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CARBON REDUCERS FOR THE PROCESSES OF FERROALLOY PRODUCTION IN THE ELECTRIC FURNACE

REDUKTORY WĘGLOWE DLA PROCESÓW WYTAPIANIA ŻELAZOSTOPÓW W PIECACH ELEKTRYCZNYCH

The article presents the requirements regarding the carbon reducers used in the processes of melting ferroalloys by means of electrothermal methods. The quality and the constancy of the carbon reducers' properties have a significant impact on the course of electrothermal processes of melting ferroalloys. The influence is particularly significant in the commonly used continuous processes. The paper describes the properties of such carbon reducers as: metallurgical coke, hard coal, semi-coke, petroleum coke and charcoal. The paper also presents the influence of the reducers' chemical composition and granulation on the process of melting ferroalloys in electric furnaces. The following properties of the above mentioned reducers were investigated: electric resistance, reactivity and durability.
Keywords: carbon reducers, Ferroalloys, EAF

W artykule przedstawiono wymagania odnośnie własności reduktorów węglowych stosowanych w procesach wytapiania żelazostopów metodami elektrotermicznymi. Jakość i niezmienność własności reduktorów węglowych wywiera istotny wpływ na przebieg procesów elektrotermicznego wytapiania żelazostopów zwłaszcza w powszechnie obecnie stosowanych procesach ciągłych. W pracy omówiono własności takich reduktorów węglowych jak: koks metalurgiczny, węgiel kamienny, półkoks, koks naftowy i węgiel drzewny. Omówiono wpływ składu chemicznego i granulacji reduktorów na przebieg procesów wytapiania żelazostopów w piecach elektrycznych. Zbadano takie własności wymienionych powyżej reduktorów węglowych jak rezystancja elektryczna, reakcyjność i wytrzymałość.

1. Introduction

In ferroalloy metallurgy carbothermal reduction methods are used to melt the alloys of silicon, manganese, chromium, etc. The interaction between carbon reducers and metal oxides underlies ferroalloy production using carbothermal methods. The interaction includes among others chemical, catalytic and heat exchange processes. In the processes of melting ferroalloys using the electrothermal method the carbon reducer has two functions:

– It is a source of carbon which is essential for the reduction processes to take place. The fulfilment of this function is dependent on proper carbon content and the reactivity of the reducer.

– It regulates the properties of the charge mixture in the melting pot. The reducer should have high electric resistance and be in the form of chunks in order to fulfil the requirements of the technological ferroalloy melting. The high electric resistance makes it possible to use the power of the furnace transformer. The chunks make the charge mixture gas permeable.

As far as the reducer's character is concerned, a number of both naturally and artificially obtained carbon materials are used in the ferroalloy melting processes. The first group contains such materials as hard coal, brown coal, anthracite, peat and waste wood. The second group contains metallurgical coke, special coke (with the addition of quartz sand, iron ore, chalk and other activators), semi-coke, petroleum coke, pitch coke, peat coke, charcoal and other materials containing carbon. In order to assess the utility of carbon reducers in the production of ferroalloys using the elecrothermal method one needs to consider the following properties:

– chemical composition
– granulometric composition
– reactivity
– electric resistance
– strength properties

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TABLE 1

The chemical composition of reduction materials for the production of ferroalloys

Reducing agent	Chemical composition, wt%				Chemical composition of ash, wt%					
	W^c	A^s	V^b	S^b	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	P_2O_5
Coke	12.8	11.3	1.8	0.69	34.35	25.90	19.00	8.85	3.30	1.20
Semi-coke	4.7	9.3	4.5	0.63	23.55	18.20	27.83	9.32	–	–
Petroleum coke	1.4	0.8	8.1	4.23	46.3	24.3	14.2	6.0	4.5	0.75
Coal	3.0	3.2	33.2	1.43	29.5	15.1	22.9	7.5	4.0	0.56
Charcoal	6.0	0.7	14.5	0.31	1.9	3.4	0.85	32.7	8.4	5.12

The mixture of metallurgical coke and hard coal is most commonly used in Poland in the process of producing ferroalloys by means of electrothermal method. The properties of metallurgical coke, which is produced with the aim of melting pig iron in the blast-furnace, do not fully fulfil the requirements of the processes taking place in low shaft electric furnaces used in ferroalloy metallurgy. As a result, it is necessary to use mixtures of coal materials in these processes. Such mixtures fulfil the requirements of the technological processes of different ferroalloy production better.

