The effect of the composition of magnesia flux on the sinter structure and properties

A N Shapovalov\textsuperscript{1}, E V Ovchinnikova\textsuperscript{1}, V B Gorbunov\textsuperscript{1}, R R Dema\textsuperscript{2} and O B Kalugina\textsuperscript{2,3}

\textsuperscript{1} National University of Science and Technology «MISIS», Moscow, Russia
\textsuperscript{2} Nosov Magnitogorsk State University, Magnitogorsk, Russia

Email: alshapo@misis.ru

**Abstract.** The metallurgical properties of magnesian fluxes of the Khalilovo deposit with different ratios in the composition of magnesite and serpentine are studied. The results of laboratory study experiments the effect of magnesian fluxes properties of the Khalilovo deposit on the sinter production from the ore of the Kursk Magnetic Anomaly at the plant of JSC Ural Steel are presented. It is revealed that the use of experienced fluxes contributes to the sinter strength, increase the yield ratio and specific capacity. Thus, using experienced fluxes instead of Bakal siderite, an increase in the yield of sinter is provided by 3-5\% \textit{(rel.)} as a result of acceleration of solid-phase reactions involving magnesite and serpentine. At the same time, the sinter productivity increases from 1.04 to 1.08-1.15 t/m\textsuperscript{2}/h, that is, by 4-10\% \textit{(rel.)}. The use of experienced magnesian fluxes supports to increase the drum strength of the sinter by 4-6\% abs. Improving the strength characteristics of the sinter when using the magnesian fluxes of the Khalilovo deposit is due to the formation of a “reinforcing” of hedenbergite solid solutions as well as homogenization of the solidifying melt and crystallization of it in the form of a glass phase of rankinite composition, which together limit the formation of $\beta$-Ca$_2$SiO$_4$.

1. Introduction

One of the main ways to increasing the efficiency of blast-furnace smelting is the optimization of the basicity and the magnesia content in the slag [1-6], the correction of which is carried out by changing the composition of the sinter, as a rule. In the practice of sintering production, various materials based on magnesite, dolomite, olivine, dunite, serpentine, etc. are used as sources of magnesia [7-12]. The choice of magnesia flux is made on the basis of its chemical and mineralogical composition, properties and transport accessibility.

As a magnesian component in the production of iron sinter at the plant of JSC Ural Steel, siderite ores of the Bakal deposit with a content of 30-32\% Fe and 10-12\% MgO are used. The main ore-forming mineral of Bakal siderite is sideroplesite - (Mg, Mn, Fe) CO$_3$, its percent is 75-80\%. The remaining 20-25\% are dolomite, silicates in the form of shale, quartz, opal, etc. This material has an unstable chemical composition and a high content of large fractions (more than 10 mm), which adversely affects the agglomeration process and the quality of the sinter. At the same time, near from JSC Ural Steel, the Khalilovo serpentine-magnesite deposit with a content of MgO up to 40\% is being developed. The main ore-forming mineral of the Khalilovo deposit is serpentine (Mg$_6$[Si$_4$O$_{10}$(OH)$_2$]OH$_6$), its ratio in the ore is 55-90\%; carbonates — dolomite (10-14\%) and magnesite (5-40\%) are concomitant. In order to estimate the effectiveness of using magnesian fluxes...
from serpentine-magnesites of the Khalilovo deposit for sinter production, we conducted a study on the effect of magnesian flux (with different magnesite content) on the agglomeration process and sinter quality.

2. Materials and methods
Fluxes from serpentine-magnesites of the Khalilovo deposit with different magnesite contents of 10, 30, 50, and 70% were used as experimental materials. This choice is due to the current multi-stage technology for the enrichment of serpentine-magnesites, which makes it possible to obtain a product with different magnesite content at various stages of processing. The chemical compositions of the experimental fluxes, as well as the Bakal siderite, are given in table 1.

