereby improving the mechanical properties of the steel. For example, lanthanum [7] may have to act as a modifier of the inclusions, improving their shape and size and hindering the generation of high stress concentrations around such inclusions and improving the fatigue strength of the steel [7]. In steel metallurgy, cerium is commonly used; it also acts as a deoxidiser and removes sulphur, prevents the negative effects of hydrogen, phosphorus, arsenic and lead. At the same time, it has an important effect in the casting process, improving the microstructure of the steel ingots and contributing to changing the properties of non-metallic inclusions by modifying them; this includes changing the shape, size, and distribution of the inclusions. Research by Yu et al. [6] confirmed that the dosage of cerium into liquid steel resulted in the modification of pre-existing MnS and SiO_2 inclusions, which were transformed into fine $Ce_2O_3 \cdot SiO_2$ and Ce_2O_2S precipitations [6]. A similar phenomenon was observed by Wang, who studied the effect of yttrium on the modification of alumina inclusions. The results of industrial and laboratory tests of steels with REM elements can vary for the same steel grades, so for each steel grade the selection of REM and the way they are dosed should be determined experimentally. When REM are dosed, depending on the steel composition and heat removal conditions, a non-uniform distribution of REM-containing non-metallic inclusions is observed once the optimum amounts of this additive are exceeded [1].

2. Materials and methods

This paper presents the results of computer simulations on the deoxidation and desulphurisation because of the introduction of mischmetal into pre-deoxidised steel. The simulations were conducted by means of the WYK_Stal software, the results of which give comparable results to experiments conducted in real time during industrial refining in a 140 Mg ladle. The WYK_Stal computer program has been developed at AGH University of Krakow to support steel smelting and refining technology in terms of selecting optimal process parameters and introducing alloying additives [8]. By using parameters such as ladle size, mixing method and coefficients specific to these processes, a detailed study of the processes during deoxidation and desulphurisation, the formation and removal of non-metallic inclusions into the slag can be carried out. The software covers phenomena such as transport of reactants, dissolution, diffusion, chemical reactions in liquid steel, slag and at the steel-slag interfacial interface. Individual reactants can be introduced into the metal bath continuously or in batches. The addition of metallic components, e.g., Al or ferroalloys, can also be declared; other types of additions can also be introduced into the slag. For calculations, the software uses specific modules containing calculation models, databases of physico-chemical parameters of reactants and steel components, thermodynamic quantities of chemical reactions. User can declare changes in temperature, pressure and mixing intensity in the software or to make these changes during the simulation [9-12]. Fig. 1 shows the block diagram of the WYK_Stal software [8, 12]. Tables 1 and 2 present the standard Gibbs energy relationships for selected REM elements (La and Ce) and the interaction parameters of the reactants in steel. [12-18]

Table 1.
Standard Gibbs energy for a reaction

Reactions	ΔG_i^o /(J·mol^{-1})
$2[Ce] + 3[O] = Ce_2O_3(s)$	-1430 200 + 359T
$2[Ce] + 2[O] + [S] = Ce_2O_2S(s)$	-1352 700 + 331T
$[Ce] + [S] = CeS(s)$	-394 428 + 121T
$3[Ce] + 4[S] = Ce_3S_4(s)$	-1494 441 + 439T
$2[Ce] + Al_2O_3(s) = 2[Al] + Ce_2O_3(s)$	-1073 900 +326T
$Ce_2O_2S(s) + [O] = Ce_2O_3\ (s) + [S]$	-77 500 + 28T
$Ce_2S_3(s) + [Ce] + [S] = Ce_3S_4\ (s)$	-420 541 + 113T
$[Ce] + 5/2[O] + 1/2[Si] = 1/2Ce_2O_3(s) + SiO_2(s)$	-1106 635 + 286.11T
$[Ce] + 3/2\ [S] = 1/2Ce_2S_3(s)$	-536.420+163 86T
$[Ce] + [N] = CeN(s)$	-401 200+153.0T
$2[La] + 3[O] = La_2O_3(s)$	-1443 880 +337T
$2[La] + 2[O] + [S] = La_2O_2S(s)$	-1341200 + 301T
$[La]+[S]=LaS(s)$	-445180+141.5T
$[La]+[Al]+3[O]=LaAlO_3(s)$	-801616+28.9T

Simulations with the WYK-Stal software were conducted using model a and c for II options for the sequence of additives introduction. Model a assumes that the activity of the resulting non-metallic inclusion is 1 (a=1), model b, which was not used for the simulations, assumes that the activity coefficients of the components in the liquid metal are 1 (f=1). Model c considers the sulphur interfacial partition coefficient (Ls).

