Ireneusz SZYPUŁA, Bogdan ZDONEK

DOI: 10.32730/imz.0137-9941.18.3.3

LABORATORY STUDIES ON THE DEVELOPMENT OF COMPOSITE PELLETS FOR DEEP REFINING OF STEEL FROM NON-METALLIC INCLUSIONS

The paper presents the laboratory research on the development of a new type of refining materials in the form of composite pellets for deep refining of steel from non-metallic inclusions, measured by the total oxygen content in steel below 10 ppm and the average size of non-metallic inclusions below 3 µm. The study included the development of a technology for pelletising materials selected for composite pellets, development of a technology for drying and hardening of pellets, making a batch of pellets and a series of laboratory heats using the produced pellets, assessment of the usefulness of composite pellets for industrial research, and development of assumptions for these tests.

Keywords: *steel, non-metallic inclusions, refining, composite pellets*

BADANIA LABORATORYJNE NAD OPRACOWANIEM KOMPOZYTOWYCH GRUDEK DO GŁĘBOKIEJ RAFINACJI STALI Z WTRĄCEŃ NIEMETALICZNYCH

Przedstawiono badania laboratoryjne nad opracowaniem nowego rodzaju rafinacyjnych materiałów w postaci kompozytowych grudek do głębokiej rafinacji stali z wtrąceń niemetalicznych, mierzonej zawartością tlenu całkowitego w stali poniżej 10 ppm i średnią wielkością wtrąceń niemetalicznych, poniżej 3 µm. Opracowano technologię grudkowania materiałów dobranych na kompozytowe grudki, opracowano technologię suszenia i utwardzenia grudek, wykonano partię grudek oraz serię laboratoryjnych wytopów z wykorzystaniem wytworzonych grudek, dokonano oceny przydatności grudek kompozytowych do badań przemysłowych oraz opracowano założenia do tych badań.

Słowa kluczowe: *stal, wtrącenia niemetaliczne, rafinacja, grudki kompozytowe*

1. INTRODUCTION

The motivation for the research is the urgent need to further improve the steel refining process from non-metallic inclusions in the processes of non-metallurgical refining of steel, in real industrial conditions, and in particular the need to reduce the total oxygen content in steel to below 10 ppm. A modern process of effective removal of solid and liquid non-metallic inclusions from steel is carried out by simultaneously producing fine bubbles of gas and slag particles and intense mixing between the gas and liquid phases in the entire volume of refined steel. Effective removal of non-metallic inclusions (NMI) from liquid steel involves two solutions – one is to promote the outflow of large NMIs under the influence of Stockes's buoyancy forces; the second is the removal of small NMIs by means of adhesion to very fine bubbles. The use of gas-permeable hybrid elements [1, 2] producing much finer gas bubbles (argon) for this purpose improved the

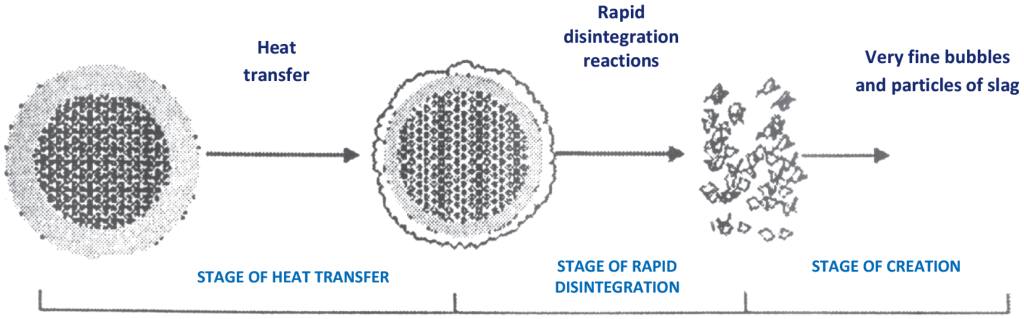

Fig. 1. Mechanism of the formation of fine bubbles and slag particles in liquid steel by means of an explosive reaction [3]

