

Article Effect of MgO Content on Heat Capacity of Synthetic BF Slag and Heat Release Behavior during Cooling Process

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Abstract: The differential scanning calorimetry (DSC) sapphire analysis was used to measure the specific heat capacity of the BF (BF) slag and observe the CaO-SiO₂-MgO-Al₂O₃-TiO₂ 5-element slag system with the binary basicity fixed at 1.17. The specific heat capacity of the BF slag and the cooling heat distribution were obtained during the cooling process when the MgO content changing from 7% to 11%. The results showed that the heat released of BF slag was more than 1.2 GJ/ton during the cooling process from 1400 °C to 35 °C, of which the sensible heat was dominant. At MgO content of 9%, the latent heat of crystallization is maximum. The cooling and heat release law of BF slag is directly associated with the phase precipitated in slag cooling and micromorphology.

Keywords: BF slag; specific-heat capacity; MgO content; heat release

1. Introduction

BF slag is the most important solid waste in the ironmaking process, and its annual emission exceeds 200 million tons per year. The molten BF slag discharged at 1500 °C contains a large number of high-quality sensible heat [1,2]. The calorific value per ton of slag is equivalent to the calorific value of 58 kg standard coal [3–5]. Therefore, BF slag has dual properties, namely, the source of energy and material resources, and the heat contained is a kind of high-quality energy, the material is important raw materials for cement production. When cooled quickly, the slag does not have sufficient time to crystallize; as such, the latent heat of solidification is not released in a promptly manner and is converted to chemical energy to maintain a glassy form. Therefore, BF slag is chemically active. Moreover, BF slag exhibits cementitious property and specific strength when treated with the raw materials for cement production. Scientific and effective utilization is important to improve energy efficiency and reduce resource consumption in the iron and steel industry. It is an important way to alleviate the bottleneck of resource shortage and promote the development of the green recycling industry.

At present, the water quenching process is used to treat the BF slag. The water quenching process exists a lot of problems and difficulty, such as high water consumption, high drying energy consumption, environmental pollution, and no heat recovery [6,7]. Inspired by the principle of coke dry quenching, researchers start to study the dry granulation of molten slag and sensible heat recovery on the basis of direct or indirect contact between the heat transfer medium and BF slag without water consumption, i.e., dry granulation, and to solve these problems. Researchers have carried out systematic research work around the particle-forming mechanism, granulation mechanism, movement, and distribution settlement behavior in the process of dry granulation [8–13]. Now, the dry granulation process is mature and provides a guarantee for the subsequent waste heat recovery.

After high-temperature slag particles are obtained on the basis of dry granulation, researchers study physical and chemical recovery methods around the waste heat recovery



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). of high-temperature slag particles [14,15]. In a physical way, taking air and water as heat transfer media, the waste heat is recovered by the gas–solid heat transfer of fluidized bed and packed bed. In a chemical way, the sensible heat of the BF slag was converted into chemical heat storage by an endothermic chemical reaction [16–20]. The physical method is mature but needs many times of energy conversion. Thus, the energy consumption and loss of energy flow are high. The chemical method has outstanding advantages, but the whole system is not mature. No matter which way is used to recover waste heat, the heat release law of the BF slag must be defined in the cooling process, thus realizing the quantity and quality of waste heat. Finally, the energy recovery concept of "temperature matching, cascade utilization" will be achieved.

Therefore, it is necessary to clarify the basic data of thermophysical properties of BF slag in different states, such as specific heat capacity, heat release law during the cooling process. The specific heat capacity is a physical quantity that reflects the ability of a substance in heat absorption and release and an attribute of material. Generally, in making rough calculations, people mostly compare based on the basic thermophysical data of the typical silicate [21,22]. However, some differences are present between them. Based on this, the specific heat capacity of the BF slag is measured systematically in this work to establish the relationship between the composition of the BF slag and its specific heat capacity.

2. Experimental

2.1. Testing Fundamentals

The specific heat capacity of materials is measured using the adiabatic calorimetry, flow calorimetry, and conduction calorimetry. DSC can be divided into the steady-state ADSC, sapphire method, and stepwise scanning methods [23–26]. Among these methods, the sapphire method is a typical indirect measurement method and is widely used due to its high reliability and high stability [27–31]. In the sapphire method, the specific heat of the known standard sapphire is used to calibrate the specific heat of other samples with known masses. In order to obtain the specific heat of the sample, three tests are required during the experiment. First, the baseline test, i.e., the blank crucible test (blank test), which is carried out. Then, the sapphire standard sample test (sapphire test) is carried out by using a blank crucible as a reference sample. Finally, the sample is tested (sample test) by using a blank crucible as a reference sample. A typical example diagram of the three DSC test curves is shown in Figure 1. The specific heat capacity of the sample is obtained by subtracting the curves. The specific calculation formula is as follows:

$$C_{p}^{\text{Sample}} = C_{p}^{Sapphire} \cdot \frac{m_{Sapphire}}{m_{Sample}} \cdot \frac{P_{Sample} - P_{Baseline}}{P_{Sapphire} - P_{Baseline}}$$
(1)

where *m* refers to mass (mg), C_p refers to specific heat capacity (J g⁻¹ °C⁻¹), and *P* refers to heat flow, DSC signal after deducting baseline in relative coordinates (m·W).

2.2. Experimental Scheme

During the experiment, the BF slag is synthesized by an analytically pure chemical reagent. The experiment focuses on the investigation of the CaO-SiO₂-MgO-Al₂O₃-TiO₂ 5-element BF slag. The specific experimental scheme is shown in Table 1 [32], and this chemical composition is the same as that in the literature. The binary basicity R (CaO/SiO₂), Al₂O₃ content, and TiO₂ content are 1.17%, 12%, and 5%, respectively; and the MgO content ranges from 7% to 11%. Firstly, slag samples were pre-melted in the MoSi₂ furnace, heated to 1500 °C, and kept for 2 h to ensure that the samples are fully mixed. Then, some slag were slowly cooling to obtain the crystallization slag. The glassy slag and crystallization slag were then dried, crushed, and ground to obtain a particle size of 200 mesh or less for tests. The glassy slag was used for the DSC tests (NETZSCH, Selb, Germany), whereas

crystallization slags were used for XRD (Rigaku Corporation, Tokyo, Japan) and SEM-EDS tests (JEOL, Tokyo, Japan), to obtain phase and microstructure characterization.



Figure 1. A typical example diagram of DSC Curves of the blank crucible, sample, and sapphire.

Table 1. Chemical composition of synthesized BF slag.

| No. | CaO (wt%) | SiO ₂ (wt%) | MgO (wt%) | Al ₂ O ₃ (wt%) | TiO ₂ (wt%) | R (CaO/SiO ₂) |
|-----|--------------|---------------------------|--------------|---|---------------------------|------------------------------|
| 1 | 40.04 | 34.22 | 7.00 | 12.00 | 5.00 | 1.17 |
| 2 | 39.50 | 33.76 | 8.00 | 12.00 | 5.00 | 1.17 |
| 3 | 38.96 | 33.30 | 9.00 | 12.00 | 5.00 | 1.17 |
| 4 | 38.42 | 32.84 | 10.00 | 12.00 | 5.00 | 1.17 |
| 5 | 37.88 | 32.38 | 11.00 | 12.00 | 5.00 | 1.17 |

The experimental conditions for specific heat capacity testing through the DSC method are as follows: the heating rate, 10 K·min⁻¹; heating from room temperature to 1400 °C; protective atmosphere, Ar gas. The corundum crucible is used.

3. Results and Discussion

3.1. DSC Curves of BF Slag with Different Contents of MgO

Figure 2 shows the DSC curves of the BF slag with different contents of MgO. It can be seen three evident endothermic and exothermic peaks in the DSC curve with increased temperature. Three peaks' local magnification are shown in Figure 3. The temperature ranges corresponded to the three peaks are 830 °C–890 °C, 1160 °C–1230 °C, and 1300 °C–1345 °C, indicating three typical phase precipitation or crystal transformation zones in the corresponding temperature range in the heating process of water-quenched BF slag. With the increase in the MgO content, the temperature of peak 1 increases firstly and then decreases. This is because with the increase of MgO content, some low melting point compounds are easily formed in the slag. When the MgO content in the slag is too high, the melting point of the slag increases instead. In addition, endothermic and exothermic peaks exist in the range of 1300 °C–1345 °C and show an evident superposed peak trend, indicating two and more phase precipitations or crystal transformations in this temperature range.



Figure 2. DSC curves of the water-quenched BF slag with different contents of MgO.



Figure 3. Local magnification of DSC curves of the BF slag in the temperature range of endothermic peak-1, exothermic peak-2, and peak-3.

Figure 4 shows the change in the peak temperature in three crystallization regions of BF slag with different contents of MgO. With increased content of MgO in the BF slag,

the peak temperatures 1160 °C–1230 °C and 1300 °C–1345 °C two crystallization regions move to the high-temperature zone, showing an upward trend, due to the change in the theoretical crystallization temperature of the secondary phase caused by increased MgO. The peak temperature in the 830 °C–890 °C crystallization region increases first and then decreases due to the increased theoretical crystallization temperature of the main phase caused by increased MgO.



