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STUDYING PROPERTIES OF CARBONACEOUS REDUCERS AND PROCESS OF FORMING PRIMARY TITANIUM SLAGS

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Preliminary Note – Prethodno priopćenje

When smelting a rich titanium slag the most suitable are low-ash reducers, and the studies revealed the suitability for this purpose of special coke and coal. An important property of a reducer is its specific resistance. Therefore there were carried out studies for measuring electric resistance of briquettes consisting of ilmenite concentrate and different carbonaceous reducers. It is recommended to jointly smelt the briquetted and powdered burden (the amount of the powdered burden varies form 20 to 50 %), this leads to the increase of technical-economic indicators of the process.

Key words: titan, slag, reducer, property, anthracite

INTRODUCTION

Selecting a reducer plays an important role in electric-carbothermal obtaining rich titanium slag (RTS) form powder and lumpy burden. As a reducer there can be used various carbon-containing materials, for example, such as anthracite, metallurgical, pitch and oil coke, different coals and special kinds of coke [1]. In the process of rich titanium slag melting in the conditions of the ore-thermal electric furnace a reducer can possess the following mail properties:

- high reaction capacity (chemical activity);
- low electrical conductivity (high electrical resistance);
- low ash-content –and must not be very expensive and deficit [1].

From the properties cited, besides chemical activity of great importance is its specific electrical resistance and, depending on the metallurgical processing specificity, ash content and composition. In case of melting rich titanium slag it is better to use low-ash reducers, as the majority of oxides composing ash (SiO_2, Al_2O_3, CaO и MgO) are transferred to slag thus diluting the final product, i.e. slag. The reducer low electrical conductivity ensures general high electrical resistance of the burden, deep electrodes placing, stable electrical mode and uniform furnace operating. By the reducing capacity for titanium concentrates the reducers are in the following order: charcoal – gas coal – anthracite – oil coke.

Rich titanium slag melting from a powder burden is known to be accompanied by some difficulties. The matter is that a large part of ferrous oxides in the composition of ilmenite concentrate is reduced from the liquid phase. This is conditioned by the fact that the concentrate melting process advances the process of reduction [2].

In this connection at the moment to increase the raw material infusibility in the practice of rich titanium slag producing there are used agglomerate burden materials, for example, briquettes or pellets. However, the processing of the burden consisting of 100% briquettes is accompanied by sintering and cementing the briquettes on the furnace throat by the boiling melt and this throws obstacles in the burden gas-permeability. That's why it is recommended to melt combined powder and briquetted burden (powder burden from 20 to 50 %) [3], эthis will lead to improving the process technical-and economical indicators. Using the most spread method of agglomeration in metallurgy doesn't permit to achieve satisfactory results.

EXPERIMENTAL STUDIES

So, the purpose of our studies was measuring electrical resistance of briquettes consisting of ilmenite concentrate and various carbonic reducers (Table 1). Shokash ilmenite concentrate chemical composition is presented by the following data, mass %: TiO_2 - 53,7; FeO - 33,9; Al_2O_3 - 1,89; SiO_2 - 3,46; ZrO_2 - 0,16; Cr_2O_3 - 1,65; P_2O_5 - 0,06.

There have been carried out studies of the phase composition of the Shokash concentrates. As a result of X-ray phase analysis it became obvious that the main phase in concentrates is ilmenite ($FeO \cdot TiO_2$). The presence of phases $Fe_2O_3{\cdot}3TiO_2$ and $2Fe_2O_3 \cdot 3TiO_2$, as well as the absence of these samples magnetic susceptibility prove the changes (leucoxenization) of ilmenite. X-raygram of the concentrate is presented in Figure 1.

