Complex Processing of a Titanium Magnetite Concentrate with Receiving the Products Containing Iron, The Titan and Vanadium

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Abstract. Present study determines conditions for titanium magnetite concentrate processing with fairly complete titanium conversion to the slag and iron and vanadium separation in the hot metal. It is quite difficult to process titanium magnetite concentrate in the blast furnaces due to low fusibility of charge and direct electrical melting which cause process instability. Present work is devoted to development of concentrate double stage smelting process with little soda additions, including solid-phase recovery at the first stage using specific coke as a reductant, avoiding concentrate oxidation and including its preliminary thermooxidation. Mix charge made of concentrate, soda and specific coke was granulated in water, dried at 130°C, pellets were placed in graphite crucible, and later on it was set up in the centre of the furnace in alundum crucible. Temperature regimen was fixed under following parameters: temperature at the first stage was 1250°C; soaking time was 50 min; temperature at the second stage was 1500 – 1650°C; soaking time was 35 min. It is established that little soda additive (estimated 3-4% Na2O) to the charge of titanium magnetite concentrate recovery smelting behaves as a coagulant during briquetting, as a catalyst in course of solid-phase recovery, as an inhibitor of DRI briquettes secondary oxidation as slag thinner during smelting. In course of titanium magnetite concentrate reduction smelting process, soda interacts to SiO2, Al2O3, TiO2 oxides forming sodium silicates and titanates. Double-stage technology of titanium magnetite concentrate reduction smelting was used, both with soda addition, and without oxidation and preliminary iron oxidation of titanium magnetite concentrates till hematite was developed. Optimal process parameters were determined. Following parameters were obtained: hot metal yield was ∼55% of concentrate weight, slag yield – 23.3-25.8%, carbon-free slag content, wt. %: Fe=1.0-1.6; TiO2=62.7-61.9. TiO2 yield in the slag was 89.6-94.1%. Hot metal contains, %: 5.51 C; 0.36 Ti; 0.35 Mn; 0.04 Si; 0.23 V. Vanadium yield in iron was 53.0%.

1. Introduction

There is a modern powerful Ust-Kamenogorsk titanium-magnesium plant in Kazakhstan with complete processing cycle from raw materials smelting to titanium slag and further to titanium ingots. Own raw materials (concentrate from Satpayev deposit) cover only 30% of the plant requirements and 70% of concentrates is imported abroad. At the same time, there are indigenous titanium magnetite deposits in the country (Velikovskoe, Tymlay, Masalskoe, Western Sayak and others) with huge reserves that can be used as complex raw material for iron, titanium and vanadium production. Tymlay field in southern
Kazakhstan is of particular interest, its reserves are more than 1 billion tons and Fe content is 30.4%; TiO₂-10%, and after enrichment metal content is Fe-52.4%; TiO₂-16.06% [1].

It is quite complicated to smelt titanomagnetites with high titanium content in blast furnaces due to their low reducibility and low fusibility but direct electro-thermal reduction smelting process is associated with process instability, melt boiling, poor separation of hot metal, slag, etc. Instability and melt boiling is caused by intensive FeO recovery in liquid phase with a large volume of CO gas released, bloating viscous titanium slag. Conditions required to produce stable slag, which can be created only in controlled recovery period occurring in solid phase to slag formation development process. It is important to determine optimal conditions for titanium magnetite double-stage smelting technology implementation [2].

This work is devoted to development of TMC double-stage smelting process using little soda additives (3-4% Na₂O), with solid-phase recovery at the first stage, using specific coke as reductant, without TMC oxidation and including preliminary thermal oxidation.

2. Material and Methods
Concentrate was provided by "TENIR LOGISTIC" company and its chemical composition was the following (Table 1).

| Content in [%]       | Fe_total | Fe₂O₃  | FeO   | TiO₂  | Al₂O₃ | SiO₂  | MgO  | CaO  | MnO  | V₂O₅ | Remark |
|----------------------|----------|--------|-------|-------|-------|-------|------|------|------|------|--------|
|                      | 52.41    | 40.0   | 31.73 | 16.06 | 2.5   | 4.52  | 3.33 | 0.15 | 0.47 | 0.36 | 1.9    |

Calcinated soda (Na₂CO₃) of "chemically pure" grade was used as fluxing additive, it was added in estimation of 3-4% Na₂O to the concentrate weight. Specific coke from LLP "Sary-Arka" Shubarkol coal deposit was used as a reductant, its moisture content was 17.9%; ash content was 4.0%, volatile matter comprised -5.8% and C-67.5%.

X-ray phase analysis of the cakes was carried out using a D8 Advance (BRUKER), shooting machine, α-Cu, tube voltage 40/40. Obtained diffraction patterns were processed using EVA evolution software and phase decryption based on Search/match program using ASTM cards database. In course of work [3], recovered products were subjected to successive treatment with CuSO₄ and NH₄Cl solutions to eliminate metallic iron effect to the filming quality. It was not carried out in present study, in order to avoid hydrolysis of produced sodium silicates and titanates.