Rys. 1. Mechanizm tworzenia się drobnych pęcherzyków i cząstek żużla w ciekłej stali za pomocą reakcji wybuchowej (szybkiego rozpadu) [3]

Ireneusz Szypuła (iszypula@imz.pl), Bogdan Zdonek – Instytut Metalurgii Żelaza im. St. Staszica

purity of the steel, however, with the short liquid steel stirring times in the ladle, under industrial conditions, no significant results were achieved. In the latest solution [3], innovative complex (composite) pellets were used in the process of vacuum degassing of liquid steel in an RH apparatus. The operating mechanism of such a pellet is shown in Fig. 1.

A composite pellet consists of three parts. The inner part is a mixture of powdered synthetic slag, limestone and binder. The powder's median diameter d_{50} is approximately 0.10 mm. Limestone (or dolomite), evenly distributed in a synthetic slag, plays a very important role. First, it produces small CO_2 bubbles in the liquid steel under the influence of decomposition reactions (1) and (2). Secondly, the distribution of fine powder in the liquid metal causes local turbulence, contributing to the dispersion of synthetic slag particles and intensive mixing, supporting the efficiency of movement of non-metallic inclusions and their effusion into the slag.

$$CaCO_3 \;\; 825°C \rightarrow CaO + \{CO_2\} \Uparrow \quad (1)$$

$$MgCO_3 \;\; 625°C \rightarrow MgO + \{CO_2\} \Uparrow \quad (2)$$

The intermediate part is a layer of limestone which determines the force of rapid dispersal of composite pellets in liquid steel. The outer part is the CaO layer, which exerts a strong influence on the durability of the composite pellets at high temperature. In addition, the strength of composite pellets depends on the intermediate and outer parts. The use of composite pellets for refining steel in a 150 ton ladle in an RH apparatus influenced, by the effective absorption of oxide inclusions by the produced synthetic slag, the reduction of the total oxygen content in the steel to 5 ppm [3].

The aim of the study was to develop a new type of refining materials in the form of composite pellets for dynamic and deep extraction (refining) of non-metallic inclusions from steel.

2. METHODOLOGY

2.1. MATERIAL

The material for the tests was lime-aluminide slag-forming material (LAS and Al_{Ca} SLAG 70) used for refining steel containing aluminium and synthetic, molten, lime-aluminium-silicon slag (LASS) used for refining steel for products characterised by high surface quality. The chemical compositions of these materials are shown in Table 1. The dolomite used for the pelletising tests was a factory product DOLOMIT 50 – carbonate agricultural lime containing magnesium, and the lime was hydrated lime (building lime).

Prior to pelletising, the slag-forming material LAS, which is aluminium dross and skimmings from the production of aluminium, was enriched in CaO in the amount of 10% of the mixture weight (LAS10) and 25% of the mixture weight (LAS25). The addition of CaO also influenced the increase of the degree of agglomeration and bond strength after pelletising.

The slagging materials selected for the preparation of composite pellets were subjected to thermal analysis to determine the characteristic melting temperature.

The TG/DTA thermal analysis was carried out on a station that included a NETZSCH STA 449 F3 Jupiter thermal analyser and a coupled NETZSCH QMS 403 Aëolos quadrupolar mass spectrometer. The basic parameters of the experiment are:
– sample weight ~50 mg
– working gas – argon 70 ml/min
– heating rate – 10 K/min
– temperature programme – 40–1550°C.

These materials were characterised by the following melting points:
– LAS10 – 1304°C
– LAS25 – 1496°C
– LASS – 1461°C
– Al_{Ca}SLAG 70 – 1480°C.

2.2. PRODUCTION TECHNOLOGY OF COMPOSITE PELLETS

The production technology of composite pellets included:
1. Grinding and milling of slag, limestone, dolomite and lime to a grain size of 0.1 mm.