Table 1. Chemical composition of experimental magnesian materials

| Component title                                      | Bakal siderite | Magnesia flux of the Khalilovo deposit with different magnesite percentage (%) |
|------------------------------------------------------|----------------|--------------------------------------------------------------------------------|
|                                                      |                | 10  | 30  | 50  | 70  |
| Fe                                                   | 30,2           | 7,59| 6,71| 5,82| 4,93|
| FeO                                                  | 32,98          | 0,71| 0,55| 0,39| 0,24|
| SiO₂                                                 | 7,58           | 31,05| 24,15| 17,25| 10,35|
| CaO                                                  | 4,22           | 2,22| 1,75| 1,28| 0,81|
| Al₂O₃                                                | 1,9            | 0,88| 0,69| 0,49| 0,29|
| MgO                                                  | 10,4           | 38,22| 39,75| 41,28| 42,82|
| S                                                    | 0,17           | 0,027| 0,021| 0,015| 0,009|
| P₂O₅                                                 | 0,057          | 0,144| 0,112| 0,080| 0,048|
| Ignition losses                                       | 34,53          | 16,58| 24,93| 31,27| 38,61|

The studies were conducted in the laboratory of JSC "Ural Steel" on a sinter pot with a diameter of 210 mm. Mixing, moistening (up to 7.0–7.5 %) and pelletizing of the components of the sinter mix were carried out in a drum granulator 600 mm in diameter for 5 minutes with a rotation speed of 12 rpm. Iron ore concentrate and sintering ore of Mikhailovsky GOK were used as the main components of the sinter mix. The sinter mix was calculated in order to obtain the sinter with a CaO / SiO₂ basicity of 1.5 units with a MgO content of 2.0 %. The required MgO content in the sinter was ensured by the expenditure of Bakal siderite (in the base period) and experimental fluxes with different magnesite content (in the experimental periods). Maintaining the basicity at a required level was provided by adjusting the consumption of limestone. The content of return fines in the sinter mix was 25 %, and carbon it was 4.2 %.

3. Experiment
The averaged results of the experimental sintering are presented in table 2.

Table 2. Average results of experiments

| Component title                     | The results of experiments using different sources of MgO |
|-------------------------------------|----------------------------------------------------------|
|                                     | Bakal siderite | Magnesia flux with different magnesite percentage (%) |
|                                     |                | 10  | 30  | 50  | 70  |
| Sinter mix moisture, %              | 7,10           | 7,20| 7,10| 7,20| 7,30|
| Height of the sintered layer, mm    | 347            | 346 | 345 | 346 | 344|
| Sintering rate, mm / min            | 15,95          | 16,16| 16,28| 16,28| 16,36|
Comparison of the experimental results allows us to conclude that the sintering process using the experimental magnesian fluxes exceed those of the Bakal siderite. The use of experienced magnesia fluxes provides an increase in productivity by sintering rate increase and by a step-up of sinter yield. An increase in the sinter yield (with a particle size of more than 5 mm) is probably associated with improved thermal sintering conditions (confirmed by an increase of FeO content in the sinter with constant fuel consumption), as well as a change in the mechanism of mineral formation.

When using experienced magnesian fluxes, the tumbler index (TI + 5mm) and abrasion index (AI-0.5 mm) increase were observed. The index values were determined in a rotating drum according to the Russian all-Union State Standard 15137-77. The reasons for the significant improvement in the strength of the sinter obtained using serpentine-magnesite were defined by a comparative analysis of the “base” and experimental sinter microstructures.

**Microstructure of sinter**

The X-ray spectroscopy analysis of experimental sinter revealed that MgO almost completely goes into the ore part (magnetite) in all cases. At the same time, the crystallization form of the silicate bond of ore grains varies depending on the type of magnesian material. For example, figure 1 shows the fragments of microstructures of the sinter obtained with Bakal siderite (Figure 1, a) and with serpentine-magnesite with a magnesite content of 10, 30 and 50 % (Figure 1, b-d).

