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PRODUCTION OF SLAG-FORMING MATERIALS IN THE STEELMAKING SLAG REDUCTION PROCESS

WYTWARZANIE MATERIAŁÓW ŻUŻLOTWÓRCZYCH W PROCESIE REDUKCJI ŻUŻŁA STALOWNICZYCH

Research on the steelmaking slag reduction process in an electric arc furnace has been carried out for many years. The research objective is to implement into a commercial practice a process enabling to utilize constantly growing slag mass without producing waste. The main obstacle is the impossibility to obtain products ensuring adequate profitability of the process. Therefore a method was developed, which allows to apply the reduction process for processing of steelmaking slag into a slag-forming material, which can be used for producing refining slag in secondary steelmaking. The price of the slag-forming material should ensure adequate profitability of the process.

Od wielu lat prowadzone są badania procesu redukcji żużła stalowniczego w elektrycznym piecu łukowym. Celem badań jest wdrożenie do praktyki przemysłowej procesu umożliwiającego bezodpadową utylizację stale narastającej masy żużła. Główną przeszkodą jest brak możliwości otrzymywania produktów zapewniających odpowiednią rentowność procesu. Z tego powodu opracowano metodę pozwalającą na wykorzystanie procesu redukcji do przetwarzania żużła stalowniczego w materiał żużlotwórczy, który może być stosowany do tworzenia żużła rafinacyjnego w czasie pozapiecowej rafinacji stali. Cena materiału żużlotwórczego powinna zapewniać odpowiednią rentowność procesu.

1. Introduction

Many research projects have been carried out in the world [1 ÷ 4] aiming at reduction of constantly growing mass of steelmaking slag. Slag reduction in an electric arc furnace is one of the methods developed. The process may result in obtaining metallic and non-metallic phases. The metallic phase may be used as Portland clinker [1,2] or blast furnace slag substitute for Portland clinker production [3]. Due to low profitability the process has not been implemented into a commercial practice yet. Research projects aiming at obtaining products ensuring adequate process profitability are still in progress. Studies aiming at obtaining a material used for slag forming during secondary steelmaking [3] are among such projects.

2. Slag formation during secondary steelmaking

Production of liquid steel is carried out in two stages. During the first stage a molten semi-product is produced in a BOF or in an EAF, during the second stage

refining is conducted in secondary steelmaking installations. The slag formed during the first stage is cut off during tapping of steel into a ladle because it has oxygenizing characteristics and high sulphur and phosphorus content, which make the refining process impossible.

Secondary steelmaking is carried out under slag formed in a ladle. The slag should perform the following functions:

- to prevent passing of oxygen from the atmosphere to the molten metal,
- to assimilate non-metallic inclusions floating,
- to absorb sulphur diffusing from the melt,
- not to interact aggressively with the refractory lining,
- to enable stable flaming of the electric arc if it is used for reheating of the melt, - to insulate against heat losses.

In order to perform the above mentioned functions refining slag formed in a ladle should be characterized by low liquidus temperature and low viscosity. Low liquidus temperature, below 1,650 K, is obtained in calcium-aluminium slags of the following chemical constitution: 50-55%CaO, 40-45%Al₂O₃ i 2-3%SiO₂.

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A calcium-aluminium refining slag may be formed by:

- addition of ready synthetic slag,
- addition of a mixture of chemical constitution based on the CaO-Al₂O₃-SiO₂ system.

Because of metallurgical reasons it is most advantageous to use ready synthetic slag prepared beforehand. Slag like this is formed by melting lime or lime stone and alumina carriers in an EAF or by sintering them in a rotary kiln [5].

Bauxite is the easiest available alumina carrier. The chemical constitution of roasted bauxite should be as follows: 87-90% Al₂O₃, 4-7% SiO₂, 1,3-2,0% FeO, 3,6-4,0% TiO₂.

Previous experiences from a commercial practice show that along with increase in the total content of ferrous and manganese oxides in refining slag, oxide diffusion from the atmosphere to the molten steel increases. Titanium oxides brought in by bauxite cause occurrence of solid precipitates of titanium oxide and calcium oxide compounds in refining slag, increase in its viscosity and diminution of refining characteristic.