Fig. 2. Balling drum
Rys. 2. Bęben grudkujący

Table 1. Chemical composition of slags for composite pellets, wt %
Tabela 1. Skład chemiczny żużli na kompozytowe grudki, w %

Slag type	Content, %						
	CaO	SiO_2	Al_2O_3	MgO	Fe_2O_3	Al_{met}	H_2O
LAS	43.00	3.20	30.26	4.22	3.00	9.20	7.14
LASS	35.40	34.50	28.60	0.86	0.35	–	–
Al_{Ca} SLAG 70	20–30	max 6	50–60	max 8	–	–	max 4

2. Making of the inner part: mixing of slag, limestone or dolomite and binder, in an amount of 80 (slag), 20 (limestone or dolomite) and 5% (binder – molasses) and pelletising in a laboratory balling drum (diameter 500 mm, drum width 200 mm, side height 70 mm), using a speed of 20 rpm, and then on a balling disc (diameter 1500 mm, side height 200 mm, variable angle of inclination and speed of 10 rpm). The balling drum used in the study is shown in Fig. 2, and the balling disc is shown in Fig. 3 and 4.

Fig. 3. Balling disc

Rys. 3. Talerz grudkujący

Fig. 4. Pellets on a balling disc during the process of applying the outer layer

Rys. 4. Widok grudek na talerzu grudkującym w czasie procesu nakładania warstwy zewnętrznej

3. Making of the intermediate part by pelletising pellets (after making the inner part) with a diameter of more than 10 mm, adding only limestone or dolomite, until a layer with a thickness of 1–5 mm is obtained, and then.
4. Making of the outer part by pelletising pellets (with an intermediate layer) with a diameter of more than 12 mm, adding only lime, until a layer with a thickness of 1 to 5 mm is obtained.
5. Drying of raw pellets first in the air and then in a dryer to remove all moisture (water).

2.3. EXAMINATION OF PHYSICAL PROPERTIES OF PELLETS

After hardening, raw composite pellets, with a total diameter of more than 15 mm, were subjected to strength tests using the drop method, then the pellets were dried to a moisture content below 2%, acceptable when using materials in the metallurgical process.

Grain distribution, calculated chemical composition and average diameter of the final composite pellets were also determined.

Table 2 presents the physico-chemical parameters of experimental (full – final) composite pellets, with the total diameter (internal diameter + intermediate layer + outer layer).

The calculated chemical composition of the experimental (final) composite pellets was determined from the mass balance of materials used in the pelletising process and chemical composition of these materials (Table 1). The content of H_2O was obtained after the pellets were dried.

Figure 5 shows an example of composite pellets after drying, before being used for laboratory tests.

Fig. 5. Portion of PLAS10 pellets prior to dropping into a metal bath

Rys. 5. Porcja grudek GŻWG10 przed wrzuceniem do kąpieli metalowej

Table 3 presents the results of strength tests of experimental composite pellets.

Drop resistance was the number of drops of a specified number of pellets (80 samples were selected from each type of the pellets) on a metal plate from a height of 2 m until the half of the tested sample disintegrated.

In practice, this determines the possible number of pellets being poured around during transport without breaking up.

Figure 6 shows the composite pellets after a drop test.

Table 3 shows that the PLASAl$_{Ca}$SLAG composite pellets are characterised by the highest strength, while PLAS25 – the smallest.

2.4. LABORATORY HEATS WITH THE USE OF EXPERIMENTAL COMPOSITE PELLETS

In order to study the behaviour of composite pellets in the process of steel refining, 4 laboratory heats were made in a 30 kg VIM Lab 30 vacuum induction furnace.

