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EFFECT OF FERRITE PHASE ON THE FORMATION AND COEXISTENCE OF $3CaO·3Al_2O_3·CaSO_4$ AND $3CaO·SiO_2$ MINERALS

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The effect of ferrite on the formation and coexistence of $3CaO·3Al_2O_3·CaSO_4$ ($C_4A_3\$$) and $3CaO·SiO_2$ (C_3S) was investigated in this paper. The results indicate that 20 % content of ferrite phase with the composition of $C_2A_{0.5}F_{0.5}$ can facilitate the coexistence of $C_4A_3\$$ and C_3S 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 $C_4A_3\$$ 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 C_3S. 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 C_3S.

INTRODUCTION

Ye'elimite ($C_4A_3\$$) and alite (C_3S) 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 C_2S at medium hydration ages (between 7 d and 28 d). C_3S is responsible for early and medium mechanical strengths in PC. Hence, a possible approach is to bring in C_3S minerals in the production of the CSA clinker. Consequently, it is necessary to solve this issue that make the two minerals ($C_4A_3\$$ and C_3S) coexist with the clinker.

Extensive researches on the formation and coexistence of $C_4A_3\$$ and C_3S 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 C_3S. I. Odler [4, 5] investigated the SO_3-rich Portland clinkers containing simultaneously the phases $C_4A_3\$$ and C_3S, which was prepared by burning pertinent raw meals with adding small amounts of CaF_2 at 1300°C. Liu and Li [6, 7] produced the clinker at temperatures between 1250°C and 1300°C by adding CaF_2 and MgO as mineralizers. Ma [8] reported the mineral formation and coexistence of $C_4A_3\$$ and C_3S in the clinker could be achieved by adding CuO and CaF_2. 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 CaF_2 mineralizer is the main way to achieve the coexistence of $C_4A_3\$$ and C_3S in the production of clinker [11-13]. No doubt that CaF_2 could contribute more to the formation of C_3S at lower temperatures by lowering its free energy relative to C_2S [14]. However, CaF_2 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 C_3S formation in the production of clinker. The liquid phase are mainly composed of CaO, Al_2O_3 and Fe_2O_3 in burning process. The viscosity of liquid phase varies with the ionic state in the liquid composition. CaO is always dissociated into Ca^{2+} ions, while Al_2O_3 and Fe_2O_3 owing to amphoteric oxide, can be dissociated into MeO_4^{5-} or Me^{3+} ions in the melting state [17]. As shown in the following formulaes:

$$Me_2O_3 + 5O^{2-} = 2MeO_4^{5-} \quad (1)$$

$$Me_2O_3 = 2Me^{3+} + 3O^{2-} \quad (2)$$

Al (with an ionic radius of 0.57 Å) tends to form a tetrahedral MeO_4^{5-} ion, and Fe (with an ionic radius of 0.67 Å) tends to form an octahedral Me^{3+} 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 $C_4A_3\$$ and C_3S.

In this work, the composition of ferrite phase is general variation by adjusting the proportional between Fe_2O_3 and Al_2O_3 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 $C_4A_3\$$ and C_3S 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 $CaCO_3$, SiO_2, $Al(OH)_3$, Fe_2O_3 and $CaSO_4 \cdot 2H_2O$ 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 Φ 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 (4^3), (L-orthogonal experiment, 16 experiments, 3 factors, and 4 tiers), as experiment regulation, was listed in Table 2.

Table 1. Theoretic mineral composition of the samples *w* (%).

Clinker composition			
C_3S[a]	C_2S	$C_4A_3\$$	$C_2A_{1-X}F_X$[b]
15	57	23	5
15	52	23	10
15	47	23	15
15	42	23	20

[a] *Notation: C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3, $ = SO_3*
[b] *X stands for the molar of Fe_2O_3 and can vary from 0.25 to 1 (X = 0.25, 0.5, 0.75 and 1)*

Table 2. Factors and levels of orthogonal experiment.

Levels	Factor A	Factor B	Factor C
	The molar ratio of A/Fc	Burning temperature (°C)	Ferrite phase content (%)
1	3	1320	5
2	1	1350	10
3	1/3	1380	15
4	0	1410	20

[c] *A/F = Al_2O_3/Fe_2O_3*

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 $C_4A_3\$$ and C_3S 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 Fe_2O_3 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 Fe_2O_3 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.