Pure alumina is a material without harmful admixtures. Due to a very high price pure alumina is substituted by cheaper bauxite. However the price of bauxite is also high and therefore synthetic slag made from lime and alumina or bauxite by melting or sintering is expensive and in practice only used in a tundish during continuous steel casting.

During secondary steelmaking in a ladle or a ladle-furnace synthetic refining slag is formed from mixtures containing components based on the CaO-Al₂O₃-SiO₂ system. Usually they are lime and roasted bauxite of possibly low titanium oxide and ferrous oxide content. The chemical constitution of the mixture produced from lime and roasted bauxite should be as follows: 50-51% CaO, 40-41% Al₂O₃, 2-3% SiO₂, 1,5% FeO, 0,5% MgO, < 2,5% TiO₂, < 0,03% S.

3. Utilization of steelmaking slags for production of slag-forming materials

The growing prices of lime and bauxite cause that other materials for forming refining slag in a ladle or a ladle furnace are sought in the world. Processes of forming refining slag containing calcium carbide, magnesium carbide, blast furnace slag etc. [6] have been engineered. The ZEWA – zero waste process developed in Vitkovice in the Czech Republic [3] is one of the attempts to replace the currently used slag-forming mixtures. The process consists in utilization of BOF slag reduced in an EAF for forming of refining slag in a ladle furnace. During the reduction process bauxite is being

added to the melt reduced to increase the Al₂O₃ content in the product. It is planned to obtain a product of the following constitution: 44% CaO, 10-15% SiO₂, 35-38% Al₂O₃, 3% MgO. The TiO₂ content in the product is about 1.5% because the titanium oxide brought in by bauxite is not reduced during converter slag re-melting.

Converter slag is a CaO carrier in the ZEWA process. At the same time it brings in a small amount of Al₂O₃ and therefore bauxite is the main Al₂O₃ carrier. At the same time, due to the high SiO₂ content in converter slag, a high content of this component in the product is obtained, much higher than in a mixture of lime and roasted bauxite.

The SiO₂ content in the slag-forming material exceeding 10% reduces refining characteristics of the slag formed from this material because of increased likelihood to form solid precipitates of Ca₂SiO₄ type, in particular if the temperature falls down below 1,600°C. When the silicon content in steel is supplemented during refining, solid SiO₂ type precipitates are forming, which are coming out to the refining slag and are being assimilated there. It makes conditions for forming more and more solid precipitates. At the same time solid precipitates of titanium oxide and calcium oxide compounds occur in the refining slag. The growing amount of solid precipitates will cause increase in viscosity and diminution of refining characteristics of the slag.

A lower titanium oxide content in the slag-forming material may be obtained only if an alumina carrier of a lower titanium oxide content than bauxite is used. Therefore it was decided to perform a computer simulation of possibilities for obtaining a slag-forming mixture of a possibly low liquidus temperature, which could be used for forming refining slag during secondary steelmaking. It was assumed for the calculations performed that ladle slag from a BOF steelmaking shop would be the basic alumina and calcium oxide carrier. Relatively high alumina content in such slag is caused by assimilation of products of steel deoxidizing with aluminium. However the requirements for a slag-forming material cause the need to reduce ferrous and manganese oxides content in ladle slag, which can be obtained during re-melting of slag under reducing conditions. At the same time corrective additions of roasted bauxite or lime should be used in order to obtain the non-metallic phase of possibly low liquidus temperature.

Ladle slag from a BOF shop is characterized by high variability of chemical constitution. Therefore it is impossible to provide a universal method for its reducing re-melting and to provide corrective amounts of lime and bauxite additions. The carbon reducer share during the reducing re-melting of ladle slag should depend on the chemical constitution of slag and corrective addi-

tions of roasted bauxite or lime should depend on the chemical constitution of the re-melting product. This requires performing suitable calculations before commencing the reducing re-melting of ladle slag. The method of calculation with the FactSage software is presented in the examples where a ladle slag of low alumina content

/slag 1/ and a slag of high alumina content /slag 2/ were used for producing the non-metallic phase for use as a slag-forming material. The chemical constitutions of the ladle slags are presented in the table 1. The chemical constitution of the roasted bauxite and lime is presented in the table 2.