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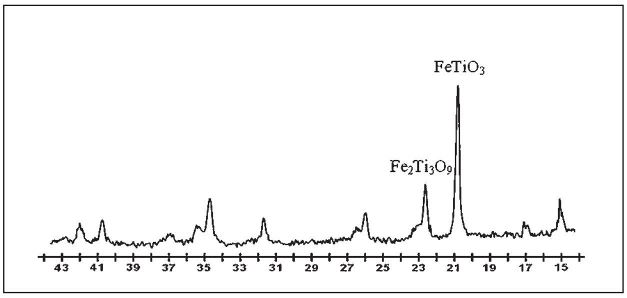


Figure 1 Concentrate X-ray-gram

The temperature of the burden softening is much lower. It is explained by that the process of reduction obviously impacts the primary slag-firming of the materials.

Table 1 **Reducers chemical composition / mass %**

Reducer	carbon	ash	volatiles	water
Cannel coal	54,25	3,55	39	3,2
Special coke	92,64	3,08	2,5	1,96
Metallurgical coke	76	13	3	8
Oil coke	87,8	0,11	7,9	4,2

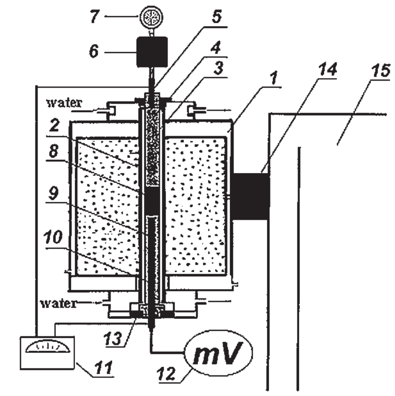
Experiments to determine electrical resistance of ore-coal briquettes were carried out on the laboratory plant (Figure 2). The pressure on the burden was 2 kgs/cm^2, heating speed was 25 - 30 deg/min, alundum tube inner diameter 0,02 m, material layer height 0,005 m.

Briquettes of d = 20 mm were produced on the laboratory hydraulic press (p = 100 kgs/cm^2). As a binder there was used 50 % solution of liquid glass (SiO_2 = 35,0 %, Na_2O = 10,5 %), that was added in the amount 5 % of the burden mass. The reducer was fed to the burden so that to reduce completely the whole iron from the concentrate. The briquettes before being fed to the alundum tube were crushed to fraction 0 - 8 mm. The experiments to measure electrical resistance were to be carried out in the conditions maximally close to the industrial ones.

In Figure 3 there is shown temperature dependence of absolute electrical resistance of ore-coal briquettes with different reducers. In the Figure it is seen that in the range of temperatures from 800 to 1 150 ˚C the briquettes from ilmenite concentrate with special coke and coal possess the largest resistance. When comparing the briquettes resistance curves we see that they are almost parallel till 1 050 ˚C, then the temps of their resistance lowering decrease significantly. At high temperatures (over 1 150˚C) the resistances of all the briquettes are comparatively equal.

The smallest electrical conductivity in the temperature range from 900 to 1 200 ˚C are of the briquettes with special coke and gas coal (see Figure 4). At the temperature over 1 200 ˚C electrical conductivity of these briquettes increases sharply. This is explained by the fact that there takes place the process of the burden melting and ferrous iron reducing product forming.

There were carried out studies to determine electrical resistance of ore-coal briquettes used at present in RTS producing practice.



1-resistance furnace; 2-graphite tube; 3-alundum tube; 4-upper graphite electrode; 5-electrode copper tip; 6-weight; 7- indicator;8 -burden; 9- thermocouple; 10-lower graphite electrode; 11-Ohmmeter; 12-potentiometer; 13-asbestos plate; 14-copper buses; 15-furnace transformer