The lining of the crucible is a monolithic ceramic insert, made of $Al_2O_3 \cdot MgO$ magnesia-spinel mix, em-

Table 2. Physico-chemical parameters of experimental (full) composite pellets

Tabela 2. Parametry fizyko-chemiczne doświadczalnych (pełnych) grudek kompozytowych

Pellet type	Calculated content in the entire composite pellet, %						Diameter d, mm		
	CaO	SiO_2	Al_2O_3	MgO	Al_{met}	H_2O	d_{avg}	d_{min}	d_{max}
$PLASAl_{Ca}SLAG$	35.0	5.2	47.8	6.3	0	3.5	18	15	22
PLAS10	53.75	2.56	24.2	3.38	7.36	5.71	25	22	28
PLAS25	58.48	2.28	21.6	4.39	6.57	5.1	16	14	18
PLASS	40.71	30.0	24.9	0.75	0	0	19	16	22

Table 3. Strength of experimental composite pellets determined using the drop method

Tabela 3. Wytrzymałość doświadczalnych grudek kompozytowych wyznaczona metodą zrzutową

Pellet type	Drop resistance number of drops (number of damaged)	Observation
$PLASAl_{Ca}SLAG$	1 – (5), 2 – (15), 3 – (15)	Highly resistant pellets
PLAS10	1 – (10), 2 – (33), 3 – (18)	After hitting the sheet, the lining falls of only at the point if impact
PLAS25	1 – (all disintegrated)	Highly fragile pellets
PLASS	1 – (60), 2 – (16), 3 – (4)	The pellets disintegrate into halves or even smaller pieces

Fig. 6. Composite pellets after a drop test: a) P 25 pellets, b) Al_{Ca} SLAG 70 pellets, c) P 10 pellets, d) LASS pellets

Rys. 6 Widok grudek kompozytowych po próbie zrzutowej: a) grudki G 25, b) grudki AlCa SLAG 70, c) grudki G 10, d) grudki ŻWGK

bedded in the coil using a dry whipped mix and then burned.

Laboratory melts were carried out on a specific chemical composition of steel, shown in Table 4.

The pellets were introduced into the crucible at atmospheric pressure (with the furnace open).

Table 5 presents the chemical composition of the basic charge material for the experimental heats, which was Armco iron.

After melting the charge at a vacuum of 0.50 mbar and with argon chamber pressure of 250 mbar, addition of alloy additives ($C_{graphite}$, FeMn, FeSi and Al) and heating of the metal bath to 1580°C, the induction furnace chamber was opened (Fig. 7) and the same number of composite pellets was added in batches, and once the slag melted, the bath was held underneath the slag made of composite pellets for at least 4 minutes. The slag was sampled and the liquid steel was cast into a casting mould (Fig. 8). A slice with a thickness of 10–15 mm was cut at half height from the cast round ingot as shown in Figure 9. From this slice, at a distance of 1/3 of the side length from the outer edge, a 20 × 20 mm^2 sample was cut for a microsection for morphology testing of non-metallic inclusions (Fig. 10).

Table 4. Chemical composition of the steel used for testing with composite pellets, wt %
Tabela 4. Skład chemiczny stali stosowanej do prób z grudkami kompozytowymi, %

C	Mn	Si	F	S	Cr	Ni	Cu	Al
0.09	0.90	0.20	max	max	max	max	max	max
0.11	1.10	0.25	0.015	0.020	0.12	0.10	0.25	0.01

Table 5. Chemical composition of Armco iron used as charge material in test heats, wt %
Tabela 5. Skład chemiczny żelaza armco użytego w wytopach doświadczalnych stali, %

C	Si	Mn	Al	F	S	Cr	Ni	Cu	O ppm	N ppm
0.03	0.007	0.22	0.046	0.009	0.004	0.03	0.02	0.01	18	35

Fig. 7. Adding composite pellets in portions into liquid steel
Rys. 7. Dodawanie kompozytowych grudek porcjami do ciekłej stali

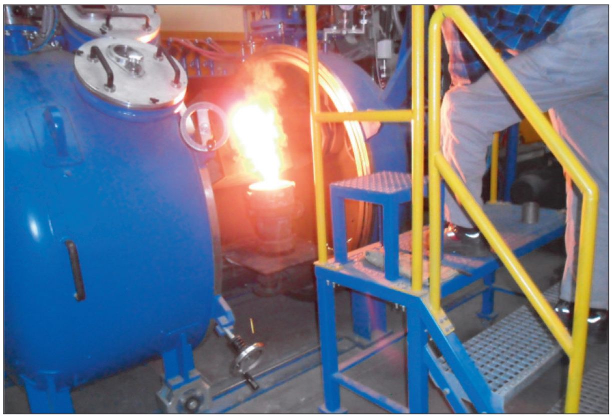

Fig. 8. Casting liquid steel into the casting mould
Rys. 8. Odlewanie ciekłej stali do wlewnicy