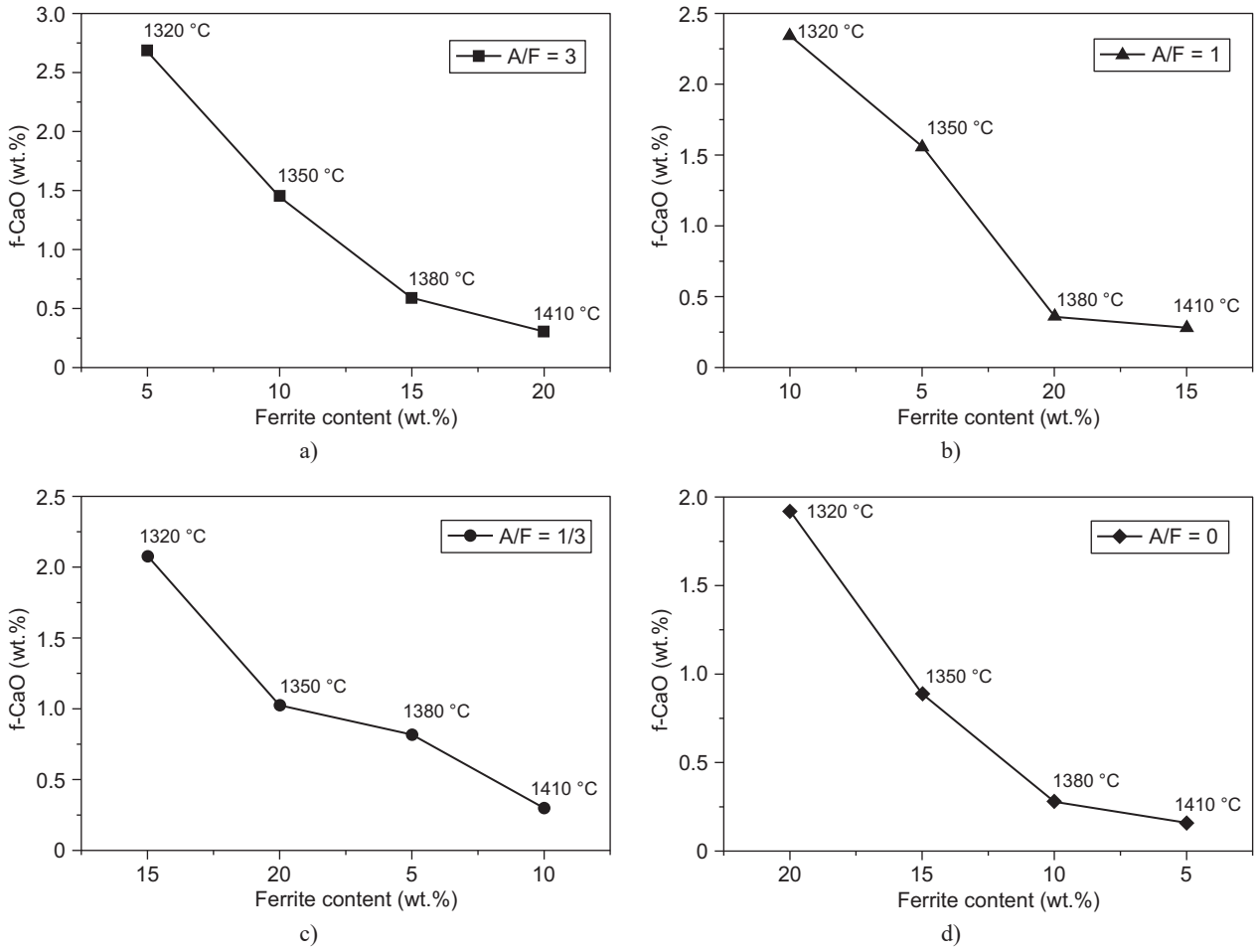


Figure 1. The effect of ferrite phase on free lime content in clinkers.

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)

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

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_2O_3 can enhance the absorption of f-CaO, improve the burnability of clinker and accelerate the C_3S formation in the clinker.

