

M. DZIARMAGOWSKI*, B. ZAWADA**

POSSIBILITIES FOR THE UTILISATION OF STEELMAKING SLAGS FOR THE PRODUCTION OF SLAG-FORMING MATERIALS

MOŻLIWOŚCI WYKORZYSTANIA ŻUŻLI STALOWNICZYCH DO WYTWARZANIA MATERIAŁÓW ŻUŻLOTWÓRCZYCH

The paper presents existing methods and findings of own research on the utilisation of steelmaking slags for the production of slag-forming materials used in secondary steelmaking. The research conducted concerned the possibilities for the utilisation of BOF slag and ladle slag for this purpose. On the basis of calculations and tests performed it has been found that reduced ladle slag of high Al_2O_3 content blended with lime and bauxite additions can be used for the production of slag-forming compounds. The amounts of lime and bauxite added should be determined on the basis of calculations performed with computer thermodynamic databases.

W pracy przedstawiono dotychczasowe metody oraz wyniki badań własnych wykorzystania żużli stalowniczych do wytwarzania materiałów żużlotwórczych wykorzystywanych w czasie pozapiecowej rafinacji stali. Przeprowadzone badania dotyczyły możliwości wykorzystania w tym celu żużła konwertorowego oraz żużła kadziowego. Na podstawie przeprowadzonych obliczeń i badań stwierdzono, że do wytwarzania mieszanek żużlotwórczych można wykorzystywać zredukowany żużel kadziowy o wysokiej zawartości Al_2O_3 po wymieszaniu z dodatkami wapna i boksytu. Dodatki wapna i boksytu powinny zostać określone na podstawie obliczeń prowadzonych w oparciu o komputerowe bazy danych termodynamicznych.

1. Introduction

Research projects with the objective of utilizing the non-metallic phase from the converter slag reduction process in the EAF as a slag-forming material for secondary steelmaking have been conducted in the world for a number of years. The objective of the research is to develop a process which enables the single-stage production of a slag-forming material. The production method of a material like this consists in the reduction of converter slag with addition of bauxite or bauxite and lime. It brings about a limitation of the mass of the slag melted, thus increasing process costs. Furthermore, it is not possible to correct the chemical composition of the final material after the process is completed.

Due to the aforesaid it has been decided that a double-stage method of producing slag-forming compounds on the basis of reduced steelmaking slag be developed. The developed method restricts or completely eliminates any addition of lime or bauxite during the reduction process, and the required chemical composition

of the slag-forming material results from the blending of the reduced non-metallic phase with lime and bauxite after the process is completed.

2. Characteristics and production of slag-forming materials

During BOF or EAF steel tapping the furnace slag is cut off and new slag is formed in the ladle. This slag should have high refining qualities and a low liquidus temperature, particularly if no ladle furnace is available and the refining processes are carried out in the ladle.

The refining slag formed in the ladle should contain as small amount of ferrous and manganese oxides and titanium oxides as possible. An increase in the ferrous and manganese oxide content in the refining slag causes an increase in the penetration of oxygen from the atmosphere to the molten steel, and an increase in the titanium oxide content causes the formation of solid precipitates of titanium oxides and calcium oxide compounds, which

* FACULTY OF METALS ENGINEERING AND INDUSTRIAL COMPUTER SCIENCE, AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, 30-059 KRAKÓW, 30 MICKIEWICZA AVE., POLAND

** FACULTY OF ELECTRICAL ENGINEERING, AUTOMATICS, COMPUTER SCIENCE AND ELECTRONICS, AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, 30-059 KRAKÓW, 30 MICKIEWICZA AVE., POLAND

increases the slag viscosity and reduces refining qualities.

The refining slag can be formed in the ladle by:

- adding a ready calcium-aluminium synthetic slag,
- adding a lime and bauxite compound of a chemical composition based on the CaO-Al₂O₃-SiO₂ system. Calcium aluminates are formed during the transition of the added material into a liquid state on the steel surface in the ladle or the ladle furnace.