Figure 4. Change in the peaks' temperature in the crystallization region of the BF slag with different contents of MgO.

3.2. Specific Heat Capacity and Heat Cooling Release of BF Slag with Different Contents of MgO

On the basis of Equation (1), the specific heat capacity of the BF slag is calculated, and the result is shown in Figure 5. The specific heat capacity of BF slag is divided into four ranges with stable specific heat capacity by three crystallization regions during the whole heating process, namely, Range-1 ($35 \degree C-730 \degree C$), Range-2 ($900 \degree C-1170 \degree C$), Range-3 ($1220 \degree C-1285 \degree C$), and Range-4 ($1345 \degree C-1400 \degree C$). Then, the expression of specific heat capacity in the corresponding ranges is fitted, and the result is shown in Table 2. Fitting results are highly correlated. The specific expressions are as follows:

Range-1:
$$C_{p_1} = a + b \times 10^{-2} T + c \times 10^{-5} T^2 \left[J \cdot g^{-1} \cdot {}^{\circ} C^{-1} \right]$$
 (2)

Range-2:
$$C_{p2} = a + b \times T + c \times 10^{-2} T^2 + d \times 10^{-6} T^3 \left[J \cdot g^{-1} \cdot {}^{\circ}C^{-1} \right]$$
 (3)

Range-3:
$$C_{p3} = a + b \times T + c \times 10^{-3} T^2 \left[J \cdot g^{-1} \cdot {}^{\circ}C^{-1} \right]$$
 (4)

Range-4:
$$C_{p4} = a + b \times 10^{-2}T + c \times T^2 + d \times 10^{-4}T^3 \left[J \cdot g^{-1} \cdot {}^{\circ}C^{-1} \right]$$
 (5)



Figure 5. The calculation result of specific heat capacity of BF slag with different contents of MgO.

| [ab] | le 2. | Th | e re | latio | nshi | p | between | specifi | c hea | t caj | pacity | 7 and | tem | pera | ture | <u>.</u> |
|------|-------|----|------|-------|------|---|---------|---------|-------|-------|--------|-------|-----|------|------|----------|
|------|-------|----|------|-------|------|---|---------|---------|-------|-------|--------|-------|-----|------|------|----------|

