EFFECT OF FERRITE PHASE ON THE FORMATION AND COEXISTENCE OF 3CaO·3Al₂O₃·CaSO₄ AND 3CaO·SiO₂ MINERALS


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The effect of ferrite on the formation and coexistence of 3CaO·3Al₂O₃·CaSO₄ (C₄A₃$) and 3CaO·SiO₂ (C₃S) was investigated in this paper. The results indicate that 20 % content of ferrite phase with the composition of C₂A₀.₅F₀.₅ can facilitate the coexistence of C₄A₃$ and C₃S solid solutions at 1350°C. There are other trace elements that incorporate into clinker minerals and form solid solutions. In addition, the dark and polygonal C₄A₃$ solid solution is not dissolved in liquid phase at 1350°C. It can promote the burnability of the raw mixes and provide a favorable condition for the formation of C₃S. However, it has an adverse effect on the coexistence of two clinker minerals with the changing of ferrite compositions. This will provide the important basis for the preparation of the calcium sulphoaluminate cement clinker containing C₃S.

INTRODUCTION

Ye’elimite (C₄A₃$) and alite (C₃S) are the most important cementitious minerals of calcium sulphoaluminate cement (CSA) and Portland cement (PC) respectively. CSA has the high early strength, small volume shrinkage during hydration and corrosion resistance [1-3]. However, the mechanical strength of mortar shows a slow increase owing to the low reactivity of C₃S at medium hydration ages (between 7 d and 28 d). C₃S is responsible for early and medium mechanical strengths in PC. Hence, a possible approach is to bring in C₃S minerals in the production of the CSA clinker. Consequently, it is necessary to solve this issue that make the two minerals (C₄A₃$ and C₃S) coexist with the clinker.

Extensive researches on the formation and coexistence of C₄A₃$ and C₃S minerals with doping minor elements has been carried out, which could lower the viscosity and the formation temperature of liquid phase, and promote the formation of C₃S. I. O. Alper [4, 5] investigated the SO₃-rich Portland clinkers containing simultaneously the phases C₄A₃$ and C₃S, which was prepared by burning pertinent raw meals with adding small amounts of CaF₂ at 1300°C. Liu and Li [6, 7] produced the clinker at temperatures between 1250°C and 1300°C by adding CaF₂ and MgO as mineralizers. Ma [8] reported the mineral formation and coexistence of C₄A₃$ and C₃S in the clinker could be achieved by adding CuO and CaF₂. In addition to using the mineralizer, Shen [9, 10] prepared alite-ye’elimite cement clinker by a secondary heat treatment step at 1250°C after regular Portland clinker firing at 1450°C. In current researches, adding the CaF₂ mineralizer is the main way to achieve the coexistence of C₄A₃$ and C₃S in the production of clinker [11-13]. No doubt that CaF₂ could contribute more to the formation of C₃S at lower temperatures by lowering its free energy relative to C₂S [14]. However, CaF₂ has its own drawbacks, for instance, environment pollution owing to fluoride ion, corrosion of the refractory materials in cement kiln, and low the hydraulic activity of cement [15, 16], which is restricted in the industrial applications.

The composition and content of liquid phase have the significant influence on the C₃S formation in the production of clinker. The liquid phase are mainly composed of CaO, Al₂O₃ and Fe₂O₃ in burning process. The viscosity of liquid phase varies with the ionic state in the liquid composition. CaO is always dissociated into Ca²⁺ ions, while Al₂O₃ and Fe₂O₃ owing to amphoteric oxide, can be dissociated into MeO₄⁻ or Me³⁺ ions in the melting state [17]. As shown in the following formulaes:

\[ \text{Me}_2\text{O}_3 + 5\text{O}^- = 2\text{MeO}_4^- \]  \hspace{1cm} (1)
\[ \text{Me}_2\text{O}_3 = 2\text{Me}^{3+} + 3\text{O}^- \]  \hspace{1cm} (2)

Al (with an ionic radius of 0.57 Å) tends to form a tetrahedral MeO₄⁻ ion, and Fe (with an ionic radius of 0.67 Å) tends to form an octahedral Me³⁺ ion. The tetrahedral valence bond of Me–O is strong and increases the viscosity of liquid phase, which is difficult to be
broken in the viscous flow. However, the valence bond of Me–O in octahedron is weak, and decreases the viscosity of liquid phase. Hence, composition and content of ferrite are the noteworthy concern for the formation of C₄A₃$ and C₃S.

In this work, the composition of ferrite phase is general variation by adjusting the proportional between Fe₂O₃ and Al₂O₃ in raw mixes, where ferrite content is designed as 5 %, 10 %, 15 % and 20 %, respectively. The intention is to achieve the formation and coexistence of C₄A₃$ and C₃S by changing the viscosity and the formation temperature of liquid phase. The coexistence of two minerals is beneficial for durative development of strength in clinker. It will be also beneficial to saving energy and reducing emission from manufacture.