Table 3 shows the results of x-ray analysis of the sinter phases obtained with different magnesian materials.
Figure 1. Sinter microstructure with using Bakal siderite (a) and serpentine-magnesite with 10 % magnesite (b), 30 % (c) and 50 % (d)

Table 3. Chemical composition of sinter ligament-phases with different magnesian fluxes (wt%)

| Spectrum number (fig. 1) | O     | Mg    | Al    | Si    | Ca     | Fe     | Phase part                                      |
|--------------------------|-------|-------|-------|-------|--------|--------|-------------------------------------------------|
| 59                       | 37,97 |       | 16,2  | 44,63 | 1,03   |        | Dicalcium silicate                               |
| 60                       | 38,02 |       | 16,44 | 43,76 | 1,32   |        | Dicalcium silicate                               |
| 61                       | 37,64 |       | 16,36 | 44,3  | 1,47   |        | Dicalcium silicate                               |
| 62                       | 38,74 | 2,45  | 18,55 | 24,74 | 12,33  |        | Glass phase of low basic capacity                |
Calcium ferrite

Sinter with magnesia flux containing 10% magnesite (Figure 1, b)

|   |   |   |   |   |   |
|---|---|---|---|---|---|
| 63 | 31.89 | 0.4 | 2.02 | 4.67 | 12.09 |
| 81 | 40.16 |   |   | 19.48 | 39.13 |
| 82 | 39.87 |   |   | 19.84 | 39.24 |
| 83 | 37.88 | 1.96 |   | 15.73 | 17.72 |
| 84 | 40.5  |   |   | 19.56 | 39.02 |

Glass phase of rankinite composition

Sinter with magnesia flux containing 30% magnesite (Figure 1, c)

|   |   |   |   |   |   |
|---|---|---|---|---|---|
| 153| 37.84 | 2.15 | 16.52 | 44.69 | 0.71 |
| 154| 35.46 |   |   | 16.91 | 46.37 |
| 157| 35.99 |   |   | 14.38 | 18.64 |

Glass phase of rankinite composition

Hedenbergite

Sinter with magnesia flux containing 50% magnesite (Figure 1, d)

|   |   |   |   |   |   |
|---|---|---|---|---|---|
| 201| 36.00 | 0.15 | 19.94 | 41.78 | 1.99 |
| 203| 35.93 | 0.19 | 19.59 | 40.96 | 3.33 |
| 204| 36.73 | 0.16 | 20.06 | 41.65 | 1.40 |

Glass phase of rankinite composition

|   |   |   |   |   |
|---|---|---|---|

Glass phase of rankinite composition

Mellit

An experimental sinter microstructure analysis allows us to conclude that the improvement in the strength of the sinter with serpentine-magnesite arises due to the simultaneous occurrence of the processes:

− formation of hedenbergite solid solutions (in the ferrites absence) [8, 13], which provides strengthening of the sinter cake;

− homogenization of the solidifying melt and its crystallization in the form of a glass phase of rankinite composition, which limits the formation of $\beta$-Ca$_2$SiO$_4$.

When a siderite from the Bakal deposit used as a magnesian material, the process of mineral formation is restrained by the lower activity of free MgO emerged during the decomposition of magnesium carbonate, as well as by the formation of refractory spinels of the magnesiomagnetite and magnesioferrite type [14-16].

Magnesium oxide, which is part of serpentine-magnesium-magnesite, is involved in the formation of silicate phases. The formation of refractory spinels at the MgO and iron oxides interaction takes place only at the stage of melt crystallization. The magnesite increase in the content of the serpentine-magnesite leads to an increase in the proportion of solid solutions of hedenbergite in the sinter.

4. Conclusions

The use of magnesia fluxes from serpentine-magnesites of the Khalilovo deposit contributes to the strengthening of the sinter, increasing the yield of the useful and specific productivity. Improvement of the sinter strength characteristics and indicators of the sintering process occurs due to the formation of a "reinforcing" of hedenbergite solid solutions, as well as the homogenization of the solidifying melt and its crystallization in the form of a glass phase of rankinite composition, both of these processes together limit the formation of $\beta$-Ca$_2$SiO$_4$.