| T [°C] | $C_p = a + b \times 10^{-2} T + c \times 10^{-5} T^2$ | | | R ² T [°C] | | $C_p = a$ | $C_p = a + b \times T + c \times 10^{-2} T^2 + d \times 10^{-6} T^3$ | | | | |
|---|--|--|-------------------------------------|--|---|--|--|--|---|--|--|
| (Range-1) | а | b | С | . It | (Range-2) | а | b | с | d | R | |
| 37-712 | 1.9823 | -0.54 | 0.40 | 0.9913 | 907-1082 | -446.56 | 1.3509 | -0.14 | 0.50 | 0.9984 | |
| 37-722 | 2.1408 | -0.31 | -0.08 | 0.9933 | 900-1169 | -338.3 | 1.0508 | -0.11 | 0.40 | 0.9837 | |
| 46-715 | 3.5320 | -0.49 | -0.03 | 0.9908 | 900-1152 | 184.83 | -0.571 | 0.06 | -0.20 | 0.9977 | |
| 46-720 | 2.6046 | -0.49 | 0.20 | 0.9922 | 890-1051 | 327.2 | -0.9905 | 0.10 | -0.30 | 0.9666 | |
| 40-726 | 1.9726 | -0.25 | -0.04 | 0.9905 | 916-1098 | 160.02 | -0.4609 | 0.04 | -0.10 | 0.9727 | |
| | $C_p = a + b \times T + c \times 10^{-3} T^2$ | | | | | | | | | | |
| T [°C] | $C_p = a$ | $+b \times T + c \times 10$ | $(-3T^2)^{-3}$ | R^2 | T [°C] | $C_p = a$ | $a+b\times 10^2T+a$ | $c \times T^2 + d \times 10$ | $^{-4}T^{3}$ | R ² | |
| T [°C] (Range-3) | $\frac{C_p=a}{a}$ | $+b \times T + c \times 10$ b | $\frac{(-3T^2)^{-3}T^2}{c}$ | - R ² | T [°C] (Range-4) | $\frac{C_p=a}{a}$ | $a+b\times 10^2T+c$ b | $c \times T^2 + d \times 10$ | $\frac{-4}{d}T^3$ | R ² | |
| T [°C] (Range-3) | $\frac{C_p = a}{a}$ 582.7 | $+b \times T + c \times 10$ b -0.9665 | $\frac{c}{0.40}$ | - R² | T [°C] (Range-4) 1352–1400 | $\frac{C_p = a}{a}$ 28,111 | $\frac{a+b\times10^2T+a}{b}$ | $\frac{c \times T^2 + d \times 10}{c}$ | $\frac{-4}{d}T^{3}}{d}$ | <i>R</i> ² | |
| T [°C] (Range-3) 1222–1282 1225–1297 | | +b×T+c×10 b -0.9665 -1.5277 | $\frac{c}{0.40}$ | - R² 0.9955 0.9963 | T [°C] (Range-4) 1352–1400 1348–1400 | | b = -0.6142 = 0.1199 | $\frac{c \times T^2 + d \times 10}{c}$ 0.0447 -0.0087 | $-4T^{3}$ <i>d</i> -0.10 0.02 | R² 0.9642 0.9931 | |
| T [°C] (Range-3) 1222–1282 1225–1297 1208–1295 | $ \begin{array}{c} C_p = a \\ \hline a \\ 582.7 \\ 934.6 \\ 472.1 \\ \end{array} $ | +b×T+c×10 b -0.9665 -1.5277 -0.8009 | $rac{c}{c}{0.40}{0.60}{0.30}$ | - R² 0.9955 0.9963 0.9961 | T [°C] (Range-4) 1352–1400 1348–1400 1347–1400 | $ \begin{array}{c} C_p = a \\ \hline a \\ \hline 28,111 \\ -5496 \\ 18,920 \end{array} $ | <i>b</i> -0.6142 0.1199 -0.4121 | $c \times T^2 + d \times 10$ c 0.0447 -0.0087 0.0299 | $-4T^3$ <i>d</i> -0.10 0.02 -0.07 | R² 0.9642 0.9931 0.9876 | |
| T [°C] (Range-3) 1222–1282 1225–1297 1208–1295 1219–1296 | $ \begin{array}{c} C_p = a \\ \hline a \\ \hline 582.7 \\ 934.6 \\ 472.1 \\ 423.9 \\ \end{array} $ | +b×T+c×10 b -0.9665 -1.5277 -0.8009 -0.7198 | $rac{c}{c}{0.40}{0.60}{0.30}{0.30}$ | - R² 0.9955 0.9963 0.9961 0.9944 | T [°C] (Range-4) 1352–1400 1348–1400 1347–1400 1347–1400 | $ \begin{array}{c} C_p = a \\ \hline a \\ \hline 28,111 \\ -5496 \\ 18,920 \\ -13,326 \\ \end{array} $ | $a+b \times 10^2 T+a$ b -0.6142 0.1199 -0.4121 0.2902 | $ c \times T^2 + d \times 10 c 0.0447 -0.0087 0.0299 -0.0211 $ | $-4T^3$ <i>d</i> -0.10 0.02 -0.07 0.05 | R² 0.9642 0.9931 0.9876 0.9859 | |

Based on the above expression of specific heat capacity, the heat released from each ton of BF slag can be obtained during the cooling process of BF slag from 1400 °C to 35 °C. Therefore, the latent heat of phase transformation and the change in specific heat capacity caused by different aggregation states of the matter before and after phase transformation should be considered. The heat change should be calculated in seven sections, namely, 35 °C–720 °C, 720 °C–900 °C, 900 °C–1170 °C, 1170 °C–1220 °C, 1220 °C–1285 °C, 1285 °C–1345 °C, and 1345 °C–1400 °C. The specific calculation formulas are as follows.

$$\Delta H_1 = \int_{35}^{720} C_{p1} dT = \int_{35}^{720} a + b \times 10^{-2} T + c \times 10^{-5} T^2 dT$$
(6)

$$\Delta H_2 = \Delta_{\rm fus} H_1 = \int_{720}^{900} {\rm DSC}_{\rm Peak-1} {\rm dT}$$
(7)

$$\Delta H_3 = \int_{900}^{1170} C_{p2} dT = \int_{900}^{1170} a + b \times T + c \times 10^{-2} T^2 + d \times 10^{-6} T^3 dT$$
(8)

$$\Delta H_4 = \Delta_{\text{fus}} H_2 = \int_{1170}^{1220} \text{DSC}_{\text{Peak-2}} dT$$
(9)

$$\Delta H_5 = \int_{1220}^{1285} C_{p3} dT = \int_{1220}^{1285} a + b \times T + c \times 10^{-3} T^2 dT$$
(10)

$$\Delta H_6 = \Delta_{\rm fus} H_3 = \int_{1285}^{1345} {\rm DSC}_{\rm Peak-3} {\rm dT}$$
(11)

$$\Delta H_7 = \int_{1345}^{1400} C_{p4} dT = \int_{1345}^{1400} a + b \times 10^2 T + c \times T^2 + d \times 10^{-4} T^3 dT$$
(12)

$$\Delta H_{\text{totals}} = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6 + \Delta H_7 \tag{13}$$