2. The chemical composition of carbon reducers used in the ferroalloy melting processes

The chemical composition of carbon reducers is assessed on the basis of the results of three analyses: technical analysis, elementary analysis and the analysis of the chemical composition of the ash. The technical analysis encompasses such elements of the reducer as the amount of humidity, ash, volatile parts as well as sulphur and phosphorus. The elementary analysis assesses the elemental composition of the organic substance. The analysis of the ash provides the chemical composition of the mineral admixture of the carbon reducers. Table 1 shows the results of the technical analysis and the chemical composition of the ash from carbon reducers used in the process of ferroalloy melting [1, 2].

The differences in humidity among carbon reducers stem from their different physical and chemical properties, different production methods, transport methods and storage as well as granulation used. The increase in humidity content makes the thermal balance of the ferroalloy melting process worse due to the thermal losses taking place during evaporation and partial dissociation of water. The increase in humidity may also lead to an increase in hydrogen content in the alloy. The use of humid air creates difficulties while sifting fine harmful fraction of the carbon material. The variable amount of humidity in carbon reducers is also a common cause of mistakes made during the selection of the charge material.

Drying carbon reducers used in ferroalloy production in electrothermal processes does not bring the expected results. Drying is an expensive process. In its course a significant amount of fine fraction is produced. Transport and dosage of the dry reducer results in an increase in dusting of the production area. The use of dry reducer is also the cause of the disturbance in the work of the electric furnace. The disturbance consists in an excessive increase in surface temperature of charge layers and in a decrease of electrodes' immersion in the charge.

The beneficial effect of constant small amount of humidity in carbon materials used for ferroalloy production by means of electrothermal methods makes certain steelworks humidify the previously dried carbon reducers up to a set humidity level before it is charged into the furnace.

In industrial practice the carbon reducers with a wide range of volatile parts are used. Depending on the composition of carbon mixtures and carbonization the metallurgical coke can contain volatile parts ranging from 0.9 to 2.8% [1]. The hard coal, which is more and more commonly used as a reducer in electrothermal processes of ferroalloy production, can contain even above 40% of volatile parts [1]. The increased content of volatile parts, which are emitted in the process of heating the carbon reducers, may be the cause of the disturbances in the furnace work. The emitted volatile parts of the carbon reducers settle on the surface of the cold charge in the form of pyrolytic carbon [3]. It leads to scorching the charge and a decrease in its gas permeability as well as to a decrease in the reactivity of the carbon reducers and to a detrimental decrease in electric resistance of the charge. The use of raw carbon materials or carbon materials processed to a small degree is, however, grounded in economic reasons and such technological reasons as their high electric resistance, reactivity and most commonly low tendency for granulation. Taking into consideration the above mentioned unfavourable influence of high content of volatile parts on the furnace's work, it is necessary to limit their presence in carbon reducers, especially those fractions which are conducive to the emission of pyrolytic carbon (tar, benzene, methane).

Carbon reducers with significantly different ash contents are used to produce ferroalloys. Petroleum coke, pitch coke and charcoal have the minimal content of the ash (0.6-2.5%). Metallurgical coke usually contains 10-15% of the ash [1]. The basic elements of the ash from carbon reducers include silicon, aluminium, calcium, magnesium, iron, titanium, phosphorus and sulphur compounds. The metal compounds, which can be found in the ash, include mainly oxides. They are reduced by carbon and they are transferred to the alloy contaminating it at the same time. Apart from influencing the chemical composition of the melted alloy, the mineral admixtures influence the properties of the carbon reducers. Oxide compounds of a number of elements present in the ash have a positive (Fe, Ca, Mn, alkali) or negative (Al, Si) influence on the reactivity of carbon reducers. Some compounds from the ash influence in a catalytic way the course of graphitization of the carbon materials. The mineral admixtures of the carbon reducers also influence the chemical composition of the slag phase produced during ferroalloy melting. Ash is not in every case a ballast of the carbon reducer. In many cases it influences positively the reactivity and electric resistance of carbon reducers. The selection of carbon reducers on the basis of the ash content and ash's chemical composition should be done individually in the case of each melting process and in the case of different uses of the ferroalloys.