The ready calcium-aluminium synthetic slag is very expensive and therefore it is usually used only in the tundish. During secondary steelmaking in the ladle or the ladle-furnace a synthetic refining slag is formed from lime and roasted bauxite compounds of various chemical compositions: 12-55% CaO, 2-6% SiO₂, 0,5 - 10% MgO, 1,5-3,0% FeO, 40 - 70% AL₂O₃, 0,2 - 6,0% TiO₂, 0 - 0,1% P₂O₅, 0,02-0,20% S. The liquidus temperature of the slag formed from such compounds is 1600 - 1700°C.

The growth in the price of lime and bauxite has meant that other materials for the formation of synthetic refining slag in the ladle or ladle furnace have been sought. Most of the compounds used are patent protected. For example, the following materials, which can form a synthetic refining slag, are specified in US patent 5271339: 0-30% magnesium, 0-60% calcium carbonate, 0-35% sodium carbonate, 0-20% glass, 0-25% fluorite, 0-40% aluminium oxide, 0-10% coke, 2-55% calcium carbide, 0-35% lime, 0-9% blast furnace slag, 0-50% calcium aluminate. The patent also gives three examples of synthetic slag formation in the ladle. US patent 41982229 presents a method of utilizing calcium carbide for the formation of refining slag in the ladle. The main objective of the proposed method is to dephosphatize steel. US patent 41982229 presents a method of refining slag formation resulting from blast furnace slag, lime and dolomite being put onto the surface of molten steel in the ladle.

Carbonate materials are used for the formation of refining slag in the patents discussed. During slag formation these materials disintegrate and require a certain amount of heat, which may not be possible if no ladle furnace is available. Also the use of fluorite to reduce slag viscosity is detrimental, due to the hazardous emissions of fluorine compounds. In some examples of slag-forming material production one can observe the use of blast furnace slag, which causes an increase in the SiO₂ content in the slag formed and a reduction of its refining qualities.

The ZEWA – zero waste – method is a method that includes the application of waste materials for slag-formation. This method consists in melting convert-

er slag with lime and bauxite additions under reducing conditions [1, 2].

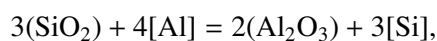
The slag-forming material obtained with the ZEWA method has a high SiO₂ content, exceeding 10%. This results in a reduction of the refining qualities of the obtained material. A decrease in SiO₂ content, and at the same time in the ferrous and manganese oxide content, is only possible if larger amounts of lime and bauxite are added. Increasing additions of these materials, in particular of lime, in the process causes a growth in energy consumption and in manufacturing costs. Moreover, the high variability of the chemical composition of the converter slag, virtually uncontrollable during the reducing melting process, means that additions of calcium and bauxite can only be roughly approximated. As a result a slag forming material of reduced refining qualities is obtained.

In our own research into the steelmaking slag reduction process general conditions for the production of a slag-forming compound with the use of ladle slag of a specified chemical composition as the basic calcium oxide and aluminium oxide carrier have been determined. These conditions are presented in the paper [3].

3. Determination of the possibilities for the utilisation of steelmaking slag for the production of slag-forming compounds

The method presented in the paper [3] only allows for the determination of the possibilities for the utilisation of reduced ladle slag of a specified chemical composition to obtain a slag-forming material. Implementation of the presented method within industrial practice still requires the determination of restrictions regarding the chemical composition of the slag reduced, the percentage of the carbon reducer and the reduction process temperature, as well as the range of the chemical composition of the slag-forming compound which can be obtained.