 ΔH_1 , ΔH_3 , ΔH_5 , and ΔH_7 refer to physical sensible heat, which can be obtained through the relationship between specific heat capacity and the temperature of the BF slag. ΔH_2 , ΔH_4 , and ΔH_6 refer to the latent heat of phase transformation, which can be obtained through the integral area of endothermic and exothermic peaks of the DSC curve.

When the temperature drops from 1400 °C to 35 °C, the distribution of the heat released from per ton of BF slag is shown in Table 3. The heat released by the BF slag in the cooling process exceeds 1.2×10^6 kJ/ton, which indicates that the heat in the BF slag is a high-quality heat source with a high recycling value. With increased MgO content, the amount of total heat released shows an upward trend first and then downward. When the MgO content increase from 7% to 11%, the ΔH_1 shows an increasing trend, from 0.43×10^6 to 1.29×10^6 kJ/ton, while the ΔH_3 decrease from 0.15×10^6 to 0.02×10^6 kJ/ton. This may be because with the increase of MgO, the phase of the slag changed. The change of Δ H mainly depends on the phase and crystallization of the slag. In addition, the ΔH_1 of slag with 7% and 8% is lower than other slags. This may be because when the MgO content is low, the slag does not crystallize sufficiently, resulting in less heat release.

Table 3. Heat release of per ton of BF slag from 1400 °C to 35 °C.

| MgO% - | Heat Release (×10 ⁶ kJ) | | | | | | | | | |
|--------|------------------------------------|--------------|--------------|--------------|--------------|--------------|--------------|-------------------------|--|--|
| | ΔH_1 | ΔH_2 | ΔH_3 | ΔH_4 | ΔH_5 | ΔH_6 | ΔH_7 | $\Delta H_{\rm totals}$ | | |
| 7% | 0.4324 | -0.0139 | 0.1474 | 0.0088 | 0.3756 | 0.0112 | 0.2895 | 1.2788 | | |
| 8% | 0.6803 | -0.0130 | 0.2192 | 0.0378 | 0.1610 | 0.0124 | 0.2897 | 1.4134 | | |
| 9% | 1.0713 | -0.0133 | 0.3702 | 0.0282 | 0.5283 | 0.0139 | 0.3029 | 2.3281 | | |
| 10% | 0.7369 | -0.0123 | 0.0549 | 0.0066 | 0.3241 | 0.0103 | 0.2347 | 1.3798 | | |
| 11% | 1.2908 | -0.0138 | 0.0244 | 0.0053 | 0.1828 | 0.0120 | 0.0691 | 1.5982 | | |

The proportion of heat of each component can be obtained by normalizing the heat release of the BF slag in each component. At the same time, considering that the BF slag after cooling can be still used as the raw material for cement production, no crystal precipitation is required in the cooling process. Therefore, the physical sensible heat values, namely, ΔH_1 , ΔH_3 , ΔH_5 , and ΔH_7 , are summarized as recoverable heat; and the latent heat values, specifically, ΔH_2 , ΔH_4 , and ΔH_6 , are summarized as nonrecoverable heat. Finally, the distribution of cooling heat of the BF slag is obtained (Figure 6).

From the whole heat distribution, the proportion of sensible heat (ΔH_1 , ΔH_3 , ΔH_5 , and ΔH_7) is far more than that of the latent heat (ΔH_2 , ΔH_4 , and ΔH_6) of crystallization. Among them, more than 90% of heat is physically sensible heat. The proportion of latent heat, as nonrecyclable heat, increases first and then decreases with increasing MgO content. This result indicates that the content of MgO in the BF slag is increased, which helps to precipitate increased crystals during the cooling process for the latent heat of crystallization to increase and the physical heat to decrease. The release of sensible heat reaches stability when the content of MgO is over 9%. Therefore, it can be inferred that the heat release law of the BF slag in the cooling process is related to the phase composition and micro morphology of the slag.



Figure 6. Distribution of heat released in each stage of BF slag cooling.