Option 1: Sequence of introduction of alloying additives: 5 min - 30 kg Al, 20 min - 70 kg mischmetal. Option 2: Additives introduction sequence 5 min - 30 kg mischmetal, 20 min - 70 kg Al. The following parameters were assumed to simulate the REM elements insertion and deoxidation process: process time 30 min, liquid steel ladle mass 140 Mg, ladle slag mass 100 kg, steel temperature at the start of the process 1670 K, pressure 1 atm. The initial oxygen content of the non-metallic inclusions was assumed to be 0.0001 % and the dissolved oxygen content of the steel 0.01 %.

Table 2.
The values of e_j^i for liquid iron at 1 873 K

e_j^i	C	O	S	P	Si	Mn	Al	N	Ce	La
O	-0.45	-0.20	-0.133	0.07	-0.131	-0.021	- 3.90	0.057	-12.1	-12.1
S	0.11	-0.27	-0.028	0.029	0.063	-0.026	0.035	0.01	-1.88	-2.79
Ce	0.351	-106	-8.225	1.77	-	0.13	-2.67	-	0.0066	
Mn	-0.07	-0.083	-0.048	-0.035	-3.0	0	-2.4	-0.091	-0.5	-
Al	0.091	-6.6	0.03	0.033	0.0056	0.035	0.045	-0.053	-6.1	-0.511
Si	0.18	-0.23	0.056	0.11	0.11	0.002	0.058	0.090	-7.7	
La	-0.279	-105	-12.13	1.734	-	0.28	-2.649			-0.013

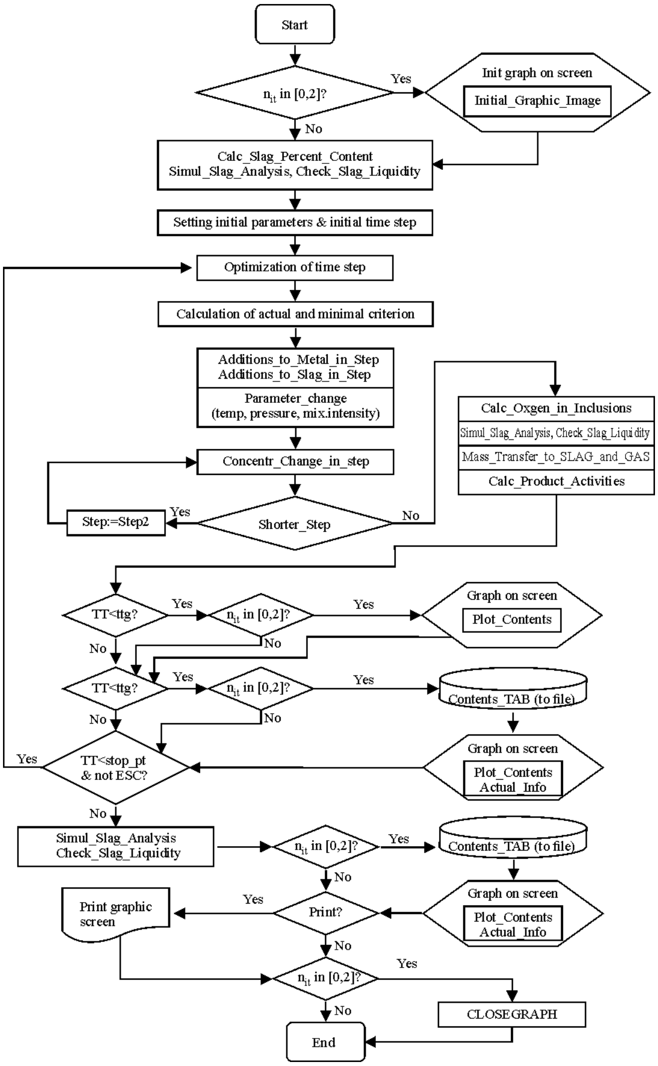

Fig. 1. Block diagram of the Wyk_Stal software

Table 3.
Chemical composition of melted steel, wt. %

C	Si	Mn	P	S	Cu	W	Ca	Al
0.029	0.013	0.14	0.023	0.018	0.036	0.028	0.003	0.019

The experimental part was carried out in a laboratory vacuum furnace. The melt consisted of steel with the composition shown in Table 3. Thus 2.57 g of mischmetal was added to a melt weight of 788 g with the chemical composition shown in Table 4; at the same time, a vacuum of 0.13 Pa was applied.