EXPERIMENTAL

Sample preparation

In order to eliminate the effect of other impurities, analytical-grade CaCO₃, SiO₂, Al(OH)₃, Fe₂O₃ and CaSO₄·2H₂O were used to synthesize the cement clinker. The prepared raw meals were homogenized in a ball mill bottle with agate balls for 4 h. The raw meals were mixed with water and pressed under a pressure of 16 MPa into a disk with Ф 45 × 3 mm. The dried disks were sintered in a resistance furnace at different temperatures (1320, 1350, 1380 and 1410°C) for 60 min. Subsequently, the cement clinker was removed from the furnace immediately and cooled rapidly by a fan. The theoretic mineral composition of the clinker was listed in Table 1. Choosing orthogonal list L₁₆(4³), (L-orthogonal experiment, 16 experiments, 3 factors, and 4 tiers), as experiment regulation, was listed in Table 2.

Characterization

Free lime tests

The content of free lime (f-CaO) in clinker was estimated using alcohol-glycerin method.

X-ray diffraction (XRD)

All clinker samples were ground into fine powder to perform laboratory X-ray powder diffraction studies. XRD data were collected on a Bruker AXS D8-Advance diffractometer with Cu Kα radiation generated at 35 kV and 45 mA at room temperature. The powders were step scanned from 5° to 60° with a step size and time per step of 0.02° and 0.5 s, respectively.

Differential scanning calorimetry-thermogravimetric analysis

Thermal analysis was monitored on a Mettler-1600 HT instrument with a combined TG and DSC system. A portion of the raw materials powder was heated from 25°C to 1400°C at a heating rate of 10°C∙min⁻¹ under air atmosphere.

Scanning electron microscopy analysis

SEM imaging using backscattered electrons requires a polished specimen for optimum performance [18]. The clinker sample was embedded and polished. After polishing, the clinker sample was cleaned using a clean polishing cloth. The final polished cross-sections were covered with carbon to provide a conductive surface for SEM imaging. Observation of mineral morphological feature, in particular C₄A₃$ and C₃S minerals, was carried out on a scanning electron microscope (SEM, S4800, Hitachi). The element distributions of clinker minerals were evaluated by energy dispersive spectra analysis (EDS).

RESULTS AND DISCUSSION

The burnability of cement clinker

The content of f-CaO in clinker is a good indicator of the burning degree [19]. The f-CaO content of clinker samples with the amount of ferrite phase at different temperatures are presented in Figure 1. As the sintering temperatures and the F/A molar ratio increased, the content of f-CaO in clinker obviously decreases, and the trend is more obvious when Fe₂O₃ proportion ranges from 0.5 to 1. Moreover, the increase in ferrite content can promote the absorption of f-CaO at a relatively low temperature. The effect of Fe₂O₃ on the f-CaO content is attributed to the decrease in the formation temperature of liquid phase, which corresponds to the analysis of DTG-DSC measurement in later part of this paper.
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Burnability index (BI) also reveals the burnability of raw meals [20]. BI value can be calculated with contents of f-CaO in the clinker samples burnt at different temperatures from the formula: (3)

$$BI = 3.75 \frac{(A + B + 2C + 3D)}{\sqrt[4]{A - D}}$$

where A, B, C and D are the content of f-CaO in the clinkers calcined at 1320, 1350, 1380 and 1410°C [21]. The low value of BI implies a good burnability. The clinker samples with good burnability are with BI value lower and equal to 60 [20]. BI values with the different compositions of ferrite phase is shown in Figure 2. With the F/A molar ratio increased, BI values of clinker samples generally decrease from 18.86 to 12.53. This results indicate that high amount of Fe$_2$O$_3$ can enhance the absorption of f-CaO, improve the burnability of clinker and accelerate the C$_3$S formation in the clinker.

The phase analysis of the cement clinker

XRD is used to analyze the phase composition of clinker samples. The XRD patterns of clinkers with the different composition and content of ferrite phase are shown in Figure 3. The clinker samples were burned at 1320, 1350, 1380 and 1410°C. From Figure 3a, the clinker samples at different temperatures show similar mineral compositions. The clinker minerals are C$_3$S, C$_4$A$_3$S, C$_2$S and C$_2$A$_{0.5}$F$_{0.5}$ solid solutions by analysis of Jade software. When the content of ferrite is 20 %
at 1320°C, the diffraction peak of C₄A₃S is lower than other samples. It might be due to the fact that the actual composition of ferrite is C₂A₀.₅F₀.₅ (brownmillerite, 2θ = 12.16°, d = 7.27 Å). Hence, more Al₂O₃, which is used to generate C₄A₃S, is consumed and forms brownmillerite in burning process. The diffraction peak of C₃S (2θ = 29.38°, d = 3.03 Å) is obviously high when the temperature reach to 1380°C and 1410°C, respectively. This result is consistent with the observations of SEM in later part of this paper.