Acknowledgements

The work was financially supported by the Ministry of Education and Science of the Russian Federation, the project № 11.2054.2017/4.6 of the state assignment for 2017-2019.

References

[1] Grigor’ev F F, Chernyatin A N, Kopyrin I A et al 1979 Optimizing the content of lime, magnesia, and alumina in blast-furnace slags Metallurgist 23:8 536-39

[2] Fedchenko V M and Shparber L Y 1986 Slag regime of a blast furnace Metallurgist 30 351-53

[3] Shiua J S, Liu S H. And Ho C K 2012 Effect of Magnesium and Aluminum Oxides on Fluidity of Final Blast Furnace Slag and Its Application Mater. Trans., JIM 53 1449-55
[4] Yao L, Ren S, Wang X, Liu Q, Dong L, Yang J and Liu 2016 Effect of Al₂O₃, MgO, and CaO/SiO₂ on Viscosity of High Alumina Blast Furnace Slag Steel research int., 87 241-49

[5] Zhang K, Wu S, Huang W, Liu X, Zhu J and Du K 2015 Effect of MgO on Emergence of Blast Furnace Primary Slag with Comprehensive Furnace Burden In: Jiang T. et al. (eds) 6th International Symposium on High-Temperature Metallurgical Processing Springer, Cham

[6] Nakamoto M, Tanaka T, Lee J and Usui T 2004 Evaluation of viscosity of molten SiO₂–CaO–MgO–Al₂O₃ slags in blast furnace operation ISIJ Int. 44 2115–19

[7] Panigraphy S C, Rigaud M A J and Dilewijns J 1985 The effect of dolomite addition on the properties of sinters produced from a high aluminous iron ore Steel Res. Int. 56 35–41

[8] Ovchinnikova E V, Gorbunov V B, Shapovalov A N, Maistrenko N A and Bersenev I S 2018 Magnesia Sinter with Flux Based on Magnesium Silicate Steel in Translation 48 34-38

[9] Raygan Sh, Abdizadeh H, Dabagh A and Pourabdoli M 2013 Influence of talc additive on cold strength and reducibility of iron ore sinters compared to bentonite Ironmaking Steelmaking 36 273-78

[10] Umadevi T, Nelson K, Mahapatra P C, Prabhu M and Ranjan M 2013 Influence of magnesia on iron ore sinter properties and productivity Ironmaking Steelmaking 36 515-20

[11] Yadav U S, Pandey B D, Das B K and Jena D N 2013 Influence of magnesia on sintering characteristics of iron ore Ironmaking Steelmaking 29 91-95

[12] Shapovalov A N, Ovchinnikova E V and Maistrenko N A 2015 Improving the Preparation of the Charge Used for Sintering at Ural Steel Metallurgist 59 204-11

[13] Li T, Sun C, Liu X, Song S and Wang Q 2018 The effects of MgO and Al2O3 behaviours on softening–melting properties of high basicity sinter Ironmaking Steelmaking 45 755-63

[14] Ovchinnikova E V, Gorbunov V B, Shapovalov A N, Pisarev S A and Durov L N 2016 Comparative study of the South Urals magnesium materials behavior at the sintering process temperature Izvestiya vuzov. Chernaya metallurgiya. Trans. Iron and steel 11 814-20

[15] Shapovalov A N, Dema R R, Nefedeyev S P, Solomonov C N and Yordanova R M 2017 Application of new surfactants sintering agglomerate Journal of Chemical Technology and Metallurgy 52 1008-16

[16] Ganin D R, Druzhkov V G, Panychev A A, Shapovalov A N, Shevchenko E A 2017 Investigation of the effect of additives serpentitomagnezit Khalilovo deposit on the performance of the sintering process at JSC "Ural Steel" Vestnik of Nosov Magnitogorsk State Technical University 15 20-26