ARCHIVES OF METALLURGY AND MATERIALS
Volume 57 2012 Issue 1
DOI: 10.2478/v10172-012-0023-6

J. JOWSA*, A. CWUDZIŃSKI*

THERMODYNAMICS ANALYSIS OF NON-METALLIC INCLUSIONS FORMATION IN THE LIQUID STEEL FLOW THROUGH CONTINUOUS CASTING TUNDISH

ANALIZA TERMODYNAMICZNA TWORZĄCYCH SIĘ WTRĄCEŃ NIEMETALICZNYCH W CIEKŁEJ STALI PRZEPŁYWAJĄCEJ PRZEZ KADŹ POŚREDNIĄ PROCESU COS

Experiments were conducted at industrial plant to determine the free and total oxygen contents in molten steel in the tundish during continuous casting blooms of sizes 280×280 mm. On the basis of industrial experiment results a thermodynamic evaluation of non metallic inclusion formation in liquid steel was performed. Software FactSage® with thermodynamic base packages were tested and applied to calculate equilibrium formation of oxides and sulphides. The results showed the effect of oxygen contents and temperature on the formation inclusion in liquid steel. Calculation results was presented in the form of suitable characteristics which were illustrated graphically.

Keywords: tundish, non-metallic inclusions, thermodynamics analysis, FactSage programme

Dla kadzi pośredniej stosowanej do odlewania wlewków kwadratowych o rozmiarach 280×280 mm przeprowadzono badania przemysłowe polegające na pobieraniu próbek metalu celem określenia zawartości tlenu w postaci rozpuszczonej i całkowitej. Na podstawie tych danych przeprowadzono analizę termodynamiczną zdolności do wydzielania się wtrąceń niemetalicznych z ciekłej stali podczas jej przebywania w kadzi pośredniej. W tym celu zastosowano program FactSage® wraz z odpowiednimi bazami danych termodynamicznych. W wynikach badań przedstawiono wpływ zawartości tlenu oraz temperatury na możliwość tworzenia wtrąceń niemetalicznych. Otrzymane wyniki badań przedstawiono w postaci odpowiednich charakterystyk, które zostały także zilustrowane graficznie.

1. Introduction

There is no doubt about the statement that the quantity, size, shape and type of non-metallic inclusions (NMI) have all significant influence on the properties of steel manufactured, and especially its mechanical properties. Therefore, various technological treatments are undertaken in the production of steel to control the NMI formation process, which are aimed at reducing NMI quantities to the lowest possible levels, as specified for a given grade and application of the steel. Several different activities have been undertaken in recent years to evaluate the influence of the steel casting process on the behavior of NMIs, regardless their nature – be it exogenous or endogenous. In the continuous steel casting, a key role is played by the tundish. It performs a number of important functions, such as enabling the uniform distribution of steel flow to individual moulds, maintaining the preset casting speed, and equalizing the temperature of steel and protecting it against excessive cooling down. It is also believed that the tundish may contribute to the removal of part of NMIs, irrespective of their origin. Explaining the problem of removal of NMIs from the tundish through their flotation to the steel surface and then assimilation by the slag and casting powder is a tough task. Industrial tests on the tundish, due to its very nature (a large facility, high temperature), meet with several limitations, which are attempted to be overcome using model studies. By building a water model of an industrial unit on a reduced scale and using suitable apparatus, the degree of NMI separation can be evaluated [1,2]. Similarly, by constructing a proper mathematical model, it is possible to carry out numerical simulations of the steel casting and NMI flotation processes, while considering the phenomenon of highly dispersed phase behavior in a continuous medium. To develop a mathematical model for steel refining with NMI removal during steel casting, it is necessary to adopt a number of

---

* DEPARTMENT OF METALS EXTRACTION AND RECIRCULATION, FACULTY OF MATERIALS PROCESSING TECHNOLOGY AND APPLIED PHYSICS, CZESTOCHOWA UNIVERSITY OF TECHNOLOGY, 42-200 CZESTOCHOWA, 19 ARMII KRAJOWEJ AVE, POLAND

parameters that result directly from the technology being in use. Part of them can be obtained by carrying out a set of uncomplicated tests (such as the measurement of temperature and casting speed); the others, however, will require greater expenditures of labor and financial resources. The latter include the development of the chemical composition of steel and the distribution of NMI size in the steel flowing through the tundish. As the authors of the present article had been for some time conducting research on NMI behavior in the tundish by the mathematical modeling method [3-5], so, in order to define some of the boundary conditions and then to verify the model, an attempt was made to carry out industrial experiments aimed at the evaluation of the NMI state, supported by appropriate thermodynamic analyses. The article reports part of the results of studies within the research project on the behavior of NMIs in the tundish.