The reduced steelmaking slag is a carrier of calcium oxide or calcium oxide and aluminium trioxide. However, at the same time, a high silica content appears in the reduced slag. If the share of the reduced slag is high, the SiO₂ content in the compound is high. After the refining slag is formed on the surface of the molten steel, deoxidised with aluminium, the following reaction occurs:



resulting in an increase in the silicon content in the molten steel and in a reduction of the desulphurising capacity of the slag [4]. Therefore the SiO₂ content in the slag reduced should be as low as possible. We can

assume that the limiting SiO_2 content in the slag reduced should not exceed 15%.

Only a small amount of sulphur, brought in by the steelmaking slag, is removed in the reduction process. Therefore the sulphur content in the slag reduced should not exceed 0.2%.

Taking account of the foregoing limitations of the chemical composition of the slag reduced we find that the converter slag and the steelmaking ladle slag of a specified chemical composition can be used for the production of steelmaking compounds.

The reduction process should be conducted in such a way that the total amount of ferrous and manganese oxides in the finished slag-forming material does not exceed 2.0%. At the same time, as the reduction process in the liquid state is much faster than in the solid state, no solid precipitates should appear in the liquid non-metallic phase which forms during the process. It

means that the reduction process temperature should be higher than the liquidus temperature of the non-metallic phase. Yet for energy reasons one should aim at conducting the process at as low a temperature as possible. Previous experiences [1, 2, 3] indicate that the liquidus temperature of the non-metallic phase can be lowered by adding bauxite. However, this causes a decrease in the share of the slag reduced in the charge and thus affects process costs unfavourably.

To determine the reducer share and the temperature of the reduction process of steelmaking slags for the production of slag-forming compounds, simulation calculations including the application of computer thermodynamic databases have been performed.

The calculations have been performed for converter slags and a ladle slag of compositions presented in Tables 1 and 2.

TABLE 1

The chemical composition of converter slags

Slag	Chemical composition, %								
	CaO	SiO ₂	MgO	FeO	Fe ₂ O ₃	MnO	Al ₂ O ₃	P ₂ O ₅	S
1.	43,69	12,85	3,47	21,32	9,14	3,01	1,71	0,96	0,08
2.	47,79	16,58	4,17	13,48	10,48	3,25	1,87	1,07	0,10
3.	44,08	13,59	3,17	18,89	11,70	3,07	1,43	0,62	0,06

TABLE 2

The chemical composition of ladle slag

Slag	Chemical composition, %								
	CaO	SiO ₂	MgO	FeO	MnO	Al ₂ O ₃	TiO ₂	P ₂ O ₅	S
4.	35,49	9,25	5,96	8,24	7,23	30,39	0,80	0,10	0,04

In order to determine the temperature of the reduction process of the converter slags and the share of the carbon reducer, simulation calculations have been performed and their results are presented in Fig. 1. The calculations performed show that the share of the carbon reducer in the reduction process conducted at a temperature of 1800°C should be 7% of the mass of slag 1 and 3 and 6% of the mass of slag 2. At these percentages of the reducer the FeO and MnO contents in the non-metallic phase are sufficiently low.