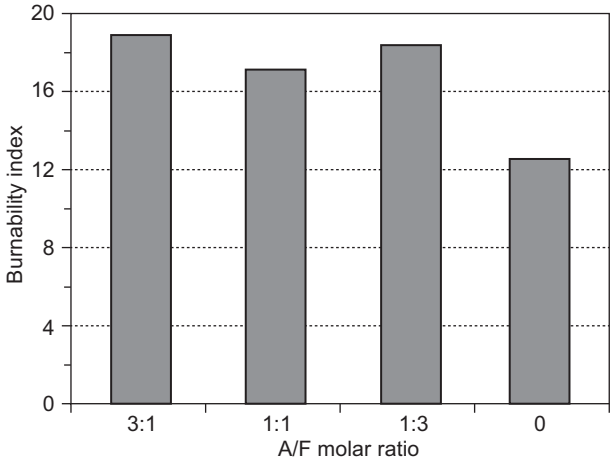


Figure 2. The effect of ferrite phase on the burnability index in clinkers.

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_2S, $C_4A_3\$$, C_3S and $C_2A_{0.5}F_{0.5}$ solid solutions by analysis of Jade software. When the content of ferrite is 20 %

at 1320°C, the diffraction peak of $C_4A_3\$$ is lower than other samples. It might be due to the fact that the actual composition of ferrite is $C_2A_{0.5}F_{0.5}$ (brownmillerite, 2θ = = 12.16°, d = 7.27 Å). Hence, more Al_2O_3, which is used to generate $C_4A_3\$$, is consumed and forms brownmillerite in burning process. The diffraction peak of C_3S (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 C_2S, $C_4A_3\$$, C_3S and $C_2A_{0.5}F_{0.5}$ solid solutions. The intensity of $C_4A_3\$$ peaks slightly increase in Figure 3b compared to Figure 3a. There is a relatively much Al_2O_3 being used to $C_4A_3\$$ 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 $C_4A_3\$$ and C_3S 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 C_3S, 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 $C_4A_3\$$ peaks obviously decreases. This suggests that $C_4A_3\$$ has already decomposed when the temperature is higher than its decomposition temperature. The sulfate in liquid phase generated by $C_4A_3\$$ decomposition inhibits the reaction of CaO with belite, consequently suppressing the C_3S formation [22-24]. Therefore, excessive the burning temperature does not facilitate the coexistence of $C_4A_3\$$ and C_3S.