3.3. Analysis on Phase and Micro Morphology of BF Slag with Different Contents of MgO

The Equip module of the thermodynamic calculation software Factsage 8.1 (FactSage, Aachen, Germany) is adopted for the thermodynamic calculation of crystallization in BF slag. Figure 7 shows the phase precipitation during the cooling crystallization process of the CaO-SiO₂-Al₂O₃-MgO-TiO₂ slag system under different MgO contents. This figure indicates that the major precipitated phase is melilite and CaTiO₃. In addition, CaSiO₃, CaSiTiO₅, CaAl₂SiO₈, Clinopyroxene, Wollastonite, and Titania_Spinel are observed.

The crystallization temperatures of melilite exhibit a rising trend. By contrast, the crystallization temperature of CaTiO₃ and CaSiO₃ present a declining trend. These results are mainly attributed to several low melting-point phases transforming into high melting-point phases and the melilite phase turning into the MgO-rich spinel phase with an increase in MgO content.

It can be seen the changes in the crystallization amount of the melilite phase along with temperature under different MgO contents of slag. As shown in the figure, the crystallization amount of melilite increases continuously and can reach up to 80% when temperature decreases. The crystallization speed of melilite is extremely fast when temperature ranges from 1380 °C to 1500 °C, but afterward, the crystallization rate becomes stable. The crystalline phase of CaSiO₃, CaSiTiO₅ and CaAl₂SiO₈ gradually disappeared when MgO content increases, while, the phase of Wollastonite and Titania_Spinel precipitate.

XRD, SEM, and EDS analyses are used to define the differences in phase and micromorphology of the BF slag with different contents of MgO. Figure 8 presents the phase analysis results of BF slag. XRD results show an evident amorphous peak in the slag when the content of MgO is lower than 9%, indicating that the slag is not fully crystallized at this moment. As the content of MgO increased to 9% or higher, the slag is fully crystallized. The different proportions of the amorphous phase that was rather a result of randomly different quenching rates. At the same time, the ΔH_1 of slag with high MgO content (above 9%) is higher than that of slag with lower MgO content, which further proves that the heat released by the BF slag is related to the crystallization of the slag. Typical crystalline phases include melilite, dicalcium silicate, pseudo wollastonite, and pyroxene. Among these phases, melilite becomes gehlenite at low MgO content and is converted to akermanite at 9% MgO, which is also observed with the most abundant crystallization and highest crystallization intensity. At this moment, the latent heat released is highest, which is also consistent with the abovementioned heat release law. Further analysis results show that the latent heat and specific heat capacity of gehlenite and akermanite in the crystalline phase are the same.



Figure 7. Crystallization of CaO-SiO₂-Al₂O₃-MgO-TiO₂ with different MgO contents.



Figure 8. XRD patterns of naturally cooled BF slag with different contents of MgO.

Figure 9 shows the SEM images of the microstructure of BF slag with different MgO contents and the microstructure of a typical melilite mineral [33]. Given that the crystal morphology is short columnar or tabular, it is a typical tetragonal crystal system melilite mineral. With the increased content of MgO, the number of melilite crystals in the field of view decreases continuously, and the size increases continuously because the type of melilite crystal is changed from gehlenite to akermanite. EDS analysis is carried out in the corresponding areas of SEM samples. At 9% MgO content, the SEM–EDS results of the selected area of BF slag are shown in Figure 10. The contents of the elements in the corresponding areas are counted (Table 4). At this moment, the content of Ti reaches the maximum value, and this finding is also consistent with the XRD phase analysis result.

| | Weight % | | | | | | | | | |
|----------|-----------|-----------|-----------|------------|------------|--|--|--|--|--|
| Elements | 7% MgO, A | 8% MgO, B | 9% MgO, C | 10% MgO, D | 11% MgO, E | | | | | |
| 0 | 49.63 | 54.39 | 50.30 | 48.39 | 50.45 | | | | | |
| Mg | 5.48 | 6.10 | 5.42 | 6.20 | 8.11 | | | | | |
| Al | 5.74 | 5.80 | 5.82 | 5.87 | 5.89 | | | | | |
| Si | 15.36 | 14.27 | 14.45 | 15.30 | 14.17 | | | | | |
| Ca | 21.15 | 17.20 | 21.73 | 23.03 | 18.92 | | | | | |
| Ti | 2.64 | 2.25 | 2.28 | 1.22 | 2.46 | | | | | |
| Totals | 100% | 100% | 100% | 100% | 100% | | | | | |

Table 4. SEM-EDS results of BF slag with different contents of MgO.