Vertical tube furnace RHTV 120-600/C40 Naberterm (Germany) is more suitable to create strong reducing environment for chemically resistant titanomagnetites reduction. Furnace size is following: furnace height - 95 cm, tube height - 145 cm, D_inter – 10.5 cm, tube is bottom purged with argon. There is spring valve on top of the tube stub maintaining excess pressure of 0.2 MPa in course of production process, in order to avoid air leaks. Mix charge made of concentrate, soda and specific coke was granulated in water, dried at 130°C, pellets were placed in graphite crucible, and later on it was set up in the centre of the furnace in alundum crucible. Temperature regimen was fixed with following parameters: temperature at the first stage is 1250°C; soaking time is 50 min; temperature at the second stage is 1500 - 1650°C; soaking time is 35 min.

3. Results and Discussion
In previous work [4], it was established that soda addition to the magnetite concentrate (TMC) estimated at 3-4% Na₂O performs as a coagulant during briquetting, as a catalyst during solid-phase reduction, as an inhibitor of DRI briquettes secondary oxidation and as a slag thinner.

TMC slag in terms of three refractory oxides has following composition, wt%: Al₂O₃-11.55; TiO₂-72.09; MgO-16.36, therefore it takes the field of anosovit continuous range of refractory solid solution MgTi₂O₅-magnesium anosovit in the state diagram (t_m-1652°C) – Al₂TiO₅ (t_m-1860°C). Out of existing
Impurities in anosovit formula, Ti, Al, Mg increase, but Fe, Mn, Cr, as well as SiO₂ and Na₂O impurities decrease the temperature of its melting. Therefore, top-and-bottom smelting of titanomagnetites with high titanium content is recommended to be maintained at the temperature range of 1500-1700 °C [2].

Considering relatively high content of Al₂O₃, MgO, and TiO₂, refractory oxides in TMC second stage smelting were studied at the temperatures of 1500 – 1650 °C. Carbon consumption, smelting mode (single - or double-stage) as well as temperature impacts on smelting results were tested (Table 2).

| Tapping scheme | Consumption [Spec coke] | Na₂O | Solid phase recovery t. °C | Tapping t. °C | τ. min | Yield from TMC [%] | Hot metal | MSS | MF | NMF | TiO₂ | Fe | Na₂O |
|----------------|-------------------------|------|---------------------------|--------------|-------|-------------------|-----------|-----|----|-----|------|----|------|
| Single stage   | 9.16                    | 4    | -                         | 1650         | 30    | 50.2              | 3.7       | 1.14| 17.2 | 35.2 | 5.2  |     |      |
|                | 7.32                    | 4    | -                         | 1650         | 30    | 55.8              | 1.2       | 0.94| 27.8 | 45.0 | 3.6  | 8.4 |      |
| Double stage   | 8                        | 3    | 1250 50                   | 1650         | 35    | 54.8              | 1.85      | 0.3 | 23.3 | 62.7 | 1.0  | 5.8 |      |
|                | 8                        | 3    | 1250 50                   | 1550         | 35    | 51.7              | 3.8       | 2.05| 27.6 | 38   |     |     |      |

In course of the single-stage process, reduction of specific coke consumption from 9.16 to 7.32% caused TiO₂ content increase in slag from 35.2% to 45%, but not more. During double-stage process, implementation under following parameters: temperature of 1250 °C at the first stage; soaking time of 50 min; temperature of 1650 °C at the second stage; soaking time of 35 min, produced good results, namely hot metal yield of 54.8%, TiO₂ content in the slag nonmagnetic fraction (NMF) of 62.7% excluding carbon. These process parameters were further maintained. In course of 1600 °C, experiment slag boiled over CO fume gases due to high viscosity and it plastered on the crucible walls all over the entire height, therefore it was not reduced completely. Subsequently, low yield of hot metal and high yield of metal-slag screenings (MSS), as well as magnetic fraction (MF) and NFM were obtained.

In course of 1550 °C experiment, slag boiled over the half height of the crucible then during cooling it dropped down leaving uniform slag film on the walls. Yield of smelting products was higher than in 1600°C experiment but lower than for results obtained with 1650°C.

In course of 1500°C experiment, slag phase was semisintered, half-melted. Outcomes were unsatisfactory. Thus, experiments proved that 1650°C temperature is the lowest bound for successful double-stage reduction smelting of TMC with this composition.

Probable temperature limit reduction concentrate shall be further enriched, in the case of magnesium and aluminum oxides in particular [6]. To reduce Na₂O sublimation, it was decided to add alkaline additives to TMC by pre-sintering of pelletized mixture with soda at 1000°C, with soaking time of 3 hours.

X-ray phase analysis of oxidized TMC sinter mixed with Na₂CO₃ (Na₂O consumption is 3%) showed that sodium makes a part of ferrosilicates and ferrotitanium. Ferrite sodium phase was not detected. Magnetite is almost completely oxidized to hematite, and ilmenite to pseudobrookite, facilitating their subsequent reduction. Six experiments of double-stage smelting of oxidized TMC sinter were carried out in continuous mode returning metal-slag screenings (MSS) and slag magnetic fraction to the beginning of the reduction process (Table 3).