Table 4.
Chemical composition of mischmetal, wt. %

Ce	La	Nd	Pr
52.53	29.10	13.13	5.24

3. Results and discussions

Simulation results of the change in the composition of the steel during additive dosing in the sequence 5 min - 30 kg Al, 20 min - 70 kg mischmetal for calculations according to models a and c gave the same results (Fig. 2).

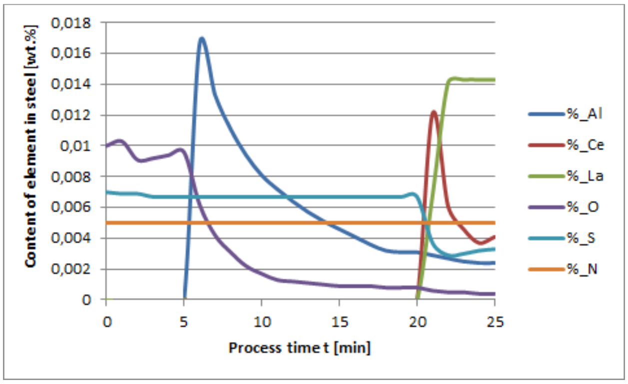

Fig. 2. The variation of chemical elements concentration in liquid steel [wt. %] vs. process duration t [min] (model a and c)

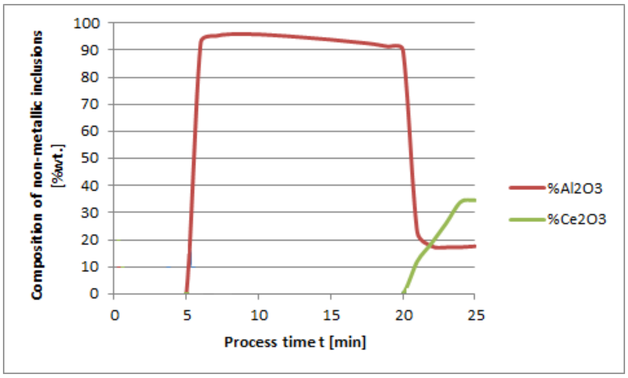

Fig. 3. The variation of chemical composition of non-metallic inclusions [wt. %] vs. process duration t [min] (model a)

The addition of Al (Fig. 2) is effective in deoxidising the steel at the 15th min after its introduction; the dissolved oxygen level in the steel is 0.001%, the addition of mischmetal at the 20th min consequently reduces it below this value (Fig. 2). As a result of dosing into the metal bath, Al_2O_3 is formed at the 5th minute of Al refining; this process is inhibited by the addition of mischmetal at the 20th minute of the process. This is followed by the release of mainly Ce_2O_3, with Al_2O_3 inclusions also present in the metal bath, which also form, but as a result of cerium's higher chemical affinity for oxygen, it takes over in its removal (model a – Fig. 3). On the other hand, calculations using model c showed that the addition of mischmetal results in the formation of CeS and Ce_2O_3 inclusions (model c, Fig. 4), i.e., the inclusion of the sulphur partition coefficient in model c gives more accurate calculation results. In doing so, it should be noted that the chemical affinity of cerium for sulphur is remarkably high, hence the presence of its sulphides is just as reasonable as that of oxides. In addition, when REM is fed into the steel in the final refining phase, there is a considerable oxygen deficit, hence the consumption of REM metals (here Ce) occurs on the formation of sulphide. This is confirmed by the results shown in Fig. 4.