2. Industrial testing conditions

The industrial tests concerned selected steel grades smelted in an electric furnace and then subjected to the standard treatment on the ladle furnace (LF) and vacuum degassing (VD) stations. The steel was cast by a continuous method to produce 280×280 mm billets (a three-strand mould) and 150×1500 mm and 225×1500 mm slabs (a single-strand mould). Industrial measurements along with taking samples for metallographic examinations were made for three casting sequences – in total, nine melts were analyzed. The measurements were taken for the first, third and fifth melts cast in a sequence. For reasons of the space of the present article, only the first three melts, of which 280×280 mm square billets were cast, will be discussed in detail. The object of testing was a wedge-type tundish of a capacity of 30 Mg. The measurements of oxygen activity in steel and FeO content of slag were taken using an instrument supplied by Heraeus Electro-Nite, furnished with pickups operating by sensing the electromotive force (EMF) in concentration cells (Celox and Celox SLAC). The overall oxygen and nitrogen contents of liquid steel were determined by using a Total Oxygen Sampling system (T.O.S) for taking rod-shaped samples. For the evaluation of the distribution of the quantity and size of non-metallic inclusions and their chemical composition, lollipop-type samples were taken. An example set of measurement results for the first melt is shown in Fig. 1, where oxygen activities in steel and FeO contents of slag in the tundish, as well as the overall oxygen content of steel are indicated in chronological order.

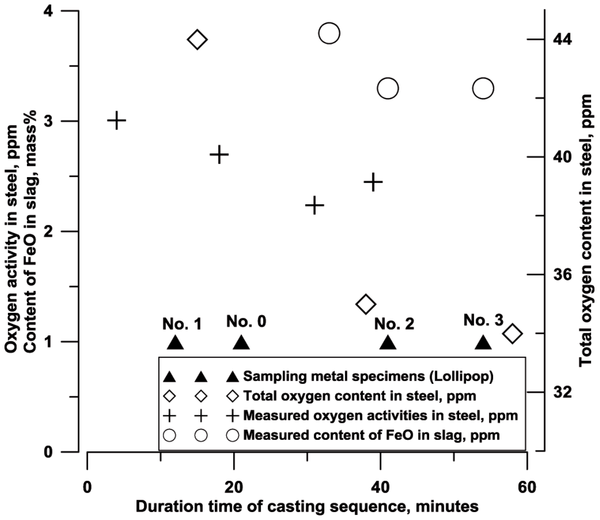

Fig. 1. Results of industrial measurements of selected parameters during casting heat no.1

A summary of the average results of steel chemical composition and industrial assays of all the measurements taken for individual melts, in the form of the ranges of measured values, is given in Table 1.

TABLE 1

Results of steel chemical composition and industrial measurements

No. Heat	Average chemical composition of steel, mass%									EMF	T.O.S.
	C	Mn	Si	P	S	Al_{tot}	Al_{sol}	Ca	[O]	(FeO)	O_{tot}
									ppm	ppm	ppm
1	0.303	0.587	0.224	0.010	0.013	0.023	0.020	0.002	2.2÷ 3.1	3.3÷ 3.8	34÷ 44
2	0.291	0.568	0.243	0.014	0.006	0.023	0.020	0.003	2.3÷ 3.1	2.1÷ 3.73	28÷ 33
3	0.302	0.591	0.273	0.014	0.014	0.032	0.029	0.003	2.0	1.3÷ 3.1	24÷ 30
4	0.174	1.283	0.234	0.013	0.008	0.031	0.028	0.004	2.5÷ 3.5	3.1÷ 3.6	30÷ 42
5	0.167	1.312	0.237	0.013	0.020	0.040	0.036	0.001	1.7÷ 1.9	2.6÷ 3.4	31÷ 45
6	0.163	1.284	0.215	0.012	0.017	0.035	0.031	0.001	1.5÷ 1.9	1.6÷ 3.8	29÷ 32
7	0.134	0.586	0.203	0.018	0.013	0.032	0.029	0.001	2.0÷ 3.3	3.1÷ 3.5	28÷ 34
8	0.131	0.568	0.263	0.015	0.018	0.035	0.033	0.001	1.9÷ 2.2	3.3÷ 4.1	26÷ 43
9	0.122	0.571	0.225	0.010	0.020	0.030	0.028	0.001	2.0÷ 2.1	3.6÷ 4.2	20÷ 25

It should be noted that the steel temperature in the tundish during concast slab casting was also measured and the steel casting speed was monitored. All the collected industrial test results provided a basis for defining the boundary conditions of numerical simulations of NMI behavior in the tundish during continuous steel casting. The results of those simulations are covered by separate publications by the authors [6, 7].