TABLE 1

The chemical constitution of the ladle slags

Slag No.	Chemical composition, %								
	CaO	Al ₂ O ₃	SiO ₂	MgO	FeO	TiO ₂	MnO	S	C
1	48.39	22.85	8.37	5.92	8.61	0.87	4.92	0.05	2.59
2	46.94	32.27	9.58	5.08	3.91	1.37	0.78	0.05	0.49

TABLE 2

The chemical constitution of the roasted bauxite and lime

Addition	Chemical composition, %								
	CaO	Al ₂ O ₃	SiO ₂	MgO	Fe ₂ O ₃	TiO ₂	Cr ₂ O ₃	CO ₂	H ₂ O
Bauxite	0.3	88.0	6.25	0.2	1.35	3.85	0.05	–	–
lime	94.0	–	1.5	0.3	–	–	–	3.0	1.2

There are two types of thermodynamic databases in the FactSage software. They contain data on pure substances and solutions. The pure substances database concerns phase components in relation to their state of aggregation and allotropic forms or isomers and the solutions database concerns solid and liquid alloys, carbides, nitrides, water based solutions, salts, ores, slags and other. Data contained in the F*A*C*T* Pure Substances Database and in the F*A*C*T* Solution Database were used for calculations. The data contained in these databases only do not allow to determine conditions of phosphorous oxide reduction but the phospho-

rous oxide content in ladle slag is very low and phosphorous can be easily reduced so it can be neglected in calculations. Results of calculations for the non-metallic phase produced from the ladle slag of low alumina content are presented in the tables 3-4. Tables 5 and 6 present results for the non-metallic phase made from the ladle slag of high alumina content and table 7 presents results for a mixture obtained from reduced non-metallic phase of high alumina and calcium content. Changes in the liquidus temperature of products in relation to roasted bauxite and lime additions are presented in Fig. 1 and 2.

TABLE 3

The liquidus temperature and mass and chemical constitution of the liquid non-metallic phase obtained in the process of reduction of the ladle slag of a low Al₂O₃ content carried out with various additions of roasted bauxite

Bauxite addition, %	Temperature, C	Chemical composition of liquid slag phase, %														Mass, g
		MgO	FeO	MnO	SiO ₂	TiO ₂	Ti ₂ O ₃	CaO	Al ₂ O ₃	MgS	CaS	FeS	MnS	Fe ₂ O ₃	CrO	
0.00%	1707.63	5.4434	0.0479	1.3391	9.9291	0.2227	0.7286	55.0584	27.1006	0.0123	0.1147	0.0001	0.0027	0.0003	–	846.83
2.00%	1653.75	5.6161	0.0456	1.3417	9.5894	0.2254	0.7593	54.5236	27.7750	0.0122	0.1086	0.0001	0.0025	0.0003	0.0000	889.9
4.00%	1616.14	6.1611	0.0388	1.3914	9.4435	0.2230	0.8088	52.9280	28.8856	0.0131	0.1037	0.0001	0.0026	0.0003	0.0001	916.87
6.00%	1575.52	6.3004	0.0331	1.4403	9.3435	0.2186	0.8616	51.6316	30.0542	0.0133	0.1003	0.0001	0.0027	0.0002	0.0001	940.02
8.00%	1557.07	6.1736	0.0287	1.4880	9.2739	0.2136	0.9154	50.5385	31.2541	0.0130	0.0981	0.0001	0.0028	0.0002	0.0001	960.47
8.50%	1559.1	6.1426	0.0278	1.4991	9.2570	0.2126	0.9283	50.2726	31.5463	0.0130	0.0975	0.0001	0.0028	0.0002	0.0001	965.58
9.00%	1564.47	6.1120	0.0270	1.5098	9.2402	0.2117	0.9409	50.0098	31.8356	0.0129	0.0970	0.0000	0.0028	0.0002	0.0001	970.68
10.00%	1564.47	6.0517	0.0255	1.5303	9.2073	0.2102	0.9657	49.4925	32.4050	0.0128	0.0959	0.0000	0.0028	0.0002	0.0001	980.89
12.00%	1570.07	5.9346	0.0232	1.5671	9.1435	0.2081	1.0129	48.4908	33.5102	0.0125	0.0939	0.0000	0.0029	0.0001	0.0001	1001.3