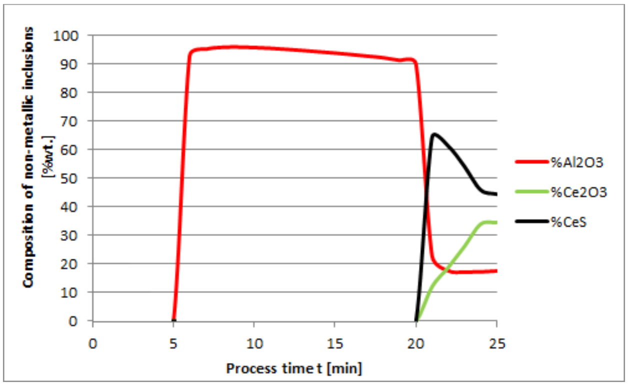

Fig. 4. The variation of chemical composition of non-metallic inclusions [wt. %] vs. process duration t (model c)

Another set of calculations was also carried out using models a and c of the WYK_Stal software, but the sequence of alloy additions was changed: 70 kg of mischmetal was added at the 5th min and 30 kg Al at the 20th min. This procedure is not economically justified due to the much higher price of using mischmetal as a deoxidiser compared to aluminum. Furthermore, it results in a higher final dissolved oxygen content in the steel. Figure 5 shows that the final oxygen content of the steel is about 0.005%, while the introduction of mischmetal at the end of the refining process (Option 1, Fig. 2) results in a much higher degree of deoxidation of 0.005% dissolved oxygen. Calculations carried out according to models a and c for changing the chemical composition of the metal bath for models a and c gave the same results (Fig. 5). The calculation results conducted for the non-metallic phase of the inclusions according to models a and c gave comparable results (Fig. 6). In this case, no cerium sulphides (CeS) was found in the non-metallic inclusion group. It is interesting to note that the calculation results did not confirm the presence of other REM-containing non-metallic inclusions in the steel.

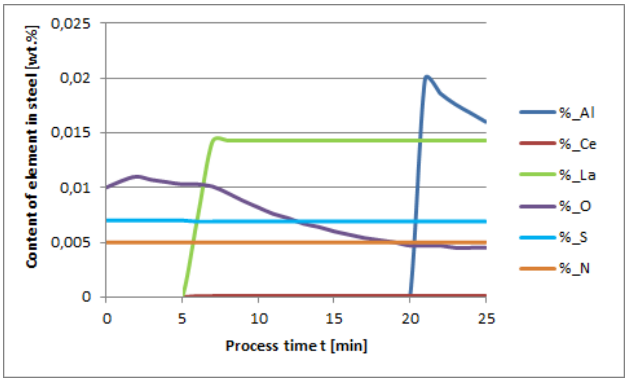

Fig.5. The variation of chemical elements concentration in liquid steel [wt. %] vs. process duration t [min] (model a and c)

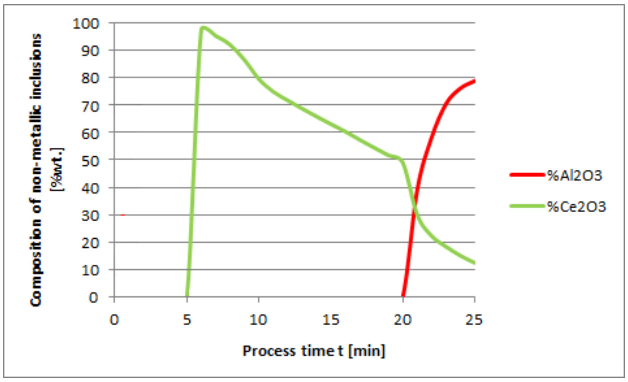

Fig. 6. The variation of chemical composition of non-metallic inclusions [wt. %] vs. process duration t (model a and c)

Microscopic examination of samples taken from the laboratory melt was carried out using an SEM microscope. Analysis of samples cut from different areas of the ingot confirmed the presence of non-metallic inclusions identified by simulation with the WYK_Stal software. The presence of non-metallic inclusions containing Ce, O and S with traces of La was observed in all samples taken from the experimental melt.

Table 5.
Result of spot X-ray microanalysis of the separation area points for sample 1

Element	Atomic conc.	Weight conc.
Ce	17.30	39.66
La	7.72	17.55
Nd	6.35	14.99
O	52.34	13.70
Fe	14.27	13.04
S	2.01	1.06

The morphology and EDS spectra of these inclusions are shown in Figs. 7-8.