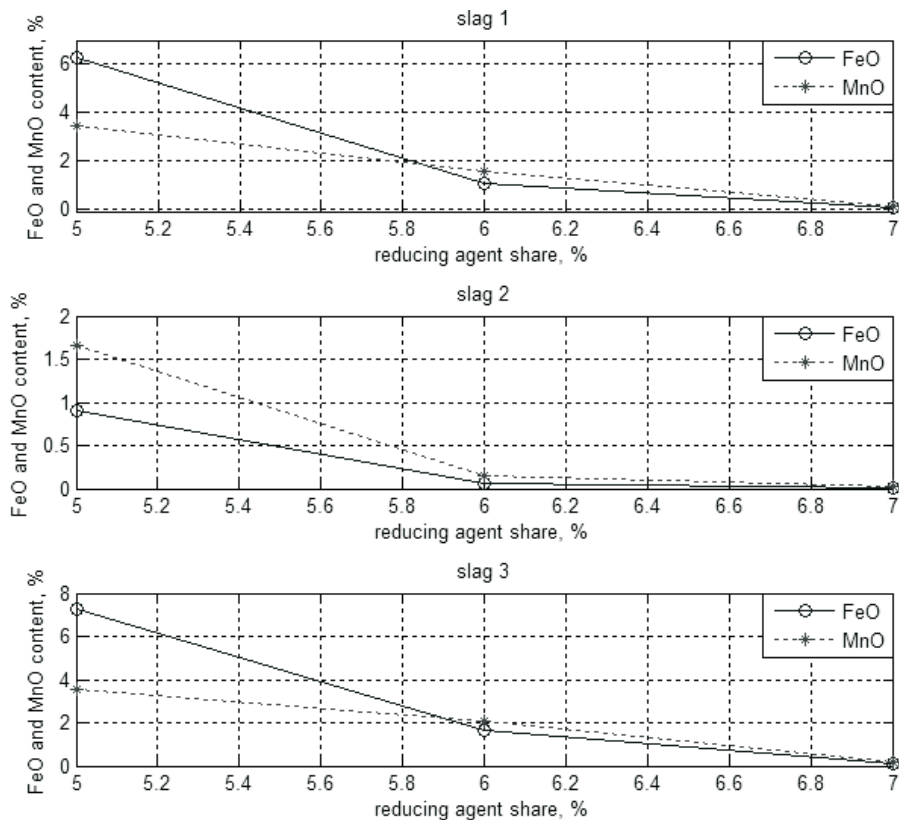


Fig. 1. The equilibrium FeO and MnO content in the non-metallic phase obtained in the reduction process of slags 1-3, conducted at a temperature of 1800°C, in relation to the share of the reducer

The slag reduction process should be carried out in a liquid state. However, as the FeO and MnO content in the phase reduced decreases, solid compounds, mainly calcium silicate, precipitate. The mass of the solid pre-

cipitates declines as the process temperature grows. The effect of temperature on the change in the solid precipitate content in the liquid slag phase during the reduction process of the converter slags 1-3 is presented in Fig. 2.

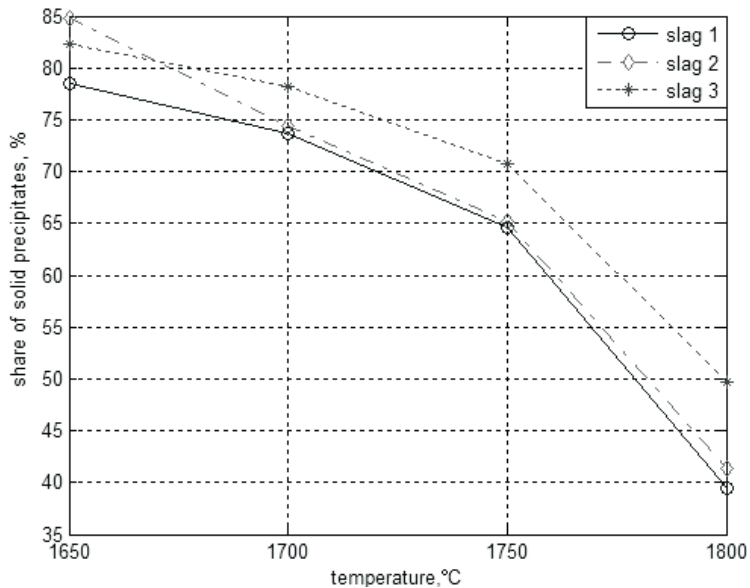


Fig. 2. The share of solid precipitates in the liquid slag phase in the equilibrium state in relation to the process temperature

By analyzing the results presented in Fig. 1 and 2 it is found that the reduction process of the converter slags 1-3 should be carried out at a very high temperature, exceeding 1800°C. The process temperature may be lowered by increasing the Al₂O₃ content in the phase reduced. To this end simulation calculations have been performed for the reduction process of slags 1-3 blended with bauxite, an Al₂O₃ carrier. The results of the simulation calculations allowing for the bauxite share in the phase reduced that enables to conduct the process at a temperature of the lowest liquidus temperature of the phase reduced to be determined are presented in Fig. 3

and in Table 3. The same share of the carbon reducer in relation to the mass of the slag reduced was maintained in the calculations performed.

