Study on structure changes of molten blast furnace slag (BFS) during cooling process

Yu LI, Xiaoming LIU, Henghu SUN and Daqiang CANG
State Key Laboratory of Advanced Metallurgy, School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083

Abstract: In the present study, blast furnace slag（BFS）re-melted respectively at 1350℃, 1450℃ and 1550℃ was water-quenched to prepare samples, along with an air-quenched sample re-melted at 1450℃ as reference. The samples were investigated by using XRD, DTA and NMR techniques. The results show that during cooling process, two structure transformation regions exist in the melts. One is high temperature transformation region (HTT region). In this region, main structures with high polymeric Q^3(3Al) and melilite units have formed from the molten slag. Under very slow or very fast cooling speed, the molten slag would fall into the region and precipitate melilite crystals, or be frozen into homogeneous glass phase. The other is a low temperature transformation region (LTT region). In this region, coexistence structure of high polymeric Q^4(2Al) or melilite units with low polymeric Q^0 units has occurred from the molten slag. Under slow or fast cooling speed, the structure features of molten slag would change from HTT to LTT region. As the result, mervinite would be crystallized with a slow colling speed, or the molten slag be frozen to generate phase-separated glass with a slow colling speed. If the molten slag falls into LTT region, the Mg^{2+} in the molten slag also changes its coordination number from 4 to 6. The change is one of driving forces for transformation from structure of akermanite ($Ca_2MgSi_2O_7$) to mervinite ($Ca_3MgSi_2O_8$) and accordingly increases the amounts of Q^0 units, contributing to the formation of phase separation structure in the molten slag.

Keywords: Structure change, blast furnace slag, temperature, cooling speed

1. Introduction

Blast furnace slag (BFS) is one of industrial byproducts generated in the process of iron ore reduction in blast furnace. A deep understanding of the slag structure is one of the key issues for improving its utilization efficiency.

Most of researchers pay attention on the relationship between slag structure and its properties in the application to different materials processing [1~4]. However only a few experiments [5~7] were conducted to study the formation process from molten slag to solid slag. In fact, the optimization of slag composition and structure in solid slag by regulation of its formation process from molten slag could be of significance for effective applications.

Molten BFS is involved in $CaO\text{-}MgO\text{-}Al_2O_3\text{-}SiO_2$（CMAS）system. Geologists have carried out lots of investigations on CMAS melts. Researches [8~10] proved significantly effect of temperature on the structure of aluminosilicate melts. When the temperature of the molten slag rises, the amount of Q^2 and Q^4 increase with the decrease of Q^3 where Q^n represents silicon structural units with n-number of bridging oxygen atoms. Investigations [11] showed that more Al^{3+} in aluminosilicate melts would promote the immiscible phases to occur. A melt in CMAS system with two immiscible liquid phases cooled under fast cooling speed would generate a glass phase with phase separated structures of a Si-rich glass phase along with Ca-rich glass phase.

In the present study, BFS re-melted respectively at 1350℃, 1450℃ and 1550℃ was water-quenched to prepare samples, along with an air-quenched sample after re-melting at 1450℃ as reference. The structure of each sample was investigated by using XRD, DTA and NMR techniques and the process of structural change in molten BFS under different cooling conditions was investigated.

2. Experimental

2.1 Sample preparation

The chemical composition of raw BFS was as follows: 42.40% CaO, 34.97% SiO_2, 12.55% Al_2O_3, 8.17% MgO and 1.92% others. Four water-quenched samples were obtained by re-melting the BFS (250 g) in a graphite crucible at different temperatures (1550℃, 1450℃ and 1350℃) for 40 min and then quenching in water. When the melted BFS at 1550 ℃ was poured in on water. The four different samples were named as W-1550f, W-1550s, W-1450 and W-1350 according to their melting temperatures. Air-quenched sample was prepared by re-melting the BFS at 1450 ℃ in the same condition, but then spreading the melt over an iron board in the air. The sample was named A-1450. After being dried, 200 g of each sample was grinded for 90 min in a ball mill (Model NZ-3, HongDing Company, China) and then sieved to −80 μm.

