Journal of Thermal Analysis, Vol. 38 (1992) 2147 -2155

THE APPLICATION OF THERMAL ANALYSIS AND CONDUCTION CALORIMETRY ON THE FORMATION AND HYDRATION OF CALCIUM ALUMINOFERRITE

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DTA was used to study the formation of calcium aluminoferrite from CaO, Al_2O_3 and Fe_2O_3 (proportion = 2 : x : 1–x), x= 0–3/4) and the effects of $C4A_3\bar{S}$ $C_{11}A_7{\cdot}CaF_2$, β–C_2S and MgO on that process. The fusion of CF and the eutectic of CaO–Fe_2O_3, CA–$C_{12}A_7$, CA–C_3A, $C_{12}A_7$–C_3A and CA–$C_2A_xF_{(1-x)}$ will be favourable for the formation. The presence of β–C_2S and MgO will decrease its formation temperature by an extra eutectic while $C_4A_3\bar{S}$ and $C_{11}A_7{\cdot}CaF_2$ will not.

The early heat evolution during the hydration of $C_2A_xF_{(1-x)}$ were measured by the conduction calorimeter made by ourselves and the products after 1 day hydration were examined by TG and DTA. The results revealed that the peak of heat evolution rise, the amount of the hydrating product iron hydrate gel decreases, CAH_{10} and $C_3(A, F)H_6$ increase with the increase of the value x. The more MgO (up to 5%) soluted in C_6AF_2 , the higher the hydration heat for this solid solution is, when TiO_2 soluted in C_6AF_2 is 2%, the hydration heat for the system reaches the highest.

Keywords: calcium aluminoferrite, conduction calorimetry, DTA, TG

Introduction

Calcium aluminoferrite, one of the four main minerals in Portland clinker, plays an important role in clinker formation and hydraulicity of cement. In some saving energy cements, such as high-ferrite cement [1] and aluminoferrite cement [2], its content is quite high.

It is believed that calcium aluminoferrite is a solid solution, of which the Al_2O_3/Fe_2O_3 ratio varies significantly with clinker systems and so does the hydration performance. But the results proposed by different authors are not uniform [3–5]. In this paper the thermal effect during the formation of the process with various $Al_2O_3/(Al_2O_3 + Fe_2O_3)$ are studied by differential thermal analysis (DTA), their hydration heat evolution are measured by conductive calorimetry and the hydration products are detected by

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DTA and thermogravimetry (TG) as well as its derivative (DTG). The influence of some impurities on these processes are also discussed.

Thermal analysis of calcium aluminoferrite formation

The formation of $2CaO{\cdot}Fe_2O_3$

Figure 1 gives DTA curves of $2CaO{\cdot}Fe_2O_3(C_2F)$ formation at different conditions. In curve *a* the endothermal at 1222°C is mainly caused by the eutectic point between

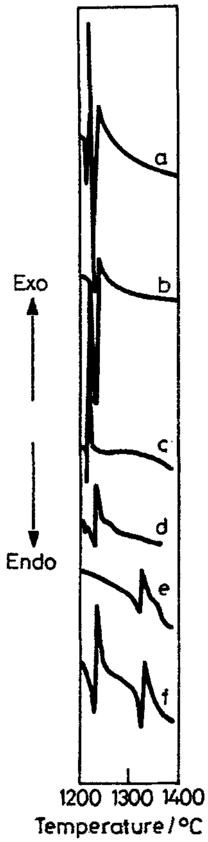

Fig. 1 DTA curves (10 deg/min, 50 mg).
a) 2C + F;
b) CF + C;
c) 2C + F + 10% β–C_2S;
d) CF + C + 10% β–C_2S;
e) 2C + F + 10% β–C_2S + 5% MgO;

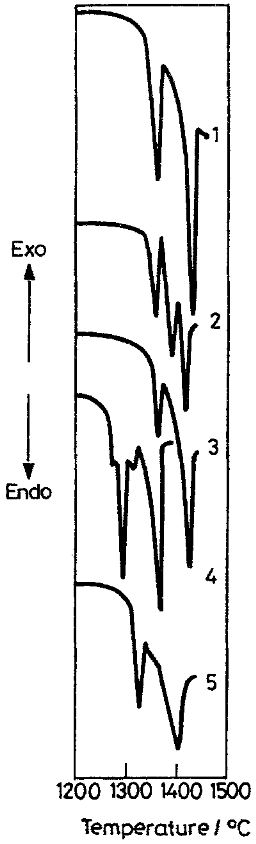

Fig. 2 DTA curves (10 deg/min, 50 mg).
1) C_2F + CA + C;
2) C_2F + CA + 10% $C_{11}A_7{\cdot}CaF_2$;
3) C_2F + CA + C + 10% C_4A_3S;
4) C_2F + CA + C +10% β–C_2S
+ 5% MgO;

$CaO–Fe_2O_3$ which accelerates the formation of both CF and C_2F (the exothermal peak at 1225°C). XRD has proved that both of CF and C_2F appear as soon as the decomposition of $CaCO_3{\cdot}CF$ melts at 1237°C in both curves *a* and *b*, which is helpful for rapid formation of C_2F (exothermal at 1240°C). In fact, C_2F can easily be synthesized at 1250°C [6].

At the presence of 10% β–$2CaO{\cdot}SiO_2$ (β–C_2S), the eutectic point between C_2S–CaO–Fe_2O_3-CF at 1212°C makes C_2F form directly and quickly (see a sharp exothermal peak at 1217°C in curve *c*). But if CF is previously synthesized, the eutectic temperature of C_2S–CF–C is 1209°C and CF melts at 1228°C which results in C_2F forming totally.