The XRD patterns of the clinker samples with the A/F molar ratio of 1/3 are shown in Figure 3b. Likewise, clinker samples mainly consist of C₂S, C₄A₃S, C₃S and C₂A₀.₅F₀.₅ solid solutions. The intensity of C₄A₃S peaks slightly increase in Figure 3b compared to Figure 3a. There is a relatively much Al₂O₃ being used to C₄A₃S crystal owing to increasing of A/F molar ratio in the raw mixtures. When the content of ferrite is 20 % at 1350°C, the diffraction peaks of C₄A₃S and C₃S are remarkably high compared to the other clinker sample. The result illustrates that the quantity of liquid phase and its viscosity can promote the formation of C₃S, which further indicates that the A/F molar ratio with the composition of ferrite phases is important in the formation of clinker mineral. It is also in agreement with the SEM-EDS analysis. When the burning temperature is more than 1350°C, the intensity of C₄A₃S peaks obviously decreases. This suggests that C₄A₃S has already decomposed when the temperature is higher than its decomposition temperature. The sulfate in liquid phase generated by C₄A₃S decomposition inhibits the reaction of CaO with belite, consequently suppressing the C₃S formation [22-24]. Therefore, excessive the burning temperature does not facilitate the coexistence of C₄A₃S and C₃S.

The XRD patterns of the clinker samples with the A/F molar ratio of 1 are shown in Figure 3c. The clinker samples of different temperatures present similar

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Figure 3. The XRD patterns of samples with different ferrite phases.
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mineral compositions, all of them are $C_2S$, $C_4A_3$, $C_S$, $C_3A$, $C_{2A}$, and $C_{2A_{0.69}F_{0.31}}$ solid solutions by analysis of Jade software. When the molar ratio of $A/F$ increases in raw mixes, the composition of ferrite phase is $C_{2A_{0.69}F_{0.31}}$ solid solution ($2\theta = 12.26°$, $d = 7.21 Å$) in clinker samples. The main peak of $C_{2A_{0.69}F_{0.31}}$ shift to right higher angle compared with $C_{2F}$. It might be due to the fact that $C_F$ itself contains iron as $Fe^{3+}$ in both tetrahedral and octahedral sites, the latter being twice as numerous as the former. As $Al$ is added to $C_F$, it has smaller ionic radius than Fe and preferentially enters tetrahedral sites. Hence, the lattice parameters and the main reflection lines of the ferrite phase also move towards lower d-spacings (from 7.27 Å to 7.21 Å) with increasing $Al_2O_3$ content of the samples [25]. In addition, the characteristic diffraction peak of $C_{4A_3}$ ($2\theta = 18.03°$) can be observed in Figures 3c and 3d, which means changing the composition of clinker samples by excessive consumption of $CaO$ and $Al_2O_3$ in the burning process. Moreover, the diffraction peak of $C_A$ ($2\theta = 33.3°$) in clinker samples is more visible apart from the content of ferrite phase in 20 %. The result illustrates that the decomposition of $C_4A_3$ can be facilitated with increasing $Al_2O_3$ content of the raw mixes in burning process, and then inhibiting the $C_S$ formation. Furthermore, flash setting mineral $C_{12A_7}$ and $C_A$ are not normally found in clinker samples. This adversely influences the quality of cement, decreasing the fluidity and increasing the heat of hydration [26].

From Figure 3d, the clinker samples with the $A/F$ molar ratio of 3 at different temperatures present similar mineral compositions, all of them are $C_2S$, $C_4A_3$, $C_S$, $C_3A$, $C_{12A_7}$ and $C_{2A_{0.69}F_{0.31}}$ solid solutions. The diffraction peak of $C_{4A_3}$ is generally weakened and the characteristic peak of $C_S$ are almost not observed with the increasing burning temperatures. It is probably related to the decomposition of $C_{4A_3}$ at temperature higher than 1350°C [27, 28] which provides an unfavorable condition for the formation of $C_S$. In general, the intensity of diffractive peak is related to the content and crystallinity of phase [29]. Therefore, this suggests that excessive the A/F molar ratio not facilitates the formation of $C_S$ and the coexistence of $C_{4A_3}$ and $C_S$. Thus, it can be drawn that the composition and content of liquid phase have the significantly effect on the formation of clinker mineral.