3. Metallographic examination of NMI in metallic samples

In total, 36 samples in the form of sucked-in lollipop-type casts were taken for nine melts for the examination of non-metallic inclusions in the steel being cast on the tundish stand. Samples were numbered for individual melts in the order, as indicated in Fig. 1. Only 27 samples (three for each melt) were chosen out of them for quantitative and qualitative analyses, assuming that one of the samples (sample no. 0) would remain a reserve one. Metallographic examinations included measurements of the quantities of inclusions on the samples and determination of their chemical composition. The measurements of the quantities and sizes of non-metallic inclusions were taken at the Institute for Ferrous Metallurgy [7]. The NIKON EPIPHOT 200 & LUCIA G v_4.82 image analysis system was used for the measurements. The measurements were taken on non-etched microsections of a fragment of a steel sample taken (Fig. 2).

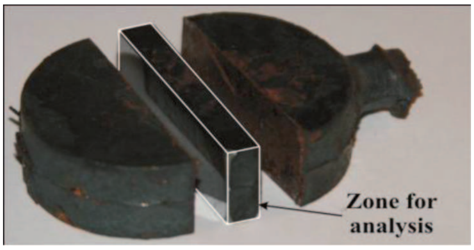

Fig. 2. Schematic illustration of cutting position for metal specimens on filled steel Lollipop sample

The image of the microsection surface visible under the NIKON EPIPHOT 200 light microscope was transferred onto the computer screen using a NIKON DS.5-U1digital camera. The optical magnification on the NIKON EPIPHOT 200 microscope was 500x, while the total magnification on the display screen was 2800x. For each sample, the following were measured: the quantity of inclusions, surface share, equivalent diameter, length, thickness, maximum Feret diameter (the projection of the object onto the X axis) and elongation (shape factor). Summaries of quantities obtained for each of the samples are as shown in Table 2.

Based on all measurements, it could be possible to plot non-metallic inclusion distribution histograms, assuming ranges of properties (min. and max.) and the number of non-metallic inclusion classes. Taking the equivalent diameter of non-metallic inclusions for evaluation, the histograms for the first, second and third melts are shown in Figs. 3-5. By evaluating the juxtapositions of different properties of the NMI size distribution for all analyzed melts it can be noticed that small inclusions occur in the cast steel, with the modal value for two classes of 1÷ 2μm and 2÷3μm – assuming their size in the form of an equivalent diameter.

TABLE 2

A tabular summary measurement quantities of NMI in sample no.1 (heat no. 1)

Number of fields	50	Size of NMI	Chemical composition NMI, mass%			
			CaS	CaO	Al_2O_3	MgO
Number of inclusions	146	2 μm	4,55	16,99	75,02	3,44
Measurement area, μm^2	639514	3 μm	5,33	18,20	73,06	3,41
Participation of area %	0,13	4 μm	1,31	27,38	68,10	3,22
Properties of inclusions:			Average	St. Dev.	Min.	Max.
equivalent diameter, μm			**2,41**	1,09	0,83	6,69
length, μm			**3,17**	1,97	0,93	16,49
thickness, μm			1,50	0,67	0,46	3,83
maximum Feret diameter, μm			3,00	1,56	0,93	12,58
elongation			1,39	0,39	1,07	3,26