The calculation results presented in Fig. 3 and Table 3 indicate that the reduction process may be carried out at a temperature below 1500°C. However, one should bear in mind that as the temperature rises the dynamic viscosity of the liquid slag phase decreases. Then the rate of diffusion of ferrous and oxygen ions into the interface between the solid carbon reducer and the liquid slag, where the following chemical reaction occurs, increases:

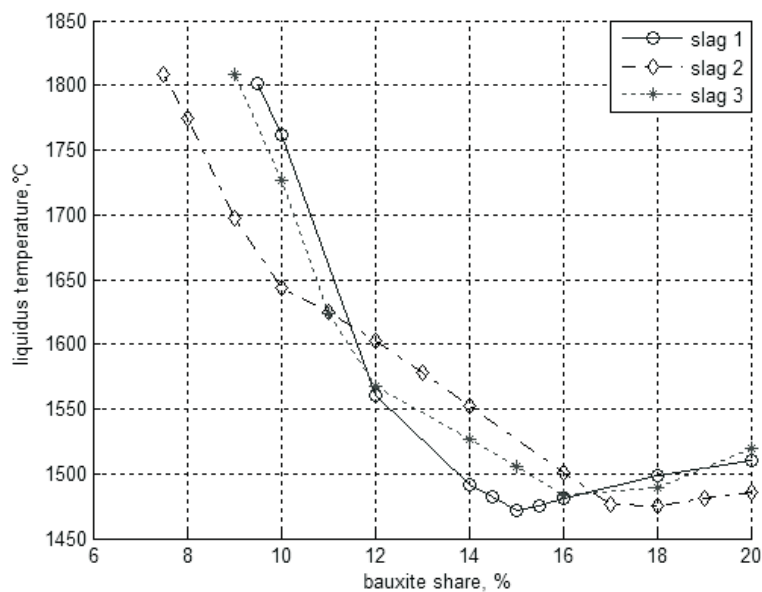
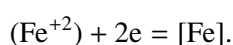
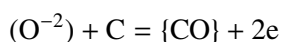


Fig. 3. The effect of the bauxite share in the charge reduced on the liquidus temperature of the non-metallic phase in the equilibrium state

TABLE 3

The lowest liquidus temperature of the non-metallic phase in the equilibrium in relation to the share of bauxite in the phase reduced

Slag	Share of bauxite, %	Lowest liquidus temperature, °C
1.	15	1472
2.	18	1475
3.	16	1483



At the same time, as the FeO content decreases, the reduction of manganese oxide begins to take place. These are diffusion processes and thus the reduction rate increases as the viscosity of the phase reduced decreases. The reduction process, therefore, should be conducted at a temperature of the liquidus temperature of the reduced phase plus 100-150°C.

Due to the abovementioned it has been decided that simulation calculations for the reduction process of slag 4, carried out at a temperature of 1650°C, be performed. The calculation results of the equilibrium content of FeO and MnO in the reduced non-metallic phase depending on the share of the carbon reducer and the liquidus temperature of the reduced phase are presented in Fig. 4.