Table 6 lists the chemical compositions of cast ingots, and Tables 7 and 8 respectively list the chemical compositions, alkalinity and total contents of FeO + MnO slags from these casts.

Fig. 9. Cast ingots from four laboratory heats
Rys. 9. Widok odlanych wlewków z czterech wytopów laboratoryjnych

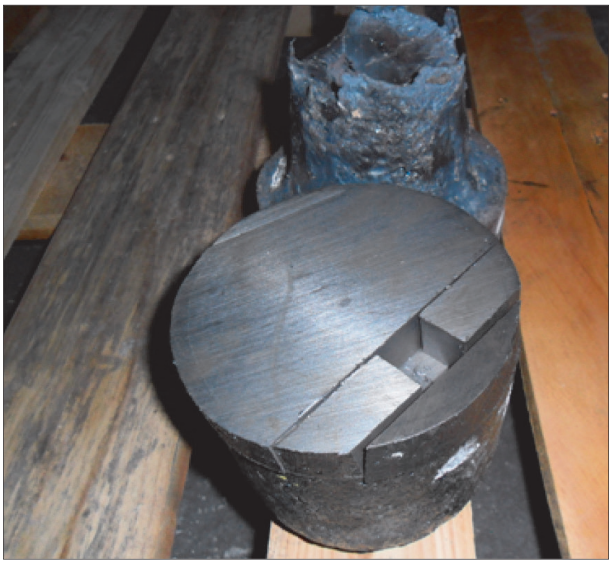

Fig. 10. Cast ingots and the sampling location for microscopic studies of morphology of non-metallic inclusions
Rys. 10. Widok odlanych wlewków i miejsce pobierania próbki do badań morfologii wtrąceń

The chemical compositions of these heats in the first two cases indicate the passing of the metal residue in the crucible from previous melts of high-alloy steels.

Table 6. Chemical compositions of cast ingots
Tabela 6. Składy chemiczne odlanych wlewków

Heat No.	Chemical composition, %								
	C	Mn	Si	F	S	Cr	Ni	Cu	Altotal
N151	0.16	1.21	0.23	0.004	0.027	0.067	0.48	0.22	0.11
N152	0.14	1.2	0.13	0.004	0.027	0.080	0.13	0.083	0.005
N153	0.13	1.02	0.21	0.004	0.009	0.090	0.030	0.055	0.007
N154	0.13	1.07	0.18	0.004	0.007	0.081	0.026	0.055	0.006

Table 7. Chemical compositions of slags from laboratory heats
Tabela 7. Składy chemiczne żużli z pieca indukcyjnego wytopów laboratoryjnych

Heat No.	Composite pellet type	Pellet weight percentage	Furnace slag chemical composition						
			CaO	SiO_2	FeO	MnO	Al_2O_3	P_2O_5	MgO
		%	%	%	%	%	%	%	%
N151	$PLASAl_{Ca}SLAG$	1.7	44.06	11.24	2.05	3.98	30.67	<0.01	2.83
N152	PLAS10	2.1	40.26	14.91	<0.01	3.82	27.84	<0.01	5.84
N153	PLASS	2.1	41.14	20.87	<0.01	4.45	21.87	<0.01	4.66
N154	PLAS25	2.1	38.10	15.62	0.84	2.34	21.01	<0.01	11.43

Table 8. Alkalinity and total content of FeO and MnO of slags from laboratory heats
Tabela 8. Zasadowości i zawartości sumaryczne FeO i MnO żużli z wytopów laboratoryjnych