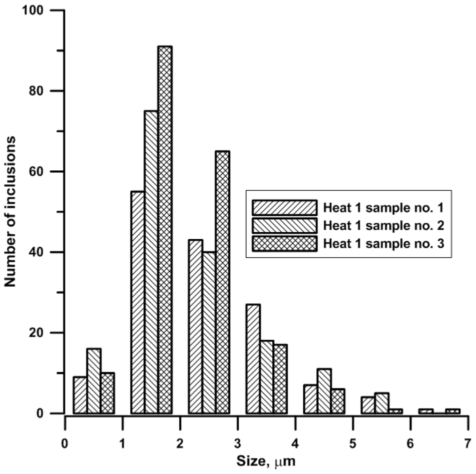

Fig. 3. Distribution of NMIs size in the samples for heat no. 1

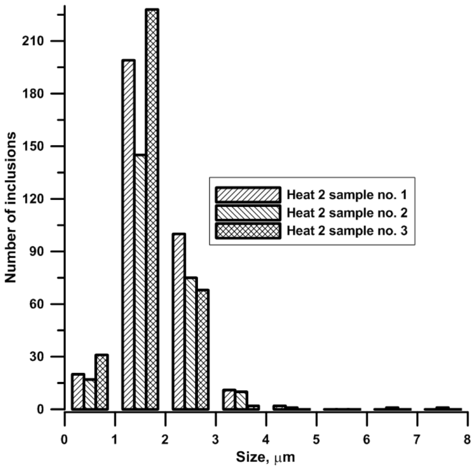

Fig. 4. Distribution of NMIs size in the samples for heat no. 2

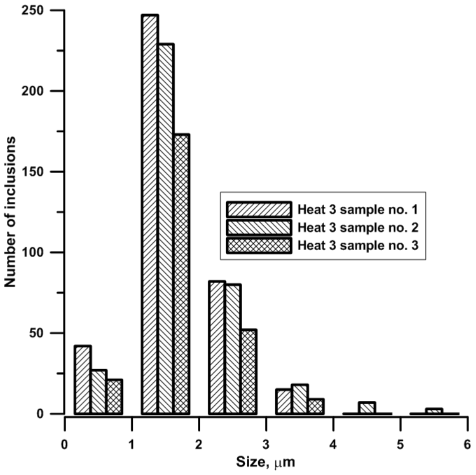

Fig. 5. Distribution of NMIs size in the samples for heat no. 3

The chemical composition of precipitates in the form of non-metallic inclusions was determined by examinations carried out at the Institute of Materials Engineering of the Czestochowa University of Technology and at the Institute of Metallurgy and Materials Engineering of the Polish Academy of Sciences. These were performed on a JOEL JSM 5400 scanning electron microscope equipped with an X-ray microanalyzer by OXFORD. The microanalysis consisted of an energy analysis of the X-ray spectrum obtained as a result of bombarding a selected location on the sample with an electron beam. The locations were selected for the edge and inner zones on the steel sample cross-section. For each of the zones, the microanalysis of chemical element composition was made for randomly chosen precipitates. The diameter or the length or width of a precipitate was also determined, which enabled the shape and chemical composition to be linked in selected precipitates. Example results for the picture of precipitates and the chemical composition analysis of a spherical non-metallic inclusion are shown in Figs. 6 and 7.

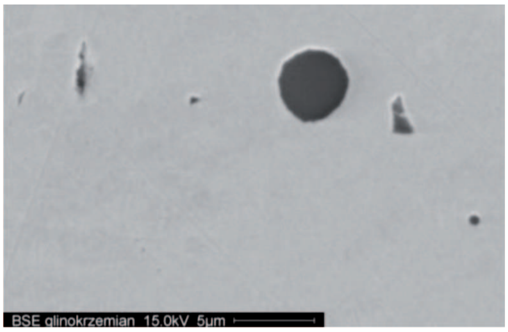

Fig. 6. Morphology of individual $Al_20_3-SiO_2-CaO-MgO$ inclusion

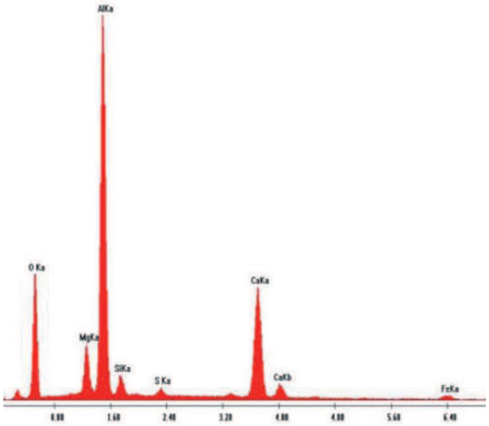

Fig. 7. Energy dispersive X-ray microanalysis (EDX) of spherical non-metallic inclusion

4. Thermodynamic prediction of stable phase in inclusions

The thermodynamic analysis covered also only the first three melts, for which it was decided to check the type and quantity of precipitated NMIs in liquid steel in the tundish and to examine their change in the steel solidification process. Computations were performed using the FactSage ver. 6.2 software program. For the thermodynamic description of the state of chemical equilibrium of the steel – NMI heterophase system, a steel solution mathematical model called ”Associate Model” was employed, which is a further extension of the Wagner-Chipman model (CWIF) and the Pelton-Bale model (UIPF) [9]. The thermodynamic database for steel was taken in the form of FSSTEL, which relies on the SGSL database derived from the **S**cientific **G**roup **T**hermodata **E**urope (SGTE) scientific consortium. The quantity of NMIs was expressed in grams, assuming a steel sample of a mass of 100 g as the base.