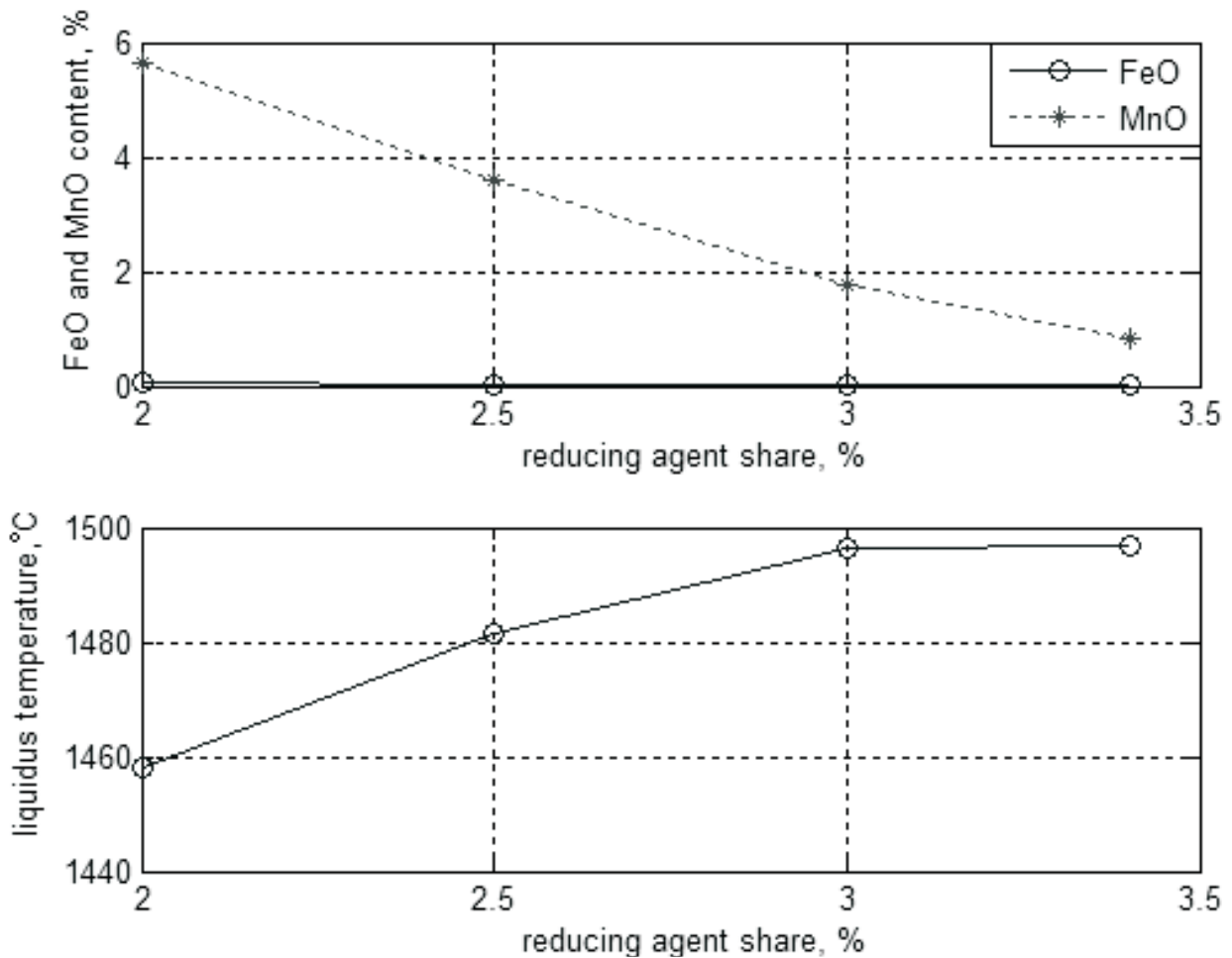


Fig. 4. The equilibrium FeO and MnO content and the liquidus temperature of the non-metallic phase obtained in the reduction process of the slag 4 in relation to the share of the reducing agent

The results of the performed simulation calculations revealed that the reduction process of the ladle slag of a high Al_2O_3 content may be carried out without adding bauxite to the charge, and the reducer share of a given chemical composition should be 3% of slag mass.