Figure 9. SEM photos of the microstructure of BF slag with different contents of MgO (**A**-7% MgO, **B**-8% MgO, **C**-9% MgO, **D**-10% MgO, **E**-11%, and a typical Melilite).



Figure 10. SEM–EDS analysis with mapping in the selected areas of BF slag with 7% MgO.

4. Conclusions

- 1. The basic database of the specific heat capacity of BF slag is improved.
- 2. The proportion of sensible heat is far more than that of latent heat of crystallization, and the heat of this part has an extremely high recovery value.
- 3. When the BF slag is cooled from 1400 °C to 35 °C, three crystallization regions correspond to the release of the crystallization latent heat, whereas four other regions correspond to the release of physical sensible heat. The physical sensible heat released at the temperature range of 35 °C–700 °C is the most.
- 4. The heat release during the cooling process of the BF slag is directly related to the phase and micromorphology. The specific heat capacity of akermanite is almost equal to that of gehlenite.

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References

- 1. Yasipourtehrani, S.; Strezov, V.; Bliznyukov, S.; Tim, E. Investigation of thermal properties of BF slag to improve process energy efficiency. J. Clean. Prod. 2017, 149, 137–145. [CrossRef]
- 2. Gao, J.; Feng, Y.; Feng, D.; Zhang, Z.; Zhang, X. Solidification with crystallization behavior of molten BF slag particle during the cooling process. *Int. J. Heat Mass Transf.* 2020, 146, 118888. [CrossRef]
- 3. Peng, L. Thermodynamic analysis of waste heat recovery of molten BF slag. Int. J. Hydrogen Energy 2017, 42, 9688–9695.
- 4. Hui, Z.; Hong, W.; Xun, Z.; Yong, Q.; Kai, L.; Rong, C.; Qiang, L. A review of waste heat recovery technologies towards molten slag in steel industry. *Appl. Energy* **2013**, *112*, 956–966.
- 5. Sun, Y.; Zhang, Z.; Liu, L.; Wang, X. Two-stage high temperature sludge gasification using the waste heat from hot BF slags. *Bioresour. Technol.* **2015**, *198*, 364–371. [CrossRef]
- 6. Peng, H.; Shan, X.; Kang, J.; Ling, X.; Wang, D. Influence of rotary disk configurations on droplets characteristics in molten slag granulation for waste heat recovery. *Appl. Therm. Eng.* **2018**, *135*, 269–279. [CrossRef]
- 7. Purwanto, H.; Akiyama, T. Hydrogen production from biogas using hot slag. Int. J. Hydrogen Energy 2006, 31, 491–495. [CrossRef]
- 8. Qin, Y.; Lv, X.; Bai, C.; Chen, P.; Qiu, G.; Zhang, J. Mechanism of Dry Molten Slag Granulation Using a Rotating Multi-Nozzle Cup Atomizer. *Steel Res. Int.* **2014**, *85*, 44–52.
- 9. Shan, X.; Peng, H.; Lin, X.; Li, J. Experimental investigation on particles characteristics in molten aluminum ligament granulation for waste energy recovery. *Energy Procedia* **2019**, *158*, 4459–4464. [CrossRef]
- 10. Ding, B.; Wang, H.; Zhu, X.; He, X.; Tan, Y.; Liao, Q. Prediction on crystallization behaviors of BF slag in a phase change cooling process with corrected optical basicity. *Fuel* **2018**, *223*, 360–365. [CrossRef]
- 11. Zhu, X.; Ding, B.; Wang, H.; He, X.; Tan, Y.; Liao, Q. Phase evolution of BF slags with variation in the binary basicity in a variable cooling process. *Fuel* **2018**, *219*, 132–140. [CrossRef]
- 12. Sun, Y.; Shen, H.; Wang, H.; Wang, X.; Zhang, Z. Experimental investigation and modeling of cooling processes of high temperature slags. *Energy* 2014, *76*, 761–767. [CrossRef]
- 13. Wang, H.; Wu, J.-J.; Zhu, X.; Liao, Q.; Zhao, L. Energy–environment–economy evaluations of commercial scale systems for BF slag treatment: Dry slag granulation vs. water quenching. *Appl. Energy* **2016**, *171*, 314–324. [CrossRef]
- 14. Xin, Y.; Yu, Q.; Han, Z.; Xie, H.; Duan, W.; Qin, Q. Kinetic and experimental characterizations of biomass pyrolysis in granulated BF slag. *Int. J. Hydrogen Energy* **2018**, *43*, 9246–9253.
- 15. Qin, Y.; Lv, X.; Bai, C.; Qiu, G. Waste Heat Recovery from BF Slag by Chemical Reactions. JOM 2012, 64, 997–1001. [CrossRef]
- 16. Yagi, J.; Akiyama, T. Storage of thermal energy for effective use of waste heat from industries. *J. Mater. Process. Technol.* **1995**, *48*, 793–804. [CrossRef]