The following was produced out of 840 g of TMC: 464.4 g of hot metal (yield 55.3), and 216.4 g of slag NMF (yield 25.8%) with 61.9% of TiO₂ content and slag yield of 94.1%. Based on x-ray phase analysis, slag in course of semi-continuous smelting process of oxidized TMC at 1650 °C consists of mainly of heat resistant compounds: sodium silicates and silicoborates, magnesium and calcium titanates, titanium dioxide and lower titanium oxides. Iron oxide FeO, previously included in sodium
ferrosilicates and ferrotitanates in oxidized sinters is replaced by sodium and magnesium oxides and recovered to metal form.

Table 3. Results of continuous double-stage reduction smelting process including preliminary soda roasting of TMC. Process parameters: t-1000 °C; τ-180 min. Solid-phase reduction: t-1250 °C; τ-50 min. Top and bottom smelting: t-1650 °C; τ-35 min. C/Fe ratio in the charge - 0,103; Na2O consumption-3% of TMC

| Sample No. | Charged. [g] | Produced. [g] | Yield of TMC. [%] |
|------------|--------------|---------------|------------------|
|            | TMC MSS MF Hot metal | MSS MF NMF Hot metal |                       |
| 1          | 200 1.9 0.2 99.07 | 8.67 1.6 57.7 | 49.5 4.33 0.8 28.85 |
| 2          | 200 1.85 0.3 100.1 | 14.1 0.77 44.2 | 50.0 7.04 0.38 22.07 |
| 3          | 73.4 5.57 0.58 45.6 | 1.95 0.15 19.72 | 62.12 2.66 0.2 26.87 |
| 4          | 111.6 8.45 0.88 69.3 | 3.65 0.45 27.54 | 62.07 3.27 0.4 24.67 |
| 5          | 112.5 8.53 0.89 Crucible bottom | 2.23 - 28.23 Crucible bottom | 1.98 - 25.1 |
| 6          | 140 7.83 0.6 150.3 | 4.04 0.38 39.05 | 59.52 2.89 0.27 27.89 |
| Total      | 840 34.3 3.47 464.4 | 4.04 0.38 216.4 | 55.3 0.48 0.05 25.8 |

Chemical composition of slag NMF [%]

| Fe | TiO2 | Na2O | C | SiO2 | Al2O3 | MgO | CaO |
|----|------|------|---|------|-------|-----|-----|
| 1.5 | 57.0 | 5.6  | 7.9 | 9.42 | 8.75  | 5.27 | 2.7 |

Chemical composition of hot metal [%] Hot metal yield [%]

| C | Ti | Mn | Si | V | V |
|---|----|----|----|---|---|
| 5.51 | 0.36 | 0.35 | 0.04 | 0.23 | 53.0 |

Table 4 provides comparative results of double-stage reduced heats of TMC directly and its oxidized cakes. It can be noticed that both options of heats are almost equal and high performance parameters were obtained both in hot metal yield (~55%), slag TiO2 content (~62%) and TiO2 slag extraction 89.6-94.1%.

Table 4. Comparative results of double-stage reduction heats

| Recovery scheme | Yield from TMC, % | Composition of carbon free slag, % | TiO2 yield of slag, % | Na2O sublimation degree, % |
|-----------------|------------------|------------------------------------|----------------------|---------------------------|
|                 | hot metal slag TiO2 Fe Na2O | Fe TiO2 Na2O |                       |                           |
| Free of sweet roasting | 54,8 23,3 62,7 1,01 5,85 | 89,6 | 56,5 |
| Including sweet roasting | 55,3 25,8 61,9 1,63 5,85 | 94,1 | 51,9 |

4. Conclusions
It is established that little soda additive (3-4% Na2O) to TMC charge in course of reduction smelting process performs as a coagulant during briquetting, as a catalyst in course of solid-phase recovery, as an inhibitor of DRI briquettes secondary oxidation and as a slag thinner during smelting.

In course of TMC double-stage reduction smelting process, soda reacts to SiO2, Al2O3, TiO2 oxides forming sodium silicates and titanates. Double-stage technology of TMC reduction smelting process both with soda addition, and without oxidation and preliminary iron oxidation of TMC to hematite was
developed. Optimal process parameters were determined: specific coke consumption-8%, or C/Fe ratio = 0.103; Na2O consumption-3%; temperature of solid-phase reduction process 1250 °C, soaking time-50 min; heating temperature -1650 °C, soaking time 35 min. Both options are almost equal and provide high performance: hot metal yield was ~55% out of concentrate weight, slag yield – 23.3-25.8%, carbon-free slag content, wt%: Fe=1.0-1.6; TiO2=62.7-61.9. TiO2 yield in slag was 89.6-94.1%. Na2O sublimation degree was 56.5% in the first and 51.9% in the second option. Hot metal contained, %: 5.51 C; 0.36 Ti; 0.35 Mn; 0.04 Si; 0.23, V yield in hot metal was 53.0%.

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