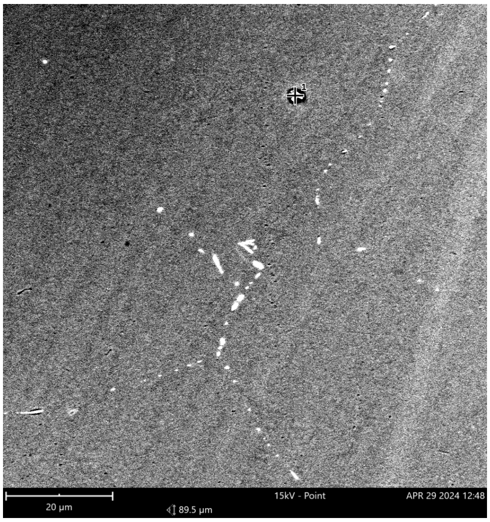

Fig. 7. Microstructure of steel with addition mischmetal obtained in scanning electron microscopy (sample 1)

In sample 1 (Fig. 7) the precipitates contained Ce, La, Nd, O and S (see table 5). After adding mischmetal to the liquid steel main reactions REM with O. This caused that complex inclusions REM-O-S were formed. Because in the chemical composition in mischmetal is dominated by cerium, it plays a major role in deoxidation and precipitates the final production of Ce-O and Ce-O-S inclusions.

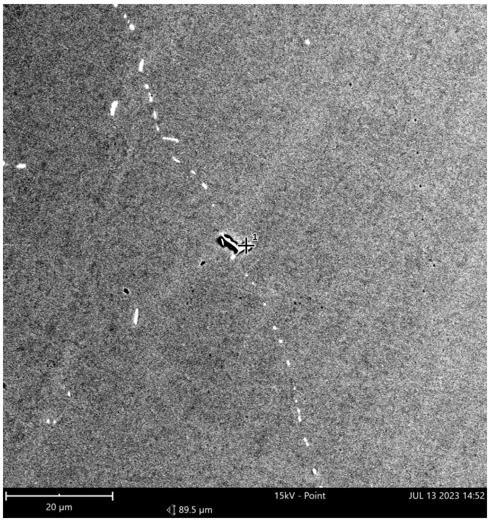

Fig. 8. Microstructure of steel with addition mischmetal obtained in scanning electron microscopy (sample 2)

Table 6.
Result of spot X-ray microanalysis of the separation area points for sample 2

Element	Atomic conc.	Weight conc.
Fe	48.13	43.23
Ce	15.74	35.46
O	30.18	7.77
La	3.12	6.97

Numerous, minor non-metallic inclusions have identified in the tested samples. Analysis of the chemical composition from the inclusions area showed that this phase contains elements: Ce, La, Nd, O and S. The analysis figure 8 reveals that after introduction mischmetal, the deoxidation products are complex REM-O inclusions: Ce-La-Nd-O with dominant inclusion Ce-O (see table 6).

5. Conclusions

The irregularly shaped Ce_2O_3 inclusions are products after deoxidation of the cerium contained in the mischmetal. The main inclusions present in the steel are Ce_2O_3 and CeS, and the presence of complex La_2O_3-Ce_2O_3 inclusions was also identified in the steel. The presence of cerium nitride, which was not identified as a reaction product during deoxidation, was also not observed in the samples, but its release occurred during ingot solidification.

The results of computer calculations using WYK_Stal software confirmed, that introduction of mischmetal in the final stage refining is the most effective method. Therefore, the oxygen content is reduced below 0.001%, and the sulphur content can be reduced to 0.004%. Considering the sulphur partition coefficient L_S enabled the identification of the formation of Ce sulphides and complex compounds containing O and S in steel (calculations for option 1 model c). The presence of cerium sulphides was also confirmed by SEM and EDS analyzes of selected steel samples.

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References

[1] Smirnov, L.A., Rovnushkin, V.A., Oryshchenko, A.S., Kalinin, G. Yu. & Milyuts, V.G. (2016). Modification of steel and alloys with rare-earth elements. Part 1. *Metallurgist.* 59(11), 1053-1061. DOI:10.1007/s11015-016-0214-x.

[2] Wang, L.M., Lin, Q., Yue, L.J., Liu, L., Guo, F. & Wang, F.M. (2008). Study of application of rare earth elements in advanced low alloy steels. *Journal of Alloys and Compounds.* 451(1-2), 534-537. DOI:10.1016/j.jallcom.2007.04.234.