- 17. Kasai Kitajima, T.; Akiyama, T.; Yagi, J.; Saito, F. Rate of Methane-steam Reforming Reaction on the Surface of Molten BF Slag: For Heat Recovery from Molten Slag by Using a Chemical Reaction. *ISIJ Int.* **1997**, *37*, 1031–1036. [CrossRef]
- Duan, W.; Yu, Q.; Wang, K.; Qin, Q.; Hou, L.; Yao, X.; Wu, T. ASPEN Plus simulation of coal integrated gasification combined BF slag waste heat recovery system. *Energy Convers. Manag.* 2015, 100, 30–36. [CrossRef]
- Jin, L.; Wang, H.; Liu, H.; Liu, H.; Hu, J. Mechanism research of calcined copper slag catalytic steam reforming jatropha oil. J. Renew. Sustain. Energy 2016, 8, 1–13. [CrossRef]
- 20. Luo, S.; Yu, F. The production of fuel oil and combustible gas by catalytic pyrolysis of waste tire using waste heat of blast-furnace slag. *Energy Convers. Manag.* 2017, 136, 27–35. [CrossRef]
- Aune, R.E.; Hayashi, M.; Nakajima, K.; Seetharaman, S. Thermophysical properties of silicate slags. JOM 2002, 54, 62–69. [CrossRef]
- Mills, K.; Yuan, L.; Li, Z.; Zhang, H.; Chou, K. A Review of the Factors Affecting the Thermophysical Properties of Silicate Slags. *High Temp. Mater. Process.* 2012, *31*, 301–321. [CrossRef]
- Liddington, R.; Bobkov, A. Differential Scanning Calorimetry (DSC). *Therm. Anal. Polym. Fundam. Appl.* 2008, 395, 1589–1611. [CrossRef]
- 24. Schlesinger, M.E.; Jacob, S. Advances in high-temperature calorimetry: A comparison. JOM 2004, 56, 37–40. [CrossRef]
- 25. Bernardes, C.; Santos, L.; da Piedade, M.E.M. A new calorimetric system to measure heat capacities of solids by the drop method. *Meas. Sci. Technol.* **2006**, *17*, 1405–1408. [CrossRef]
- 26. Li, W.B.; Xue, F.; Cheng, R.S. Modification of DSC Method for Measuring Specific Heat Capacity. *Chem. Res. Chin. Univ.* 2005, 26, 2310–2313.
- Zheng, H.; Liang, L.; Du, J.; Zhou, S.; Jiang, X.; Gao, Q.; Shen, F. Mineral Transform and Specific Heat Capacity Characterization of Blast Furnace Slag with High Al₂O₃ in Heating Process. *Steel Res. Int.* 2020, *92*, 2–10.
- Chang, Z.Y.; Jiao, K.X.; Zhang, J.L.; Ning, X.; Liu, Z. Effect of TiO₂ and MnO on Viscosity of Blast Furnace Slag and Thermodynamic Analysis. *ISIJ Int.* 2018, 58, 2173–2179. [CrossRef]
- 29. Kousksou, T.; Jamil, A.; Omari, K.E.; Zeraouli, Y.; Guer, L. Effect of heating rate and sample geometry on the apparent specific heat capacity: DSC applications. *Thermochim. Acta* 2011, *519*, 59–64. [CrossRef]
- Ding, B.; Xian-Yan, H.; Liao, Q.; He, X.; Tan, Y.; Liao, Q. Crystallization Behaviors of Blast Furnace (BF) Slag in a Phase-Change Cooling Process. *Energy Fuels* 2016, *30*, 3331–3339. [CrossRef]
- 31. Lin, B.; Wang, H.; Liao, Q.; Ding, B. Crystallization properties of molten blast furnace slag at different cooling rates. *Appl. Therm. Eng.* **2016**, *96*, 432–440. [CrossRef]
- 32. Qin, Y.; Liu, H.; Yang, Y. Structure evolution of blast furnace slag with high Al₂O₃ Content and 5 mass% TiO₂ via molecular dynamics simulation and fourier transform infrared spectroscopy. *Metall. Res. Technol.* **2018**, *115*, 1–6.
- 33. Gehlenite. Available online: https://www.mindat.org/min-1668.html (accessed on 6 June 2021).