Figure 2 Plant for measuring electrical resistance

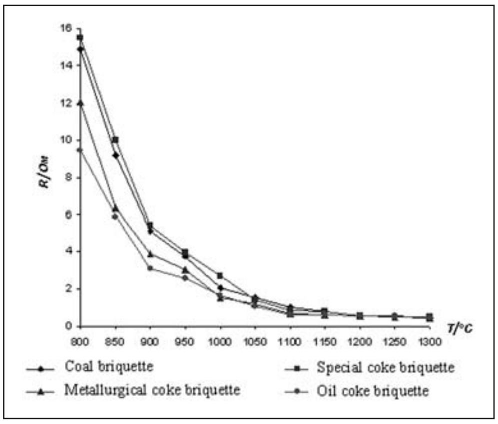


Figure 3 Electrical resistance temperature dependence

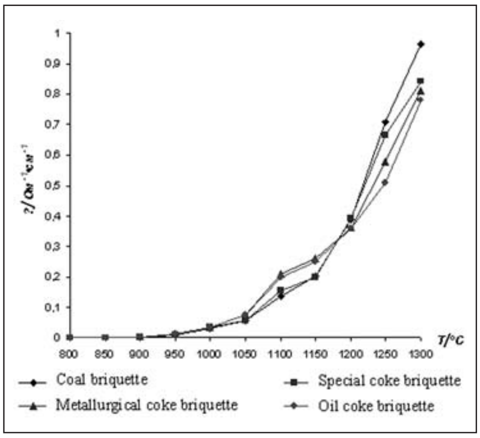


Figure 4 Electrical conductivity temperature dependence

It became clear that the most adequate reducer for RTS melting are special coke and coal, as the briquettes with these reducers possess the minimal specific electric resistance in the temperature range of the three-phase reducing, This helps to improve the conditions of ferrous oxide reducing and prevents fusible primary slags forming.

Melting rich titanium slag from ilmenite concentrates in the conditions of ore-thermal electric furnace is accompanied by some specific difficulties. This is conditioned by that a significant part of iron oxides in the composition of ilmenite concentrate is reduced from the liquid phase, i.e. the concentrate melting process advances the process of iron reduction.

The process of melting any ore material excluding eutectic compositions, is accompanied by the primary slag-forming, i.e. melting fusible eutectics that forms and develops in the process of heating a multi-phase material to high temperatures. The materials primary slag-forming characterizes its behavior in the transition into plastic state (its fluidity) that is accompanied by forming solid solutions and chemical compounds [4]. The process of slag-forming effects significantly in a varying degree the completeness of iron reduction from ilmenite concentrates. As a result at a comparatively low temperature a part of ferrous oxide can reduce from the melt which conditions this process transition into diffusion conditions, the duration of melting being increased.

Forming primary titanium slag consisting mainly of ferrous ortho-titanium ($2FeO \cdot TiO_2$), refers to short slags. By their nature they are very sensitive to the least temperature drops that in turn lead to slag recrystallization. Due to this the ore-reducing process of obtaining rich titanium slag (RTS) is expedient to carry out so that the main part of ferrous oxides reduction from ilmenite concentrate could take place before the burden melting, i.e. the reduction reaction would advance melting.

With the aim of determining the temperature of the primary slag-forming process from the Shakash concentrate, its burden with low-ash coal and ore-coal briquettes, there was used the method of quantitative evaluation. The method consists in building the material softening curve under the load in the form of the dependence $\Delta = fT$ (where Δ is shrinkage, mm) and finding a sharp changing of the sample shrinkage corresponding to the temperature of the material primary slag-forming.

A sample of ilmenite concentrate placed in the molybdenum crucible was placed then in the high-temperature Tamman furnace with a graphite heater. Under the crucible bottom there was placed a tungsten-rhenium thermocouple, covered with a ceramic envelop. Then the sample was uniformly heated with the speed 10 °C/min., besides, the pressure upon the material was 2 kgs/cm^2. The material heating was accompanied by eliminating volatiles and malting fusible compounds, due to which the concentrate shrinks that is fixed by an indication with accuracy 0,01 mm. The studied concentrate chemical composition is presented in Table 2.