2.2 Measurements

The chemical composition of BFS samples were analyzed by X-ray Fluorescence Spectrometer (Model XRF-1700，Shimadzu, Japan). The mineral phases in prepared samples were analyzed by XRD (Model D/max-RB, Rigaku, Japan) and scanned in the 2θ range from 5° to 70° with a scanning rate of 4°/min. X-ray diffractions were re-corded with a CuKα diffractometer. The measurements of NMR spectroscopes of BFS samples were obtained by a Varian Unityinova 300M spectrometer under MAS up to 5 kHz with 7mm ZrO_2 rotors. The ^{27}Al spectra were obtained at spectrometer frequency 78.20 MHz with a pulse width of 45°, spectrum width of 30000 Hz, sampling time of 0.04s and a recycle delay time of 0.1 s; The ^{29}Si spectra were obtained at spectrometer frequency 59.62 MHz with a pulse width of 45°, spectrum width of 30000 Hz, sampling time of 0.246s and a recycle delay time of 2 s.

3. Results

The XRD patterns of each sample are shown in Fig.1. W-1550f, W-1550s and W-1450 are completely amorphous with a hump characteristic of the glass phase. In the XRD pattern of W-1350 and A-1450, there are not only humps but also some characteristic peaks there in Fig.1. The peaks reveal that the main mineral components were gehlenite ($Ca_2Al_2SiO_7$) [JCPDS# 35- 0755], larnite (Ca_2SiO_4) [JCPDS# 29-0369] and akermanite ($Ca_2MgSi_2O_7$) [JCPDS# 35-0592] for W-1350, and mervinite ($Ca_3MgSi_2O_8$) [JCPDS# 35-0391] and gehlenite ($Ca_2Al_2SiO_7$) [JCPDS# 35-0755] for A-1450. It is indicated that the samples with the same chemical composition would have different minerals phases with the different cooling modes.

DTA curves of the samples in Fig. 2 show two exothermic events in W-1450 and W-1550s curves with maxima (Tc_1 and Tc_2) between 845℃ and 935℃ in the curves, indicating a phase separated structure with two glass phases in the samples [12]. Two exothermic events in BFS glass indicate two devitrification processes, namely the formation of the first crystalline phase, mervinite and the formation of the second crystalline phase, melilite. Melilite is a solid solution of akermanite and gehlenite [13,14]. For the second crystalline phase, akermanite and gehlenite in W-1350 sample had been precipitated during the quenching process as shown in Fig. 1, the W-1350 curve in Fig.2 had only one obvious exothermic peak. The W-1550f curve has a large exo-thermic area. This might indicate that W-1550f did not have two obvious devitrification processes due to the high homogeneity in its glass structure.