TABLE 4

The solid precipitates and mass and chemical constitution of the liquid non-metallic phase obtained in the process of reduction of the ladle slag of a low Al_2O_3 content at a temperature of 1558°C

Bauxite addition, %	Solid precipitates at a temperature of 1558°C				
	Solid precipitates, %	Sum of mass, g	Mass and kind of solid precipitates, g		
			CaO	MgO	$\text{Ca}_3\text{Ti}_2\text{O}_6$
0%	4.67%	41.049	22.707	18.342	–
2.00%	1.70%	15.319	–	15.319	–
4.00%	0.99%	9.0845	–	9.0845	–
6.00%	0.29%	2.717	–	2.717	–
8.00%	0.00%	0.00	–	–	–
8.50%	0.02%	0.16656	–	–	0.16656
9.00%	0.05%	0.45879	–	–	0.45879
10.00%	0.10%	1.0047	–	–	1.0047
12.00%	0.19%	1.9479	–	–	1.9479

TABLE 5

The liquidus temperature and mass and chemical constitution of the liquid non-metallic phase obtained in the process of reduction of the ladle slag of a low Al_2O_3 content carried out with various additions of lime

Lime addition, %	Temperature, C	Chemical composition of liquid slag phase, wt. %													Mass, g CrO
		MgO	FeO	MnO	SiO_2	TiO_2	Ti_2O_3	CaO	Al_2O_3	MgS	CaS	FeS	MnS	Fe_2O_3	
0.00%	1540.84	5.2132	1.3972	0.7963	9.8402	0.7386	0.6003	48.1230	33.1353	0.0112	0.0951	0.0026	0.0015	0.0455	995.92
2.00%	1535.02	5.1186	1.3765	0.7803	9.6801	0.7216	0.5912	49.0847	32.4945	0.0106	0.0938	0.0025	0.0014	0.0441	1015.6
4.00%	1533.75	5.0277	1.3570	0.7649	9.5261	0.7055	0.5821	50.0098	31.8779	0.0101	0.0926	0.0024	0.0013	0.0426	1035.2
6.00%	1533.33	4.9400	1.3386	0.7498	9.3777	0.6902	0.5732	50.9005	31.2843	0.0096	0.0913	0.0023	0.0013	0.0411	1054.8
8.00%	1532.82	4.8555	1.3213	0.7352	9.2348	0.6757	0.5644	51.7585	30.7122	0.0092	0.0901	0.0022	0.0012	0.0396	1074.5
10.00%	1532.19	4.7742	1.3053	0.7209	9.0970	0.6620	0.5557	52.5854	30.1606	0.0088	0.0889	0.0021	0.0012	0.0381	1094.1
12.00%	1531.43	4.6955	1.2904	0.7069	8.9640	0.6489	0.5472	53.3830	29.6284	0.0084	0.0877	0.0020	0.0011	0.0365	1113.8
14.00%	1530.49	4.6196	1.2767	0.6932	8.8355	0.6364	0.5388	54.1528	29.1145	0.0080	0.0865	0.0019	0.0011	0.0350	1133.5
16.00%	1529.36	4.5463	1.2643	0.6796	8.7115	0.6243	0.5307	54.8961	28.6179	0.0077	0.0853	0.0019	0.0010	0.0334	1153.1
17.00%	1538.12	4.5105	1.2586	0.6729	8.6510	0.6185	0.5267	55.2583	28.3760	0.0075	0.0848	0.0018	0.0010	0.0326	1163.00
18.00%	1582.09	4.4753	1.2531	0.6662	8.5915	0.6127	0.5228	55.6142	28.1380	0.0074	0.0842	0.0018	0.0010	0.0318	1172.80

TABLE 6

The mass of solid precipitates in the liquid non-metallic phase obtained in the process of reduction of the ladle slag of a high Al_2O_3 content at a temperature of 1530°C