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

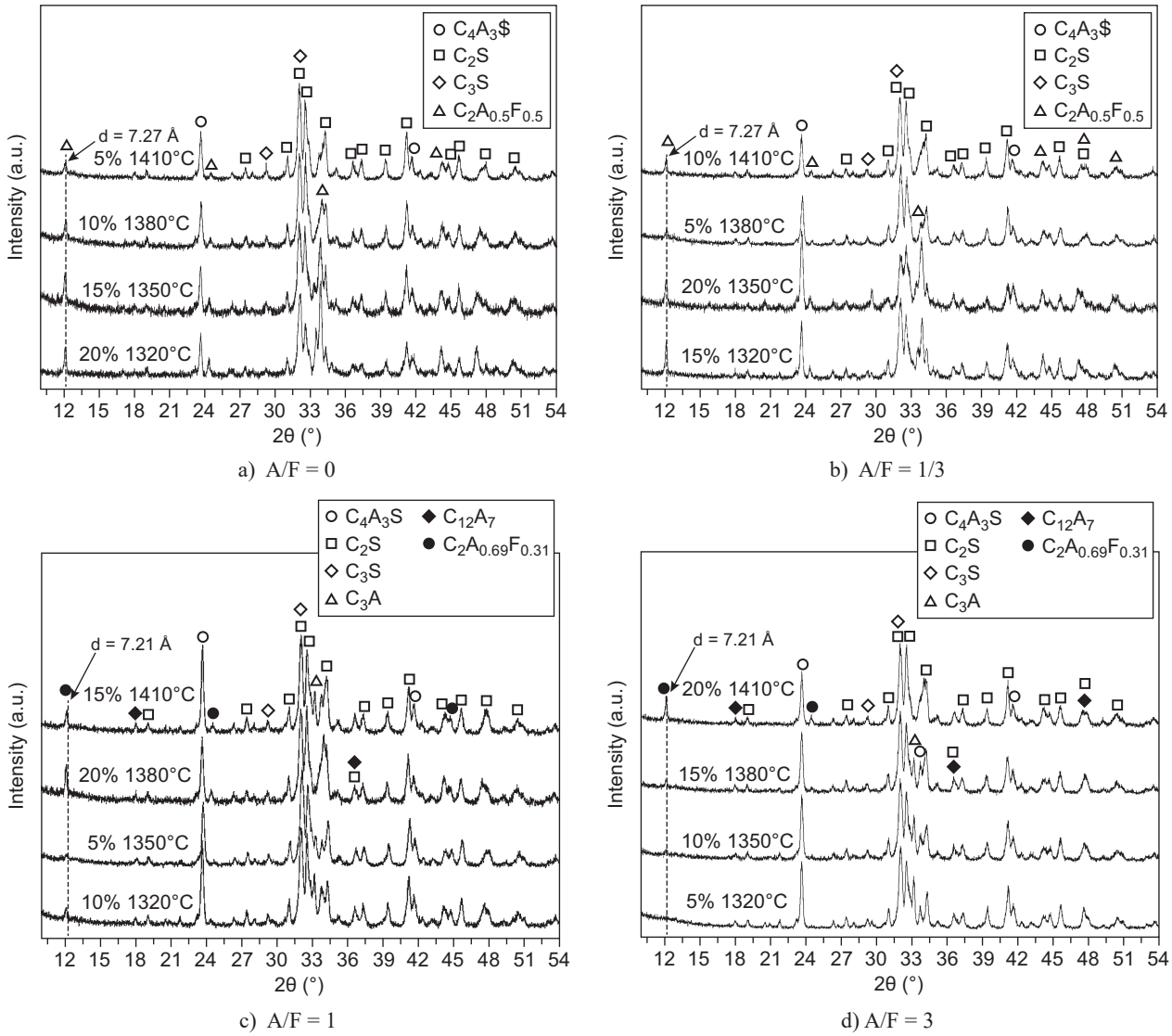


Figure 3. The XRD patterns of samples with different ferrite phases.

mineral compositions, all of them are C_2S, $C_4A_3\$$, C_3S, C_3A, $C_{12}A_7$ 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 $C_2A_{0.5}F_{0.5}$. It might be due to the fact that C_2F 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_2F, 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 (from7.27 Å to 7.21 Å) with increasing Al_2O_3 content of the samples [25]. In addition, the characteristic diffraction peak of $C_{12}A_7$ ($2\theta = 18.03°$) 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_3A ($2\theta = 33.3°$) 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_3S formation. Furthermore, flash setting mineral $C_{12}A_7$ and C_3A 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_3S, C_3A, $C_{12}A_7$ 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_3S 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_3S. 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_3S and the coexistence of $C_4A_3\$$ and C_3S. 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_3S 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_3S 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_3S in burning process, which is consistent with previous results of XRD observations.

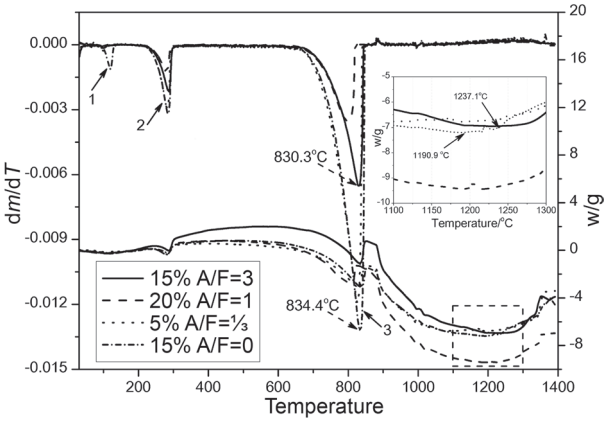


Figure 4. DTG-DSC curves of raw materials at different ferrite phases.

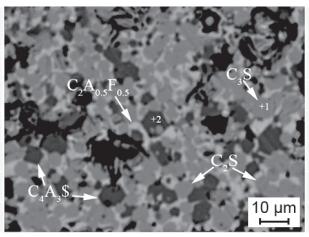
SEM-EDS analysis

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, $C_4A_3\$$, C_3S and $C_2A_{0.5}F_{0.5}$ 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_3S 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

$C_4A_3\$$ crystals are ferrite. The result indicates that $C_4A_3\$$ crystals have not dissolved in liquid phase at 1350°C and retains regular outlines with undercooling, which also coincide well with XRD results.