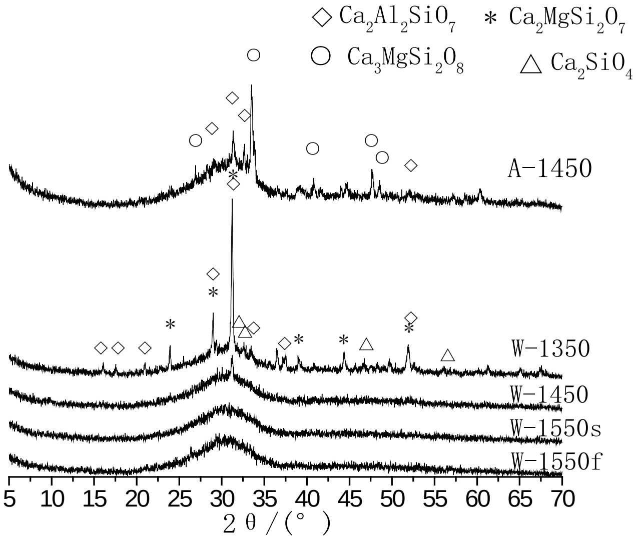

Fig.1 XRD patterns of the samples

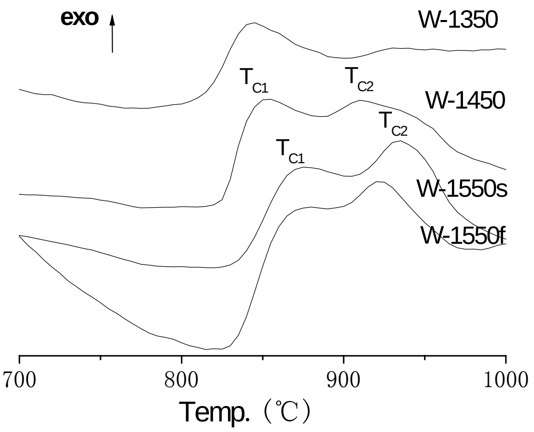

Fig. 2 DTA curves of the samples (Heating rate: 10 ℃/min) [12]

The ^{27}Al NMR spectra of the samples in Fig.3 show tetrahedral resonances ranging from 40 to 75ppm, which indicates Al^{3+} in all the samples existing in Al-O-Si bonds. The resonance centered at 58ppm falls in high field region, which means that those Al-O-Si bonds have high polymerized Al(OSi)k units with larger number of k (k=0~4) [15].

^{29}Si NMR spectra of the samples are shown in Fig. 4. For crystalline phases, melilite ($Ca_2MgSi_2O_7$ and

$Ca_2Al_2SiO_7$) with Q^1 and Q^1(1Al) units and Ca_2SiO_4 with Q^0 unit, exist in W-1350, resonances of the corresponded units should shown in its spectrum. Therefore, resonance at -71ppm, -74ppm and -77ppm are separately assigned to overlap between Q^0 and Q^1(1Al), Q^1 and Q^3(3Al), where Q^n(kAl) represents silicon structural units having n-number of bridging oxygen atoms, in which k-number of tetrahedral aluminum substituting for silicon. A series of weak resonances ranging from -95ppm~ -98ppm appear in spectra of W-1550s, W-1450 and W-1350 and they contribute to Q^4(2Al).

Compared with spectrum of W-1550f, intensity of resonances centered at -71ppm rises and one centered at -77ppm drop in each spectrum of W-1550s, W-1450 and W-1350. Therefore, it could be inferred that as the melting temperature of BFS decreasing, the amounts of Q^0, Q^1(1Al) with low polymerized structure increased and Q^3(3Al) with high polymerized structure decreased in the frozen water-quenched sample.