Lime addition, %	Solid precipitates at a temperature of 1530°C					
	Solid precipitates, %	Sum of mass, g	Mass and kind of solid precipitates, g			
			$\text{Ca}_5\text{Ti}_4\text{O}_{13}$	Fe	$\text{Ca}_3\text{Ti}_2\text{O}_7$	CaO
0%	0.32%	3.22853	2.7511	0.47743	–	–
2%	0.17%	1.71337	1.3377	0.37567	–	–
4%	0.06%	0.60267	–	0.29988	0.30279	–
6%	0.03%	0.28058	–	0.28058	–	–
8%	0.03%	0.28124	–	0.28124	–	–
10%	0.03%	0.2818	–	0.2818	–	–
12%	0.03%	0.2821	–	0.2821	–	–
14%	0.02%	0.28213	–	0.28213	–	–
16%	0.00%	0.00	–	–	–	–
17%	0.13%	1.5616	–	–	–	1.5616
18%	0.93%	10.852	–	–	–	10.852

TABLE 7

The liquidus temperature and mass and chemical constitution of the mixture obtained from the reduced ladle slag of a high Al_2O_3 and lime content

Lime addition, %	Temperature, C	Chemical composition of liquid slag phase, wt. %													Mass, g
		MgO	FeO	MnO	SiO_2	TiO_2	Ti_2O_3	CaO	Al_2O_3	MgS	CaS	FeS	MnS	Fe_2O_3	
0.00%	1540.84	5.2132	1.3972	0.7963	9.8402	0.7386	0.6003	48.1230	33.1353	0.0112	0.0951	0.0026	0.0015	0.0455	995.92
2.00%	1535.13	5.1226	1.3380	0.7816	9.6870	0.7904	0.5303	49.0739	32.5203	0.0107	0.0939	0.0024	0.0014	0.0476	1014.8
4.00%	1533.75	5.0340	1.3149	0.7672	9.5371	0.7746	0.5216	49.9784	31.9198	0.0102	0.0927	0.0023	0.0014	0.0460	1033.8
6.00%	1533.32	4.9486	1.2931	0.7533	9.3924	0.7586	0.5139	50.8501	31.3411	0.0097	0.0915	0.0022	0.0013	0.0443	1052.9
8.00%	1532.8	4.8662	1.2721	0.7399	9.2531	0.7434	0.5062	51.6907	30.7829	0.0092	0.0903	0.0021	0.0012	0.0426	1072
10.00%	1532.17	4.7868	1.2519	0.7270	9.1186	0.7291	0.4986	52.5019	30.2443	0.0088	0.0891	0.0020	0.0012	0.0409	1091.1
12.00%	1531.38	4.7100	1.2323	0.7145	8.9887	0.7154	0.4910	53.2853	29.7242	0.0084	0.0879	0.0019	0.0011	0.0391	1110.2
14.00%	1530.43	4.6358	1.2134	0.7024	8.8632	0.7025	0.4835	54.0423	29.2218	0.0081	0.0868	0.0019	0.0011	0.0373	1129.3
16.00%	1529.26	4.5641	1.1952	0.6908	8.7419	0.6901	0.4760	54.7741	28.7361	0.0078	0.0856	0.0018	0.0010	0.0355	1148.4
17.00%	1528.58	4.5291	1.1864	0.6851	8.6827	0.6842	0.4724	55.1310	28.4992	0.0076	0.0851	0.0017	0.0010	0.0346	1157.9
18.00%	1564.8	4.4941	1.1970	0.6795	8.6233	0.6403	0.5028	55.4743	28.2623	0.0074	0.0845	0.0017	0.0010	0.0318	1167.6

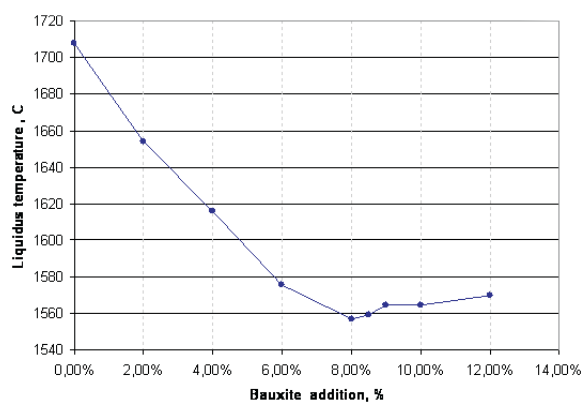


Fig. 1. The liquidus temperature of the non-metallic phase obtained with various additions of roasted bauxite during reduction process of the ladle slag of a low Al_2O_3 content