3. The granulometric composition of the carbon reducers

The specificity of the ferroalloy melting technology in electric furnaces requires the use of finer fractions of carbon material. The specificity consists in the fact that the reducer is not only a chemical reagent but it also influences the depth of electrode immersion and the distribution of power in the melting pot by means of a change in electric resistance of the charge. The choice of proper granulation depending on the used melting technology, the furnace size and the properties of the carbon reducer are significant factors contributing to the improvement of the economic results of the process. The size of the carbon reducers' grain used for the ferroalloy production should depend on such properties as reactivity and electric resistance. When the reducer is less chemically active and less electrically resistant, the grain should be finer. The favourable influence of fine fractions of the reducer on its reactivity and electric resistance is underrated by the unfavourable influence of subgrain on the melting process. It stems from worsening the gas permeability of the charge and the fact that the fine fraction is always increasingly contaminated. Due to the above mentioned reasons in the case of the metallurgical coke, for instance, the maximum size of the grain is set as 15 or even 12mm. The minimum size of this reducer is usually 3-5mm [1].

4. The reactivity of carbon reducers

The reactivity is one of the most important properties of carbon reducers used in ferroalloy production in electric furnaces. The reactivity of carbon materials is their ability to react with oxidizing agents such as carbon dioxide, vapour, oxygen, silicon oxide and silicon dioxide. The reaction occurs in set physical and chemical conditions such as pressure, temperature, the intensity of oxidizing gas flow, the size of the carbon material's grain. The reactivity of carbon reducers depends on such interrelated factors as the amount and type of admixtures, the structure of the carbon substance – the degree of its similarity to the graphite structure, porosity (the total volume of pores, their distribution depending on their size, open and closed porosity). In the case of artificially obtained carbon materials the reactivity can be influenced by the following factors: the composition of the coke mixtures and the temperature of carbonization.

So far there has not been a homogenous method of assessing the reactivity of carbon reducers used in ferroalloy production. Different oxidizing substances are used, different temperatures are measured (873-1773K), different intensity of gas flow is used. What is more, the grains of the samples differ from one another. The most commonly used method consists in applying the CO_2 flow in order to gasify the carbon materials. In the case of this method the reactivity is assessed on the basis of the mass decrement or the amount of the obtained CO [1, 2]. The process proceeds according to the reaction

$$C + CO_2 = 2CO. \tag{1}$$

The methods of assessing the reactivity of the carbon reducers, which consist in gasifying them in a flow of oxidizing gas, do not fully present the behaviour of the reducer in the working area of the furnace. During the reactivity measurement by means of gasifying the volume of the pores, the surface of the reaction and the speed of gas diffusion in the pores go up during the measurement time. In this way the results are too high. The situation taking place in the silicon melting processes is quite different. In the case of silicon melting the carbon of the reducer reacts with SiO according to the reaction:

$$SiO + 2C = SiC + CO. \quad (2)$$

The obtained product SiC has bigger volume than the carbon taking part in the reaction (2). This results in a decrease in the pore size and a decrease in the speed of gas diffusion in them. The surface of reducer is gradually covered with a layer of SiC carbide and the speed of the reaction (2) goes down. Consequently, the reactivity of carbon reducers used in silicon melting processes is often assessed on the basis of the speed of their reaction with gaseous SiO [4].