Fig. 4 ^{29}Si MAS NMR spectra of the samples

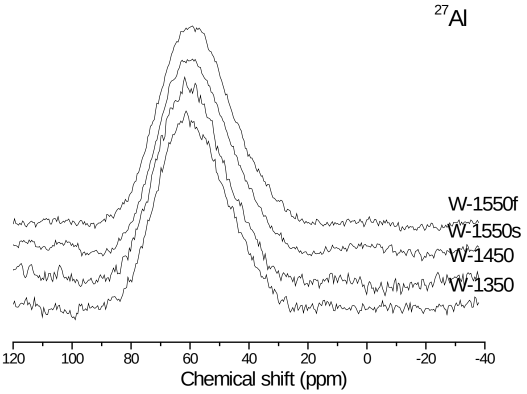

Fig. 3 ^{27}Al MAS NMR spectra of the samples

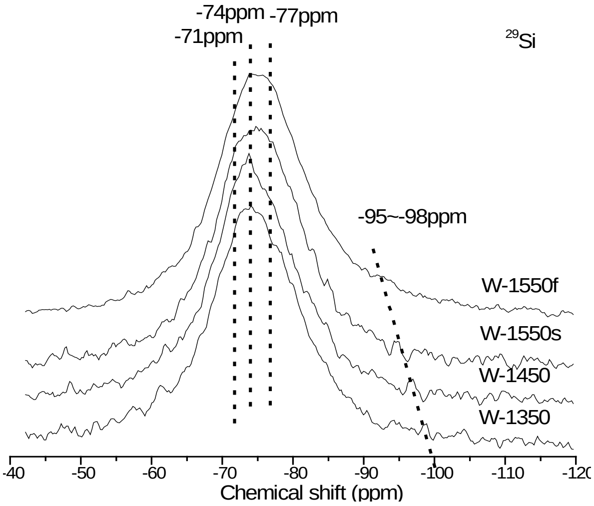

Fig.4 ^{29}Si MAS NMR spectra of the samples

4. Discussion

4.1 Two structure types of melts

Usually, a glass is in a non-equilibrium state, but its real structure can be considered in equivalence to a structure of the melt in equilibrium at a temperature higher than the glass transition temperature. This higher temperature depends on cooling speed of the melt. The faster the cooling speed is, the higher the temperature is. Because the molten BFS was water-quenched at different melting temperature in the experiment, the solid samples formed under different cooling speed. From sample W-1550f, W-1550s, W-1450, to W-1350, the cooling speed deduces as melting temperature decreased, and air-quenched sample A-1450 has the slowest cooling speed. Correspondingly each sample from W-1550f to A-1450 has the structure equivalent to that from the higher to the lower temperature of the molten slag.

The melilite structure has Q^1 unit for akermanite or Q^1(1Al) unit for gehlenite and high polymerized Al^{3+} with

$Al(OSi)_4$ units. These units are shown as resonance at -74ppm or -71ppm in ^{29}Si NMR spectrum and resonance at 58ppm in ^{27}Al NMR spectrum (see Fig. 3 and Fig. 4). An investigation [7] about effect of melilite structure on phase separation of molten BFS shows that melilite is a solid solution of akermanite ($Ca_2MgSi_2O_7$) and gehlenite ($Ca_2Al_2SiO_7$). In melilite units, the special structure of 4-coordinated Mg^{2+} for akermanite or Al^{3+} for gehlenite linking with four bridging oxygen $Al(OSi)_4$ resulting in the formation of a 5-membered ring. Therefore, melilite unit is classified as sorosilicate, but it is a layer-structure with high degree of polymerization.

W-1550f is composed of Q^1 and Q^3(3Al) units and high polymerized Al^{3+} with $Al(OSi)_4$ units. Because melilite unit is a layer- structure with high degree of polymerization, W-1550f is a homogenous structure which possesses of high polymeric Q^3(3Al) and melilite units.

W-1550s and W-1450 can be classified into the same glass phase as W-1550f, however their higher temperature decreases in turn. With the higher temperature decreasing, W-1550s and W-1450 have less Q^1 and Q^3(3Al) units, while more Q^0, Q^1(1Al) and Q^4(2Al) units than W-1550f as shown in Fig. 4. This change enlarges the structure difference of $[Si(Al)O_4]$ unit with the increasing Q^0 and Q^4(2Al) units. The enlarged difference only provides a necessary condition in structure to form phase separation of the melt in the cooling process. Therefore, both W-1550s and W-1450 have the phase separation structure, corresponding to the coexistence structure of high polymeric Q^4 (2Al) or melilite units with low polymeric Q^0 units.

When the melt was quenched at very fast cooling speed, homogenous structure with more Q^1 and Q^3(3Al) would froze into glass, such as W-1550f; when at fast cooling speed, phase separation structure with more Q^0, Q^1(1Al) and Q^4(2Al) units would froze into glass, such as W-1550s and W-1450.

Therefore, the same molten slag would possess the two structure types involving homogenous and phase separation structure.

4.2 Two structure transformation regions in molten slag

As the composition of the BFS is far away from immiscible regions in phase diagram of $CaO-MgO-Al_2O_3-SiO_2$ system [16], the phase separation can be generated by metastable immiscible phases in the molten slag during cooling process, thereby the phase separation structure in molten slag would form only under the cooling process and not exist in a stable equilibrium state.

The comparison of the XRD patterns between W-1350 and A-1450 shows the different crystalline phases, which appear in Fig. 1. This indicates for the same molten slag, two structure types could form during the cooling process with different modes.