[3] Wang, L., Lin, Q., Ji, J. & Lan, D. (2006). New study concerning development of application of rare earth metals in steels. *Journal of Alloys and Compounds*. 408-412, 384-386. DOI:10.1016/j.jallcom.2005.04.090.

[4] Wang, M., Mu, S., Sun, F. & Wang, Y. (2007). Influence of rare earth elements on microstructure and mechanical properties of cast high-speed steel rolls. *Journal of Rare Earths.* 25(4), 490-494. DOI:10.1016/S1002-0721(07)60462-1.

[5] Smirnov, L.A., Rovnushkin, V.A., Oryshchenko, A.S., Kalinin, G., Yu. & Milyuts, V.G. (2016). Modification of steel and alloys with rare-earth elements. Part 2. *Metallurgist.* 60(1), 38-46. DOI:10.1007/s11015-016-0249-z.

[6] Jiang, X., Li, G., Tang, H., Liu, J., Cai, S. & Zhang, J. (2023). Modification of Inclusions by Rare earth elements in a high-strength oil casing steel for improved sulphur resistance. *Materials.* 16(2), 675, 1-18. DOI:10.3390/ma16020675.

[7] Ning, Z., Li, C., Wang, J., Zhai, Y., Xiong, X. & Chen, L. (2023). Refinement and modification of Al_2O_3 inclusions in high-carbon hard wire steel via rare earth lanthanum. *Materials*. 16(14), 5070, 1-12. DOI:10.3390/ma16145070.

[8] Program instructions Wyk_Stal.

[9] Gerasin, S., Kalisz, D., Iwanciew, J. (2020). Thermodynamic and kinetic of simulation of Y_2O_3 and Y_2S_3 nonmetallic phase formation in liquid steel. *Journal of Mining and Metallurgy Section B: Metallurgy*. 56(1) 11-25. DOI:10.2298/JMMB190326050G.

[10] Iwanciw, J. (2002). Simulator of steelmaking processes for work in real time. Kraków: Komitet Metalurgii PAN, Wyd. Nauk. Akapit.

[11] Iwanciw, J., Podorska, D. & Wypartowicz, J. (2011). Modeling of oxide precipitates chemical composition during steel deoxidation. *Archives of Metallurgy and Materials.* 56(4), 999-1005. DOI: 10.2478/v10172-011-0110-0.

[12] Iwanciw, J., Podorska, D. & Wypartowicz, J. (2011). Simulation of oxygen and nitrogen removal from steel by means of titanium and aluminum. *Archives of Metallurgy and Materials.* 56(3), 635-644. DOI: 10.248/v10172-011-0069-x.

[13] Szucki, M., Kalisz, D., Gerasni, S., Mrówka, N.M., Iwanciw, J. & Semiryagin, S. (2023). Analysis of the effect of cerium on the formation of non-metallic inclusions in low carbon steel. *Scientific Reports*. 13, 8294, 1-9. DOI: 10.1038/s41598-023-34761-0.

[14] Adabavazeh, Z., Hwang, W. & Su, Y. (2017). Effect of adding cerium on microstructure and morphology of Ce-based inclusions formed in low-carbon steel. *Scintific Reorts.* 70 DOI: 10.1038/srep46503 (2017).

[15] Han, Q.Y. (1998). *Rare Earth, Alkaline Earth and Other Elements in Metallurgy.* IOS Press.

[16] Han, Y., Liu, Z.H., Wu, C.B., Zhao, Y., Zu, G.Q., Zhu, W.W. & Ran, X. (2023). A short review on the role of alloying elements in duplex stainless steels. *Tungsten*. 5(4), 419-439. DOI:10.1007/s42864-022-00168-z.

[17] Hino, M., Ito, K. (2010). *Thermodynamic Data for Steelmaking*. Tohoku University Press.

[18] Mao, N., Yang, W., Chen, D., Lu, W., Zhang, X., Chen, S., Xu, M., Pan, B., Han, L., Zhang, X. & Wang, Z. (2022). Effect of lanthanum addition on formation behaviors of inclusions in Q355B. *Materials*. 15(22), 7952, 1-14. DOI: 10.3390/ma15227952.