Thermal analysis

The thermal analysis curves of raw mixes at different ferrite phases are given in Figure 4. The results carried out the raw mixes are used to obtain information on the decomposition and the formation of chemical compounds during burning process. The first endothermic peak about 120°C is attributed to the decomposition of gypsum in the raw mixtures. The second endothermic peak located at approximately 285°C is proven to be the decomposition of $Al(OH)_3$ [13, 30]. The third peak between 650°C and 850°C is attributed to the decomposition of $CaCO_3$. The forth peak at approximately 1230°C is ascribed to the formation of liquid phase and $C_S$ mineral. When the content of ferrite phase is the same with 15 % in raw mixes, but its composition is different, the decomposition temperature of $CaCO_3$ in samples with $A/F$ molar ratio of 3 and 0 are 830.3°C and 834.4°C, respectively, implying that the composition of ferrite phase has a slight influence on the decomposition temperature of $CaCO_3$. However, the formation of liquid phase and $C_S$ is strongly affected by the composition of ferrite phase. The formation temperatures of liquid phase in raw mixes with 15 % content of ferrite phase are about 1190.9°C and 1237.1°C, respectively. The result further illustrates that the decrease of $A/F$ molar ratio can lower the formation temperature of liquid phase. At the same time, it provides a favorable condition for the formation of $C_S$ in burning process, which is consistent with previous results of XRD observations.

Figure 4. DTG-DSC curves of raw materials at different ferrite phases.

SEM-EDS analysis

The morphological feature of clinker minerals was observed by BSE and EDS with area scanning map to determine the distribution of clinker minerals in Figure 5. The microstructure changes markedly with different $A/F$ molar ratio and the sintering temperature. However, the microstructure revealed the formation of solid solutions inside the equilibrium phase assemblage all samples, namely, $C_2S$, $C_A$, $C_S$, and $C_{2A_{0.69}F_{0.31}}$ solid solutions. Microstructure of the clinker sample is loose at a relatively low burning temperature (1350°C) from Figure 5a. Most of the silicate phases are $C_2S$, and $C_S$ solid solution is rarely, as corroborated by the XRD analysis. The dark grains are $C_{4A_3}$ solid solutions, and their sizes are approximate 10 μm. Their outlines are also the distinct polygon in the clinker sample. The large bright and reflective crystals which partially surround the
C$_4$A$_3$S crystals are ferrite. The result indicates that C$_4$A$_3$S crystals have not dissolved in liquid phase at 1350°C and retains regular outlines with undercooling, which also coincide well with XRD results.

Compared with C$_4$A$_3$S grains at the burning temperature 1350°C (Figure 5a), the sample with the molar ratio A/F as 0 at 1380°C is smaller than 10 μm, as shown in Figure 5b, and its outline is unclear. This result suggests that a part of C$_4$A$_3$S has decomposed in the liquid phase and formed the solid solution with silicate phase, which also is consistent well with the molar ratio of element from EDS analysis [31]. In contrast, the C$_2$S and C$_3$S crystal have larger particle sizes more than 10 μm, and the sample in Figure 5b has a lower porosity.

Because the increasing amount of liquid at 1380°C can promote the formation of C$_3$S. With the ongoing increase in the burning temperature, the clinker sample shows well-formed hexagon C$_3$S crystals and large circular C$_3$S crystals, which are encompassed by ferrite phases. However, accompanied by the decomposition of C$_4$A$_3$S, its crystal size becomes small only several microns from Figure 5c. This has an adverse effect on the coexistence of C$_3$A$_3$S and C$_3$S crystals. Hence, it must be remembered that the ferrite phase plays an important role in avoiding the breakdown of C$_4$A$_3$S and facilitating the formation of C$_3$S in the sintering process.

CONCLUSIONS

In order to achieve the coexistence of C$_3$S and C$_4$A$_3$S, the effect of ferrite phase on the formation and coexistence of two clinker minerals was investigated by changing the A/F molar ratio. The following conclusions can be drawn from this study:

- When the composition of ferrite is C$_2$A$_{0.5}$F$_{0.5}$ with the A/F molar ratio of 1/3 and its content is 20 % at 1350°C, the property of liquid phase can facilitate the coexistence of C$_4$A$_3$S and C$_3$S solid solutions. However, it has an adverse effect on the coexistence of two clinker minerals with the increasing the A/F molar ratio, meanwhile, the formation of C$_{12}$A$_7$ and C$_3$A has a negative effect on the setting times of clinkers.

- Ferrite phase of the decreasing A/F molar ratio can significantly lower the formation temperature of liquid phase. Consequently, it can facilitate the burnability of the raw mixes and provide a favorable condition for the formation of C$_3$S in burning process.

- The distinctly dark and polygonal C$_4$A$_3$S solid solutions, whose sizes are approximate 10 μm, has not dissolved in liquid phase at 1350°C. However, with the increase of the sintering temperature, a part of C$_4$A$_3$S has decomposed in the liquid phase and formed the solid solution, and its crystal size becomes smaller and its outlines is also unclear.

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