According to the phase diagram of $CaO-MgO-Al_2O_3-SiO_2$ system [16], the primary phase for BFS was melilite ($Ca_2MgSi_2O_7$ - $Ca_2Al_2SiO_7$). Therefore, melilite should initially precipitate at the temperature of about 1400℃ from thermodynamic consideration, and then Ca_2SiO_4 and $Ca_3MgSi_2O_8$ successively formed when the melt was cooled.

For the sample W-1350 underwent a re-melting process at 1350℃, as the temperature lower than 1400℃, melilite would generate during the process before the melt was quenched, as shown on Fig.1.

Compared with resonances of W-1550f in Fig. 3 and Fig. 4, the resonance of W-1350 moves downfield due to the rise of resonance at -71ppm and the drop of resonance at -77ppm. It indicates that the amounts of Q^3(3Al) units decrease and Q^0, Q^1(1Al) and Q^1 increase as the re-melting temperature decreasing. This had provided plenty of nutrition for the crystallization of melilite with structure of Q^1(1Al) and Q^1.

When the molten slag was cooled at very slow cooling speed or kept below the initially crystalline temperature of about 1400℃, it had enough time to crystallize and to reach thermodynamics equilibrium state, avoiding the generation of metastable immiscible phases in melts.

The immiscible phase and subsequently phase separated structure in the molten slag would form when the melt was quenched at a reasonable cooling speed. After the phase separated structure formed in the melt, it can be frozen into a phase separated glass with a Si-rich glass phase and Ca-rich glass phase under fast cooling speed, such as W-1450 and W1550s.

A crystalline phase also could be precipitate from the melt with phase separated structure under a slow cooling speed. However, the crystallization process in a phase separated melt was different from that with homogenous structure. Because the formation of the phase separated process in the molten slag correspondingly enlarged the structure difference of $[Si(Al)O_4]$ unit with the increasing Q^0 and Q^4(2Al) units, the increase of amount of lower polymerized Q^0 units had provided plenty of nutrition for the crystallization of $Ca_3MgSi_2O_8$ with structure of Q^0. Thereby, $Ca_3MgSi_2O_8$ was generated from the molten slag under slow cooling speed, such as A-1450.

Therefore, two structure transformation regions existed in the molten slag cooling process, which is shown in Fig.5. One is high temperature transformation region (HTT regions). In this region, a homogeneous structure in the melt can form. Under very fast cooling conditions, the melt would be frozen into a homogeneous glass phase, while under very slow cooling speed, the primary phase of melilite would precipitate firstly.

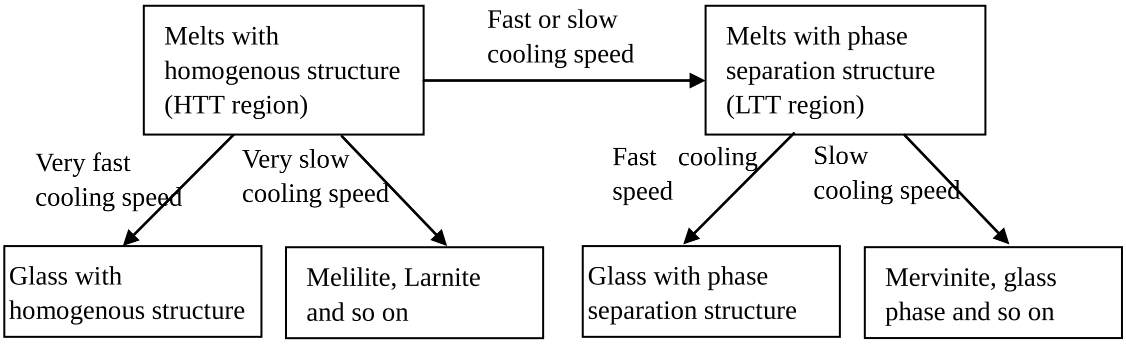

Fig. 5 Schematic diagrams of structure changes in BFS melts depending on cooling condition

When the melt was cooled under fast or slow cooling speed, the homogenous structure would change into a phase separation structure. At this time, the melt fell into low temperature transformation region (LTT region). Under fast cooling speed, it would be frozen into glass with phase separated structure, while under slow cooling speed, the crystalline phase of $Ca_3MgSi_2O_8$ would firstly precipitate.