To verify the simulation calculations, 3 kg of fragmented slag 4 were blended with the ground carbon reducer, bringing in elemental carbon in the amount of 3% of the slag mass. The size of the fragmented slag particles did not exceed 50 mm and the size of the ground reducer particles did not exceed 5 mm. The resulting compound was melted in a single-electrode electric arc furnace. The process was carried out in a graphite crucible and, at a temperature of 1650°C , took 13 minutes. After the process had been completed a liquid non-metallic phase without solid precipitates and a liquid metallic phase were obtained. The crucible content was poured out onto a steel plate and was cooled down with compressed air while being poured out. After separation of

the reduced metal, 2.5 kg of the non-metallic phase was obtained. Its chemical constitution was: 42,35% CaO , 10,95% SiO_2 , 7,20% MgO , 0,1% FeO , 2,01% MnO , 36,40% Al_2O_3 , 0,89% TiO_2 , 0,05% P_2O_5 , 0,04% S , 0,01% C .

A high SiO_2 content was obtained in the reduced non-metallic phase. This reduces the refining qualities of the slag that may be obtained as a result of the addition of the non-metallic phase onto the surface of the liquid steel in the ladle. To obtain a slag-forming material of a lower SiO_2 content it is necessary to blend it with an addition of lime or roasted bauxite. Additions of these materials should be specified so that the obtained compound has a possibly low liquidus temperature and a low SiO_2 content. Fig. 5 shows the results of the simulation calculations of the liquidus temperature of compounds obtained with various additions of lime and roasted bauxite, and Fig. 6 shows the change in the SiO_2 content.

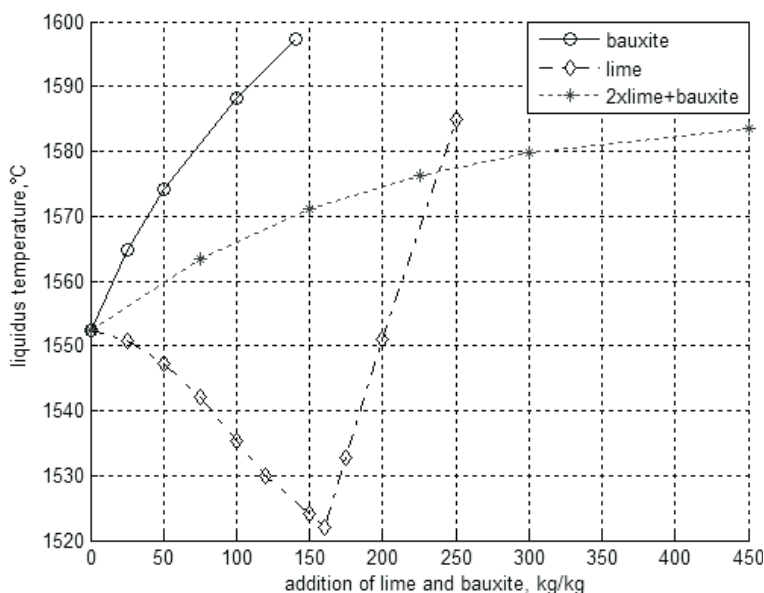


Fig. 5. The effect of the addition of lime and bauxite on the liquidus temperature of the slag-forming compound obtained on the basis of slag 4