Heat No.	Composite pellet type	CaO/SiO_2	CaO/Al_2O_3	$CaO/SiO_2 + Al_2O_3$	FeO + MnO
		–	–	–	%
N151	$PLASAl_{Ca}SLAG$	3.9	1.4	1.05	6.03
N152	PLAS10	2.7	1.4	0.94	3.82
N153	PLASS	2.0	1.9	0.96	4.45
N154	PLAS25	2.4	1.8	1.04	2.34

In the other two heats using clean crucibles, chemical compositions meet the requirements set out in Table 4. The steel laboratory heats were mainly intended to examine the behaviour of composite pellets of slags after adding to the bath under steel refining conditions, at a temperature of 1580–1620°C. Therefore, the final results of phosphorus and sulphur content do not reflect the effectiveness of desulphurisation and dephosphorisation processes, as well as the effectiveness of steel refining and reduction of total oxygen content due to very short periods of liquid steel holding under slags formed from composite pellets.

The analysis of the data contained in Table 6 shows that virtually all slags from composite experimental pellets had more impact on dephosphorisation of heats and on their sulphurisation from alloy and slag-forming additives and residual steel from previous heats, with $PLASAl_{Ca}SLAG$ and PLAS10 pellets – significant impact, and PLASS and PLAS25 – slight impact. The significant increases in sulphur, nickel and copper in heats N151 and N152 result, as already mentioned, from the contamination of the crucible lining, as these heats were produced as 'rinsing' the crucible after previous melts of high-alloy steels.

The slags resulting from the melting of composite pellets were characterised by, as shown in Tables 7 and 8, CaO/SiO_2 alkalinity from 2.0 to 3.9, high Al_2O_3 content and in the case of dolomite pellets (PLAS25) – high MgO content. These slags, with the $CaO/(SiO_2 + Al_2O_3)$ alkalinity of 0.94–1.05, were characterised by high fluidity. The contents of FeO + MnO in these slags, ranging from 2.34 to 6.03, indicate the oxidative nature of these slags, mainly due to the moisture content in the composite pellets, as well as the CO_2 emission during melting of the pellets. The achievement of balance by the slag coming from the addition of composite pellets

Table 9. Results of quantitative studies of NMIs in steel with composite pellets
Tabela 9. Wyniki badań ilościowych WN w stali z udziałem grudek kompozytowych

Heat No.	Slag type	Surface fracture of NMIs	Average diameter	Number of NMIs	d_{min}	d_{max}
		%	µm	pcs/mm^2	µm	µm
N151	$PLASAl_{Ca}Slag70$	0.17	1.61	2936	0.99	7.75
N152	PLAS10	0.18	3.01	838	0.99	10.61
N153	PLASS	0.07	2.64	328	0.99	12.78
N154	PLAS25	0.06	2.44	369	0.99	7.41

Table 10. Results of morphology studies of NMIs in steel with composite pellets
Tabela 10. Wyniki badań morfologii WN w stali z zastosowaniem grudek kompozytowych

Heat No.	Slag type	Morphology of non-metallic inclusions Type
N151	$PLASAl_{Ca}Slag70$	MnS – very fine, Al_2O_3 $Al_2O_3 \cdot TiO_2$ – very fine
N152	PLAS10	MnS – very fine, SiO_2 + MnS – fine $Al_2O_3 \cdot SiO_2$ + MnS – very fine
N153	PLASS	MnS – fine Al_2O_3 + MnS – very fine
N154	PLAS25	$Al_2O_3 \cdot SiO_2 \cdot CaO \cdot MgO$ – large ($d \cong 26$ µm) $Al_2O_3 \cdot SiO_2$ + MnS – very fine MnS – fine, $Al_2O_3 \cdot SiO_2$ + MnS – fine

takes much longer than 4 minutes. For this reason, the total oxygen content was not studied because the total oxygen content can only be obtained with deep vacuum degassing with strong mixing at the interface – refining slag – metal.