4.3 Coordination change of Mg^{2+} in melts

When homogenous structure of the molten slag changed into phase separation structure with two immiscible liquid phases, melilite unit and Q^3(3Al) unit decreased and Q^0 and Q^4(2Al) increased. As Mg^{2+} is of 4-coordination in melilite (akermanite) and 6-coordination in mervinite, the coordination number of Mg^{2+} had correspondingly changed from 4 to 6.

Therefore, Mg^{2+} would exist as 4-coordination cation in HTT region and as 6-coordination cation in LTT region. When the molten salg was cooled at very slow cooling speed or kept at temperature in HTT region, such as the cooling condition of W-1350, the $Ca_2MgSi_2O_7$ with 4-coordinated Mg^{2+} would precipitate from it. While when the molten slag was quenched at slow cooling speed, such as the cooling condition of A-1450, the $Ca_3MgSi_2O_8$ with 6-coordinated Mg^{2+} would precipitate from it.

The crystallization property of the BFS has been investigated [6, 13] by conducting temper experiments, the results also showed that two crystallization regions exist in the BFS system. One is a lower-temperature crystallization region about 860℃ where $Ca_3MgSi_2O_8$ with 6-coordination would come into being. The other is a higher-temperature crystallization region about 980℃ where $Ca_2MgSi_2O_7$ with 4-coordination number would form significantly and $Ca_3MgSi_2O_8$ would disappear.

During the cooling process, the change of Mg^{2+} coordination was one of the driving forces for transformation from structure of $Ca_2MgSi_2O_7$ to structure of $Ca_3MgSi_2O_8$. This transformation only increases the amounts of Q^0 units, which is also contributed to the formation of phase separation structure in melt.

Orsini[14] has found the required proportion of Mg^{2+} for the transformation. His result showed that for glass with composition of $2CaO \cdot (1-x)MgO \cdot xAl_2O_3 \cdot (2-x)SiO_2$, which is $Ca_2MgSi_2O_7$ when x=0, and is $Ca_2Al_2SiO_7$ when x=1, $Ca_3MgSi_2O_8$ would not generate from the glass unless enough Mg^{2+} existed in glass in the range of $x \leq 0.6$.

5. Conclusions

The present study was carried out on the structures of four water-quenched BFS samples after re-melting respectively at 1350℃, 1450℃ and 1550℃ and an air-quenched sample after re-melting at 1450℃. The process of structural change in molten BFS under different cooling conditions was investigated. The conclusions were drawn as follows.

During the cooling process, two structure transformation regions existed in the molten slag. One was HTT regions. In this region, the homogeneous structure in the melt formed. Under very fast cooling conditions, the melt would be frozen into a homogeneous glass phase, while under very slow cooling speed, the primary phase of melilite would initially precipitate.

When the molten slag was cooled under fast or slow cooling speed, the homogenous structure would change into a phase separation structure. At this circumstance, the melt fell into LTT region. Under fast cooling speed, it would be frozen into a glass with phase separation structure, while under slow cooling speed, the crystalline phase of $Ca_3MgSi_2O_8$ would precipitate.

The main structures in HTT region were high polymeric Q^3 (3Al) and melilite units, and in LTT region were the coexistence structure of high polymeric Q^4 (2Al) or melilite units with low polymeric Q^0 units.

When the molten slag fell into LTT region, Mg^{2+} ions in the melt also changed the coordination number from 4 to 6. The change was one of driving forces for transformation from a structure of mervinite ($Ca_2MgSi_2O_7$) to $Ca_3MgSi_2O_8$. This transformation would increase the amounts of Q^0 units therefore to contribute to the formation of the phase separation structure in melt.

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