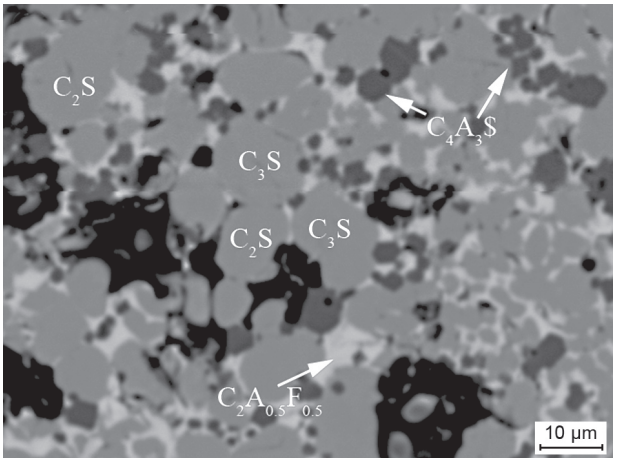
Compared with $C_4A_3\$$ grains at the burning temperature 1350°C (Figure 5a), the sample with the molar ratio A/F as 0 at 1380°C is smaller than 10 μm, as shown in Figure 5b, and its outline is unclear. This result suggests that a part of $C_4A_3\$$ has decomposed in the liquid phase and formed the solid solution with silicate phase, which also is consistent well with the molar ratio of element from EDS analysis [31]. In contrast, the C_2S and C_3S 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_3S. With the ongoing increase in the burning temperature, the clinker sample shows well-formed hexagon C_3S crystals and large circular C_2S crystals, which are encompassed by ferrite phases. However, accompanied by the decomposition of $C_4A_3\$$, its crystal size becomes small only several microns from Figure 5c. This has an adverse effect on the coexistence of $C_4A_3\$$ and C_3S crystals. Hence, it must be remembered that the ferrite phase plays an important role in avoiding the breakdown of $C_4A_3\$$ and facilitating the formation of C_3S in the sintering process.

Point +2 element	Molar ratio
Ca	24.33
Al	23.35
O	44.07
S	4.43
Fe	1.60
Si	2.23

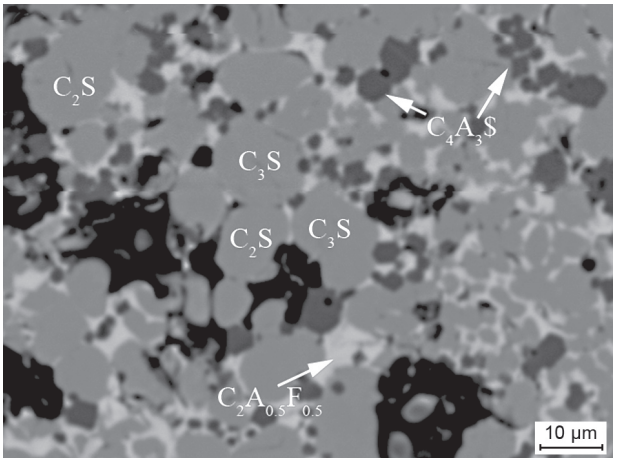


Point +1 element	Molar ratio
Ca	41.02
Si	11.47
O	42.52
Al	3.54
Fe	0.68
S	0.77

a) with 20 % ferrite phase (A/F = 1/3)



b) with 10 % ferrite phase (A/F = 0)



c) with 5 % ferrite phase (A/F = 0)

Figure 5. BSE image of samples with different ferrite phases.

CONCLUSIONS

In order to achieve the coexistence of C_3S and $C_4A_3\$$, 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 $C_2A_{0.5}F_{0.5}$ 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 $C_4A_3\$$ and C_3S 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_3A 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_3S in burning process.
- The distinctly dark and polygonal $C_4A_3\$$ 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 $C_4A_3\$$ has decomposed in the liquid phase and formed the solid solution, and its crystal size becomes smaller and its outlines is also unclear.

Acknowledgements

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