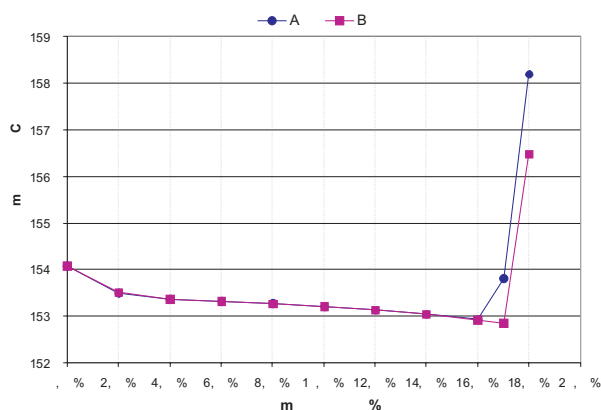


Fig. 2. The liquidus temperature of the non-metallic phase obtained with various additions of lime during the process of reduction of the ladle slag of a high Al_2O_3 content and the mixture obtained from reduced ladle slag of a high Al_2O_3 content and lime.

A – non-metallic phase, B – mixture

During calculations it was assumed that the temperature of the reduction process was 1,600°C and the carbon reducer share during reduction of the ladle slags

of low and high Al_2O_3 content was respectively 2.59% / 26 g/ and 0.49% / 5 g/.

The results of the calculations performed allow to generally determine conditions for producing a

slag-forming mixture with the use of ladle slag from a BOF shop as the basic calcium oxide and alumina carrier. The conditions can be presented as follows:

1. The ferrous and manganese oxides content in ladle slag is higher than their required content in the slag-forming mixture and therefore ladle slag should be re-melted in reducing conditions.
2. The carbon reducer share and the temperature of the reduction process of slag of variable chemical constitution should be determined as a result of a previous computer simulation.
3. During a computer simulation of the reduction process corrective additions of roasted bauxite or lime should be determined in order to obtain a slag-forming mixture of possibly low liquidus temperature.
4. During the reduction process such addition of roasted bauxite or lime should be used, which enables to obtain a non-metallic phase of the liquidus temperature lower than the reduction process temperature after completion of the process.
5. The balance of roasted bauxite or lime should be mixed with fine non-metallic phase obtained in the reduction process.

The presented conditions only allow to determine the amounts of components necessary to obtain a slag-forming mixture which can be used during secondary steelmaking. During production of the mixture on a commercial scale one should also take into account the cooling method of the reduction process product, its degree of fineness and the degree of fineness of roasted bauxite and lime additions after completion of the reduction process.

The product obtained during reducing re-melting of slag should be intensively cooled with compressed air so that it does not disintegrate autogenously due to a transformation of the $\beta 2\text{CaO}\cdot\text{SiO}_2$ allotropic form into the γ form, which is connected with the increase in volume [7]. This transformation occurs during slow cooling and results in obtaining of a powdery fraction, which cannot be used in secondary steelmaking.

The degree of fineness of the ready slag-forming mixture should be the same as the degree of fineness of mixtures used in the industrial practice. In general, the mixture should not contain a powdery fraction.

The high SiO_2 content, which is higher than in the existing mixtures, is a drawback of the slag-forming mixture made from ladle slag. The only possibility to reduce the SiO_2 content is selecting for production a ladle slag mixture from production of steel of low silicon additions.

4. Conclusion

The presented method allows to determine conditions for production of slag-forming mixture for secondary steelmaking. The basic assumption of the proposed method is re-melting of ladle slag from a BOF shop, which is the alumina and calcium oxide carrier, in reducing conditions in an electric arc furnace. During the process and after its completion corrective additions of roasted bauxite or lime should be used to obtain a product of a possibly low liquidus temperature. The reduction process conditions and the amount of corrective additions are determined on the basis of calculations with the FactSage software.

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