The carbon reducers presented in table 1, which are used in ferroalloy production in Poland, were subjected to reactivity tests using the gasifying method in the CO_2 flow. The tests were carried out in the temperature of 1173K. The intensity of CO_2 flow was 1 litre per minute. The reducer sample was crumbled so that the grains would have the size of 2-3mm. The sample was then dried in the temperature of 373K during one hour. A 40g sample was placed in the pipe of silit furnace made of heat-proof steel. The sample was subjected to argon blowing until it reached the temperature of 1173K. It was also subjected to argon blowing during the cooling down after the measurement. The gasifying time amounted to 20 minutes. After cooling down the reducer samples were weighed and the reactivity was assessed on the basis of the mass decrement. The results of carbon reducer reactivity measurements were shown in Figure 1 [5].

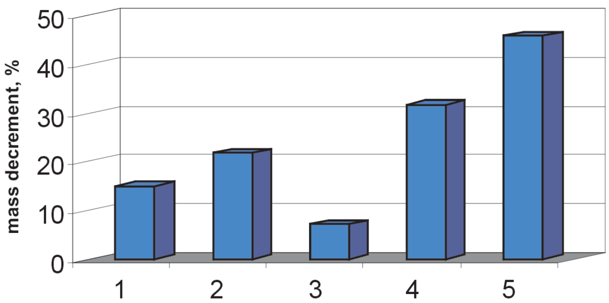

Fig. 1. Reactivity of carbon reduction materials: 1– coke, 2– semi-coke, 3– petroleum coke, 4 – coal, 5 – charcoal

5. The electric resistance of the carbon reducers

The electric resistance is one of the most important parameters of the charge mixtures used in ferroalloy production by means of electrothermal method. It influences the power and temperature distribution in the working area of the furnace. When the electric resistance is high, the furnace works under an arc regime with electrodes being immersed in the charge. The zone of the highest temperatures is near the furnace core and the surface of the charge has a comparably low temperature. It is a proper distribution of temperature for a low shaft electric furnace used for ferroalloy production. In the case of low electric resistance the majority of the energy supplied to the furnace is transformed into heat in the charge (Joule – Lenz heat). The furnace works under the resistance regime with electrodes shallowly immersed in the charge. The surface of the charge has high temperature and the lower areas of the furnace have comparably lower temperatures. Such a distribution of temperatures leads to difficulties in initiating the flow-down, increased heat losses, smaller amounts of obtained alloy and in extreme situations it leads to a total disturbance in the work of the furnace [6].

The electric resistance of the carbon reducer is a decisive factor when it comes to the electric conductivity of the charge mixture. In the industrial practice carbon reducers which differ in terms of electric resistance are used to produce ferroalloys. The carbon reducers obtained in high temperatures, i.e. coke, have the lowest resistance. In room temperature it is from several to over a dozen Ω·cm depending on the carbonization temperature and the composition of the coke mixture. Semi-coke, formed coke and coke with mineral admixtures have the electric resistance ranging from 35÷2000 Ω·cm. Charcoal, petroleum coke, hard coal and certain low-temperature types of semi-coke have the electric resistance ranging from $10^6 \div 10^{10}$ Ω·cm [1].

The electric resistance in pouring state is the sum of the following two: the real electric resistance of the carbon reducer and the resistance of the contacts between its grains. The finer the grains, the more contact between them. The resistance in that case goes up, too.

The electric resistance of the carbon materials decreases during heating. It is related to such accompanying changes as humidity emission, volatile parts emission, the degradation of organic compounds and graphitization.

The carbon reducers shown in table 1 had their electric resistance assessed in the function of temperature. The electric resistance of the presented carbon reducers was assessed in the room temperature and in the following temperatures: 473, 673, 873, 1073 and 1272 K. The samples' grains had the size of 10÷15 mm. The measurement of the electric resistance of the carbon reducers was conducted using the Wheatstone bridge. The sample of the tested reducer was placed in the pipe of the silit furnace between two copper electrodes. The sample had the diameter of 35mm and the height of 100 mm. The protective argon atmosphere was created during the electric resistance test in higher temperatures. The results of the tests in temperature function are shown in Figure 2 [7].