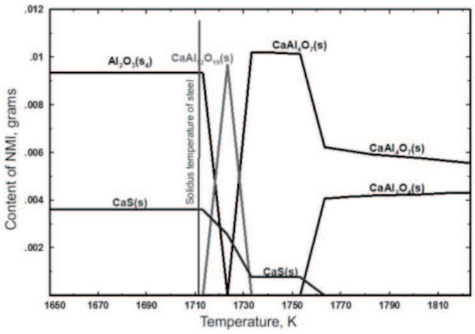

Fig. 8. Computed equilibrium sequence of precipitation of stable phases in NMIs (grams) during steel solidification for heat no. 1

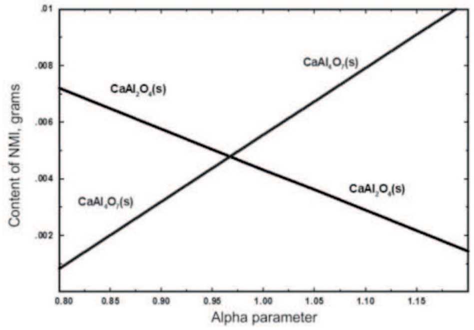

Fig. 9. Relationship between computed quantity of NMIs (grams) and Alpha parameter at 1823K for heat no. 1

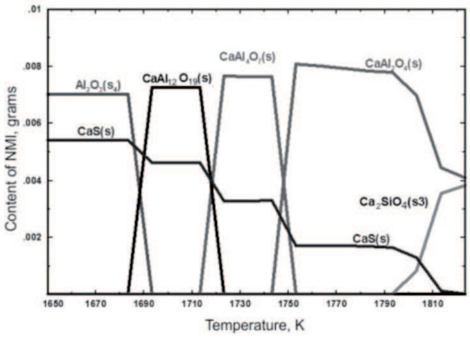

Fig. 10. Computed equilibrium sequence of precipitation of stable phases in NMIs (grams) during steel solidification for heat no. 2

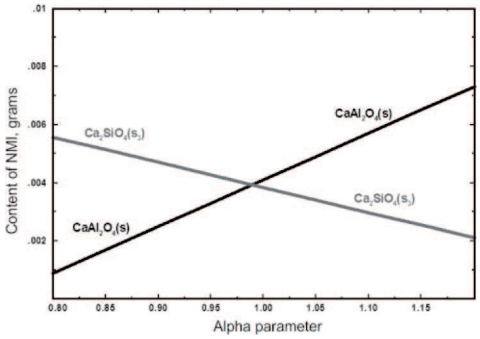

Fig. 11. Relationship between computed quantity of NMIs (grams) and Alpha parameter at 1823K for heat no. 2

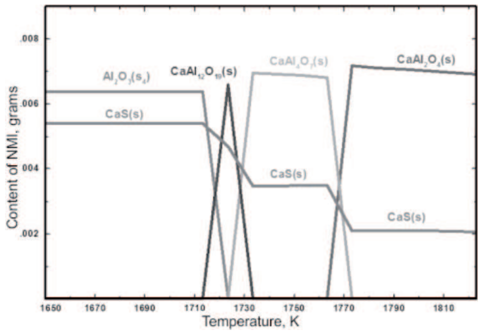

Fig. 12. Computed equilibrium sequence of precipitation of stable phases in NMIs (grams) during steel solidification for heat no. 3

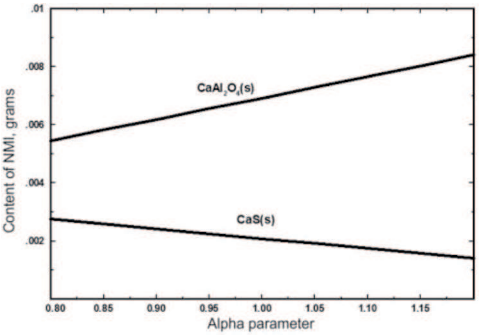

Fig. 13. Relationship between computed quantity of NMIs (grams) and Alpha parameter at 1823K for heat no. 3

Because of the fact that the oxygen content varies during the course of the steel casting process, as indicated by Table 1, a computational simulation was performed to find out how that variation influences the state of NMIs in the liquid steel (1823 K), assuming the Alpha parameter. This parameter is the analytical factor of the total oxygen content (wt%), which was taken for computations as the arithmetic mean of all measurements for a given melt. The obtained results of the computer simulation of NMI precipitation from the steel in the state of thermodynamic equilibrium for variable temperature (1650÷ 1823K) and a constant temperature and variable total oxygen content (Alpha = 0.8÷ 1.2) are illustrated in Figs. 8-13.