Table 2 **Concentrate chemical composition / wt. %**

TiO_2	FeO	Al_2O_3	SiO_2	ZrO_2	Cr_2O_3	P_2O_5
53,7	33,9	1,89	3,46	0,16	1,65	0,06

RESULTS AND DISCUSSION

The results of experiments to determine the concentrate softening temperature are graphically presented in coordinates Δ - T. In Figure 5 there is shown a temperature dependence of the materials studied shrinkage.

The experimental data processing was made by the method of anomorphing of softening curves. The method selected is a more accurate one as compared to the method of graphical differentiating the continuation of straight sections of softening curves in PS scale.

As a result of the experimental data processing there were determined then temperatures of the primary slag-forming of ilmenite concentrate and its burden with a reducer. Primary slag-forming temperatures were calculated from the breaking of the softening curve in coordinates $lg\Delta$ - lgT. In Figure 6 by the curves method of anomorphing there are presented the temperatures of primary slag-forming of ilmenite concentrate and its burden with a reducer.

By means of comparing the mineralogical structure of the materials studied before and after the breaking on the softening line shown in Figure 6, there was found that after the breaking the quality of amorphous glass increases significantly. In it there crystallizes mainly faielite with small segments of ilmenite crystallites. Thus, the breaking on the softening line manifests fusible ferrous slag forming.

In Figure 6 it can be seen that ilmenite concentrate primary slag-forming corresponds to the temperature ≈ 1 130 °C, and its burden with a reducer to ≈ 1 060 °C.

CONCLUSIONS

The burden softening temperature is significantly lower, this is explained by the fact that the reducing process greatly impacts the primary slag-forming of the materials. The burden softening temperature is significantly lower, and due to that the process of reduction impacts greatly the material primary slag-forming.

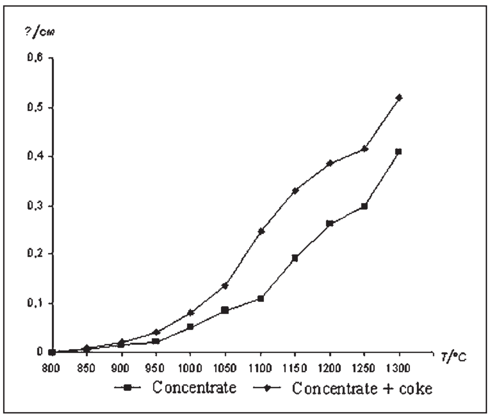
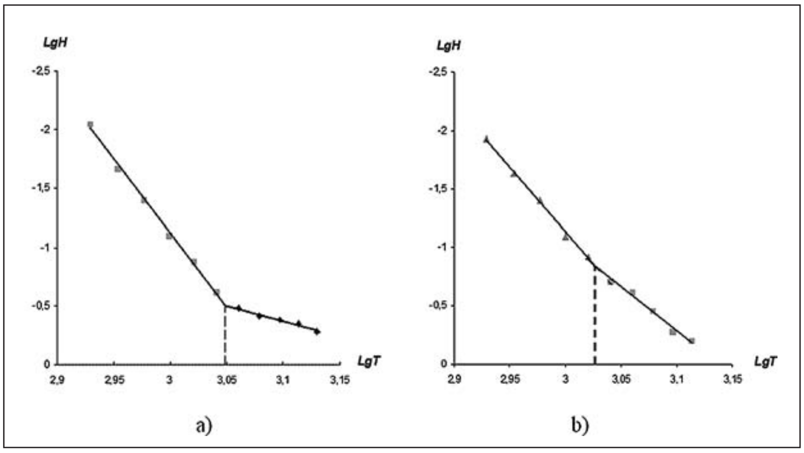


Figure 5 Temperature dependence of the materials shrinkage



a) concentrate; b) concentrate + coke

Figure 6 Method of anomorphing softening curves for determining slag-forming temperatures

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Note: The translation of the N. M. Drag, Karaganda, Kazakhstan