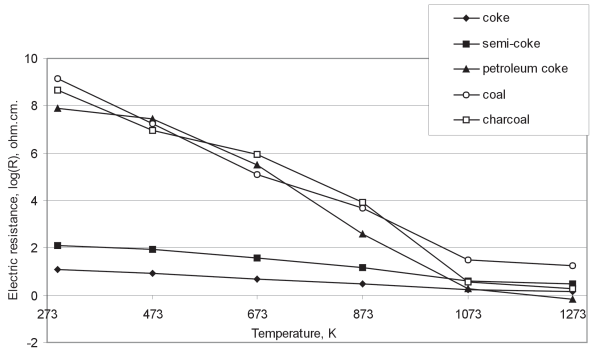

Fig. 2. Dependence of electric resistance of carbon reducing agents upon temperature

6. The strength properties of the carbon reducers

The technology of ferroalloy production in low shaft electric furnaces does not set high requirements when it comes to the strength properties of carbon reducers. These properties, however, have a significant influence on the amount of fine fraction that is produced in the process of making the reducers ready for the melting (crumbling, sifting) and during their transport and charging into the furnace.

Drum tests are the basic method for assessing the strength properties of carbon reducers. The strength and resistance to abrasion can be assessed thanks to these tests. The assessment of strength properties of carbon reducers in ferroalloy industry is carried out in drums similar to those used in Micum test for the assessment of blast-furnace coke's strength. The indices used for coke, i.e. the index of strength (M_{40}) and the index of resistance to abrasion (M_{10}), are of little use in the case of the strength of carbon reducers in ferroalloy production by means of the electrothermal method.

The drum used for strength tests had inner dimensions of $\phi300\times300$ mm. There were four angle bars attached to the inner surface of the drum. The angle bars had the following dimensions: 30×30×3 mm. The angle bars were used to crumble the reducers. The drum was set into motion by an electric motor with the speed of 25 turns per minute during four minutes. The sample of the reducer having the volume of 3 dm^3 was subjected to drumming. The reducer samples had the same grains as those used in ferroalloy production in the Polish industry. After the test the content of the drum was sieved. First the holes of the sieve corresponded to the lower border of the pieces from the sample. Then a sieve with 1mm holes was used. As a result of the sieve analysis two indices of reducers' strength were presented:

- the strength index showing the proportional share of the reducer in the sample after drumming within a given class (the grain is bigger than the lower border of the tested sample),
- the index of resistance to abrasion showing the proportional share of the fraction with grains smaller than 1mm in the tested sample after drumming.

The results of the strength tests and basic properties of carbon reducers used for ferroalloy melting by means of electrothermal methods were presented in table 2 [8].

TABLE 2

Basic properties and strength indexes of carbon-reducing materials

Reducing agent	Porosity, %	Absolut density, kg/m^3	Apparent density, kg/m^3	Grain size, mm	Weight of sample, kg	Strenght index, %	Grindability, %
Coke	49.7	1857	949	10-25	2.8	85.3	5.4
Semi-coke	44.8	1833	1012	10-40	3.0	80.4	6.4
Petroleum coke	20.4	1409	1121	6-25	3.4	75.2	10.3
Coal	4.2	1296	1307	8-31.5	3.9	81.5	4.8
Charcoal	78	1480	440	5-100	1.3	61.9	15.7

7. Conclusions

In electro thermal processes of ferroalloy production the carbon reducer is not only a source of carbon necessary for the occurrence of reduction processes but it also influences significantly the distribution of power and temperatures in the melting pot of the furnace (immersion of the electrodes in the charge). It exerts this influence by means of changing the electric resistance of the charge. It is impossible to produce carbon reducers with such properties that would make them adequate for different melting technologies. That is why the ferroalloy industry uses mixtures of carbon reducers. The mixtures are prepared so that they would fully fulfil the requirements set by the melting processes of particular alloys. The properties of the commonly used reducer, i.e. the metallurgical coke, fulfil the requirements of the blast-furnace process for which the coke is produced. It is possible to affect the properties of the charge in order to meet the requirements of the ferroalloy production processes by using mixtures of metallurgical coke with other carbon materials that have high reactivity and electric resistance such as hard coal, semi-coke or charcoal.

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