5. Summary

The examination of steel samples taken from the tundish found small-sized NMIs, rarely exceeding the size of 10μm, to be present in the samples, which represents a major hindrance to refining the steel and capturing the NMIs by the slag or casting powder present on the steel surface. This process can only be intensified by additionally equipping the tundish with flow control devices, such as impact pads. Devices of this type produce conditions favoring collisions between particles, which result in coagulation and coalescence, and thus an increase in the size of NMIs. The thermodynamic analysis made for three melts showed that, depending on the temperature, NMIs of different chemical composition, but close to the composition of chemical compounds such as Al_2O_3, $CaAl_4O_7$, $CaAl_2O_4$, $CaSiO_4$, $CaAl_{12}O_{19}$ and CaS, would precipitate from the steel. Mg-containing inclusions were cont considered in the thermodynamic computation due to the fact that there was no analysis available of steel containing this element. The computation results are confirmed by NMI atomic composition analyses made using an X-ray microanalyzer. By making the conversion of the atomic element composition to the chemical composition of basic compounds (oxides and sulfides) it is possible to asses to what extent the NMI composition as calculated from the thermodynamic analysis is consistent with the laboratory tests of steel samples. Table 2 gives chemical composition of NMIs in three sizes (2, 3 and 4μm), as determined with the X-ray analyzer. This composition indicates that oxide inclusions are similar in chemical composition to compounds of the $CaAl_4O_7$ and $CaAl_2O_4$ types, which is consistent with the computation results for melt no. 1, which are represented in Figs. 8 and 9. Completing the examination of the laboratory tests and thermodynamic computation results for the remaining melts will help determine in a greater detail the conditions favoring the processes of steel refining with NMI removal at the stage of steel transport through the tundish.

Received: 10 September 2011.

Acknowledgements

This scientific work has been financed from the resources allocated for Science in the years 2009-2011 as Research Project No. N50839043

REFERENCES

[1] R. Koitzsch, M. Warzecha, A. Rueckert, H. Pfeifer, Physical and mathematical simulation of the inclusion removal and determination of the deposition rate for the continuous casting process, ECCC 2008 Conf. Proceeding, Riccione, Italy 2008.

[2] A. Rueckert, M. Warzecha, R. Koitzsch, M. Pawlik, H. Pfeifer, Particle distribution and separation in continuous casting tundish, Steel Research International **80**, 568-574 (2009).

[3] A. Cwudziński, J. Jowsa, Numerical simulation of steel flow and behaviour of non-metallic inclusions in the six-strand tundish with stopper rod system, Materials Science Forum **638-642**, 3176-3181 (2010).

[4] J. Jowsa, A. Cwudziński, S. Garncarek, T. Merder, Modelowanie numeryczne usuwania wtrąceń niemetalicznych z ciekłej stali w kadzi pośredniej wyposażonej w urządzenia sterujące przepływem, Hutnik – Wiadomości Hutnicze 3, 83-86 (2010).

[5] A. Cwudziński, Archiv. of Metall. and Mater. **56**, 3, 611 (2011).

[6] A. Cwudziński, J. Jowsa, Modelowanie matematyczne zjawiska wzrostu wtrąceń niemetalicznych podczas przepływu stali przez kadź pośrednią, Hutnik – Wiadomości Hutnicze 9, 459-461 (2010).

[7] J. Jowsa, A. Cwudziński, Modelowanie matematyczne zachowania się wtrąceń niemetalicznych (WN) w kadzi pośredniej, Polska Metalurgia w latach 2006-2010, Komitet Metalurgii PAN, 94-102 Kraków 2010.

[8] Raport z badań nr Nr 8105 pt. Analiza ilościowa wtrąceń niemetalicznych w próbach lizakowych pobranych z ciekłej stali, IMŻ, Gliwice 2010.

[9] I.H. Jung, S.A. Decterov, A.D. Pelton, Computer Applications of Thermodynamic Databases to Inclusion Engineering, ISIJ International **44**, 3, 527-536 (2004).