In industrial practice, slags with a similar chemical composition are formed in the ladle at the beginning of the secondary treatment, and then during the refining process, they are reduced for at least half an hour. In the laboratory furnace, after melting the slag and holding the metal bath under the slag for 4 minutes, the heat was cast for safety reasons (danger of erosion of the crucible lining and leakage of liquid metal to the induction coil of the furnace).

2.5. MICROSCOPIC QUANTITATIVE AND QUALITATIVE EXAMINATION OF NON-METALLIC INCLUSIONS

The identification of the chemical composition of particles was carried out using an INSPECT F scanning electron microscope equipped with an EDS detector for analysing chemical composition in micro-areas.

The assessment of NMIs morphology was carried out using the Met-Ilo software for quantitative image analysis. The results of quantitative examination of NMIs are compared in Tables 9 and 10.

The data in Table 9 indicate that the highest purity is attributed to steel from the N153 and N154 heats, under slag from composite pellets PLASS and PLAS25, due to the NMIs surface area and number. The elevated indicators, both mentioned above, in the other two slags can indicate the transition to steel from the rinsed induction furnace lining (high Al_2O_3 contents in the slags from these heats – Table 7).

The chemical composition of NMIs indicates that despite the high content of CaO in these slags (about 40% and above), CaO was not present in the inclusions. These inclusions consisted mainly of aluminosilicates ($Al_2O_3 \cdot SiO_2$) and MnS precipitated on them or separately. In the steel sample with the PLAS25 composite pellets with dolomite, there were also complex spinel inclusions.

The above analysis shows that the best ability to refine steel is attributed to composite pellets made of aluminium dross and skimmings, with an increased content of CaO and dolomite addition, as well as pellets made of molten lime-aluminium-silicon (wollastonite) slag.

The assessment of the effectiveness of removing (refining) NMIs from steel by composite pellets requires further research on a semi-industrial or industrial scale.

3. EVALUATION OF THE USEFULNESS OF COMPOSITE PELLETS FOR INDUSTRIAL TESTING

As already mentioned, the best refining efficiency is attributed to composite pellets made of lime-aluminium-silicon (wollastonite) slag (LASS) and lime-aluminide slag, 'aluminium dross and skimmings' with the addition of lime and dolomite (PLAS25), which is why they should be considered first. Composite pellets with dolomite are, however, characterised by a very low durability, and therefore the process of producing pellets with dolomite should be further improved.

4. SUMMARY AND CONCLUSIONS

1. The study included the development of a multi-layered pelletising method with the use of a basic slag-forming material and materials (carbonates) causing rapid pellet disintegration under high temperature.
2. Four different types of experimental composite pellets were produced.
3. The behaviour of these pellets in steel refining was tested in a 30 kg laboratory induction furnace.
4. The quantitative studies of IMNs in samples from these heats showed the best efficiency of composite pellets based on molten lime-aluminium-silicon (wollastonite PLASS) slag with alkalinity $CaO/SiO_2 \cong 2.0$ and PLAS25 lime-aluminide slag based on Al dross and skimmings with lime and dolomite with alkalinity $CaO/SiO_2 \cong 2.4$.
5. Composite pellets are recommended in processes where a particularly fast production of refining slag is required, such as in RH, VTD devices as well as in the refining of high purity steels in a ladle furnace.

REFERENCES

[1] L. Kneis, B. Trummer, B. Knabl. The Hybrid Plug – An Innovative Purging Plug for Steel Ladles. *RHI Bulletin*, 2004, (1), p. 34–38.
[2] B. Trummer, W. Fellner, A. Viertauer, L. Kneis, G. Hackl. Purging Plugs for Soft Gas Bubbling: A Water Modelling Comparison of Hybrid and Slot Designs. *RHI Bulletin*, 2014, (1), p. 29–33.
[3] F.P. Tang, X.-F. Wang, Z. Li, Y. Lin, B.W. Chen, P. Fei. Novel concept of cleansing IF molten steel with dispersed in situ phase induced by composite ball explosive reaction in RH ladles. *Ironmaking and Steelmaking*, 38, 2011, (4), p. 285–290.