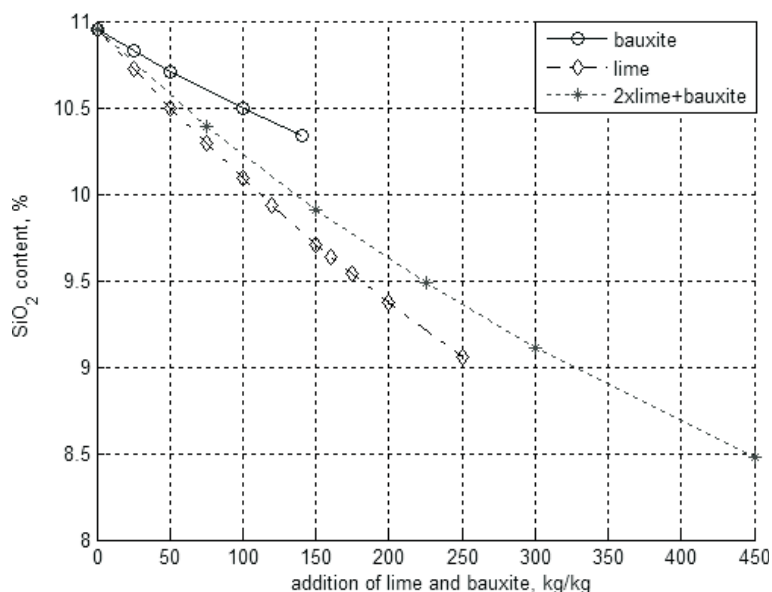


Fig. 6. The effect of the addition of lime and bauxite on the SiO_2 content in the slag-forming compound obtained on the basis of slag 4

The graphs presented enable the lime and bauxite additions to be determined in order to obtain slag-forming compounds of various chemical compositions and liquidus temperatures. When the lime addition was 0.16 kg per 1 kg of the non-metallic phase the obtained compound comprised: 49,47% CaO, 9,64% SiO_2 , 6,24% MgO, 0,09% FeO, 1,73% MnO, 31,38% Al_2O_3 , 0,77% TiO_2 , 0,004% P_2O_5 , 0,003% S, 0,008% C, and had the lowest liquidus temperature of 1522°C. The addition of 0.3 kg of lime per 1 kg of the non-metallic phase and of 0.15 kg of roasted bauxite per 1 kg of the non-metallic phase resulted in an increase in the liquidus temperature of up to 1584°C and at the same time the

composition of the compound was: 48,68% CaO, 8,48% SiO_2 , 5,02% MgO, 0,22% FeO, 1,38% MnO, 34,20% Al_2O_3 , 1,01% TiO_2 , 0,003% P_2O_5 , 0,003% S, 0,007% C, and had the lowest SiO_2 content.

4. Conclusion

The presented examples of the possibilities for obtaining slag-forming compounds on the basis of the reduced steelmaking slag conclude that ladle slags of a high Al_2O_3 content should be used in the reduction process. It helps to avoid adding bauxite to the charge, in order to lower the process temperature.

The chemical composition of the non-metallic phase obtained should be modified by adding lime, bauxite or lime and bauxite. The selection of the amount and type of materials added should depend on the assumed criterion, which may either be the liquidus temperature of the compound obtained or the SiO₂ content.

Acknowledgements

We would like to acknowledge the support of this work by the Project EEA Financial Mechanism No PL0083.

REFERENCES

- [1] A. Fleischanderl, U. Gennari, A. Ilie, Revenue from waste. ZEWA - metallurgical process for treatment of residues from steel industry and other industrial sectors to generate valuable products. *Ironmaking and Steelmaking* **31**, 6, 444-449 (2004).
- [2] A. Fleischanderl, U. Gennari, J. Borlee, M. Gimenez, F. Sorrentino, J. M. Delbecq, C. Grisvard, J. Hoffman, J. Calloens, K. Kubica, E. Roubaud, M. Raclavsky, Zewa – ein neues metallurgisches Verfahren zur Herstellung von Wertstoffen aus industriellen Reststoffen. *Stahl und Eisen* **124**, 12, 123-131 (2004).
- [3] M. Dziarmagowski, T. Kargul, Wytwarzanie materiałów żużlotwórczych w procesie redukcji żużli stalowniczych. *Archives of Metallurgy and Materials* **54**, nr. 1. (w druku) (2009).
- [4] B. Bonnevirole, P. Margueret, W. Meichsner, Optimazation of Secondary Metallurgy. *Kermetal* 97, Koszyce, Słowacja, s. 116-124.
- [1] A. Fleischanderl, U. Gennari, A. Ilie, Revenue from waste. ZEWA - metallurgical process for treat-