Curves *e* and *f* indicate a significant effect of 5% MgO on the process mentioned above. In the case of CF + C + 10% β–C_2S + 5% MgO, CF still melts at 1231°C which promotes C_2F formation (1239°C). The endothermal valley at 1322°C means the eutectic in system C_2F–C_2S–MgO and a new phase may form through the liquid (1335°C). But for the mixture 2CaO + Fe_2O_3 + 10% β–C_2S + 5% MgO, the endothermal effect by CF melting is no longer present, which implies that neither CF nor free Fe_2O_3 presents at about 1230°C. In fact, some free CaO and $MgFe_2O_4$ are detected by XRD at below 1250°C. So it can be believed that some MgO will solute in C_2F finally.

The effect of impurities on formation of C_4AF *from* C_2F + CA + C

The compounds, such as C_2F, CA, $C_{11}A_7{\cdot}CaF_2$, $C_4A_3\bar{S}$, and β–C_2S are previously synthesized and then 10% $C_{11}A_7{\cdot}CaF_2$, 10% $C_4A_3\bar{S}$, 10% β–C_2S and 10% β–C_2S + 5% MgO, are added to the mixture of C_2F + CA + C, respectively. Figure 2 gives their thermoanalytical curves by the same operation conditions with Fig. 1. In the case of C_2F + CA + C the thermal effects related to C_2F formation all disappear. The endothermal valley at 1360°C is referable to the eutectic between aluminate phases, such as CA + $C_{12}A_7$, $C_{12}A_7$–C_3A, and CA–C_3A, which accelerates the formation of C_4AF, and the other one at 1420°C is C_4AF melting point $C_{11}A_7{\cdot}CaF_2$ and $C_4A_3\bar{S}$ have no significant influence on C_4AF formation from C_2F + CA + C but both β–C_2S and β–C_2S + MgO do have one. The addition of 10% β–C_2S leads an eutectic point at 1322°C reducing the C_4AF synthesis temperature to about 1320°C and melt point to 1402°C. The addition of 10% β–Cu2S +5% mgO makes the eutectic and melt temperature further decrease to 1291°C and 1374°C, respectively, and C_4AF can be totally synthesized at about 1290°C.

The formation of calcium aluminoferrite with different Al_2O_3 / Fe_2O_3

Figure 3, is the thermoanalytical curve of mixtures of CaO, Al_2O_3 and Fe_2O_3 with $Al_2O_3 / (Al_2O_3 + Fe_2O_3) = 2/12, 4/12, 5/12, 6/12, 7/12, 8/12$ and $9/12$, respectively, and with $CaO / (Al_2O_3 + Fe_2O_3) = 2$ for all specimen. When $Al_2O_3 / (Al_2O_3 + Fe_2O_3) < 4/12$, the endothermal at 1230°C, which is the eutectic of CaO–Fe_2O_3 and may be some CF melting, accelerates the formation of $C_{12}AF_5$ and C_6AF_2 (about 1240°C). When $Al_2O_3 / (Al_2O_3 + Fe_2O_3) > 5/12$, this valley gradually decreases, which means less free Fe_2O_3

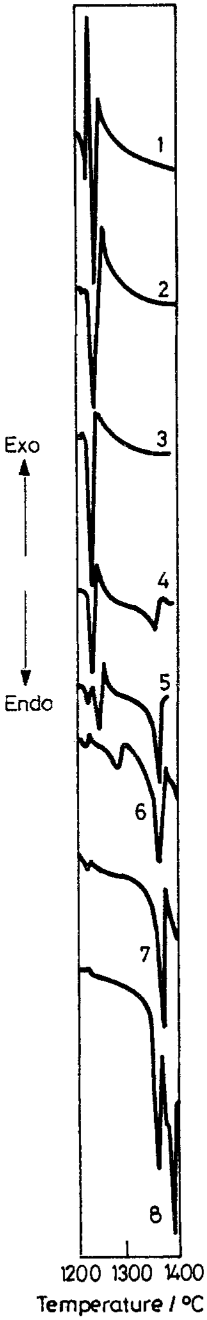

Fig. 3 DTA curves for formation of 1) C_2F; 2) $C_2A_{7/12}F_{10/12}$; 3) C_6AF_2; 4) $C_2A_{5/12}F_{7/12}$; 5) C_4AF; 6) $C_2A_{7/12}F_{5/12}$; 7) C_6A_2F; 8) $CA_{9/12}F_{3/12}$

lifted up to 1230°C. When Al_2O_3 / (Al_2O_3 + Fe_2O_3)> $7/12$, it sharply reduces to near disappearance but free CaO still can be detected by XRD at 1300°C. In these samples, the eutectic between aluminate phases at 1360°C brings about the complete formation of aluminoferrite with Al_2O_3 / (Al_2O_3)< 8, such as C_4AF and C_6A_2F. The endothermal effect in the range of 1250–1326°C is the eutectic of $C_2A_xF_{(1-x)}$–CA corresponding to the boundary line between the primary crystal fields of $C_2A_xF_{(1-x)}$ and CA in the phase diagram of the system C_2F–CA-CaO in which the end of the line is an invariant point at 1335°C, with the increase of Al_2O_3, its temperature lifts and its area reduces. On curve 9 this extremely small effect is at 1326°C and an extra endothermal at 1390°C is the melt of $C_{12}A_7$ which increases with Al_2O_3 / (Al_2O_3 + Fe_2O_3). Finally the aluminoferrite melts, the temperature of which rises with the decrease of Al_2O_3 / (Al_2O_3 + Fe_2O_3).

Calorimetry and thermal analysis of calcium aluminoferrite

Heat evolution and products of the hydration of calcium aluminoferrite with various Al_2O_3 / Fe_2O_3

The heat evolution is measured with the conductive calorimeter designed and made by ourselves according to Calvete principle and equipped with the type 3066 pen re-

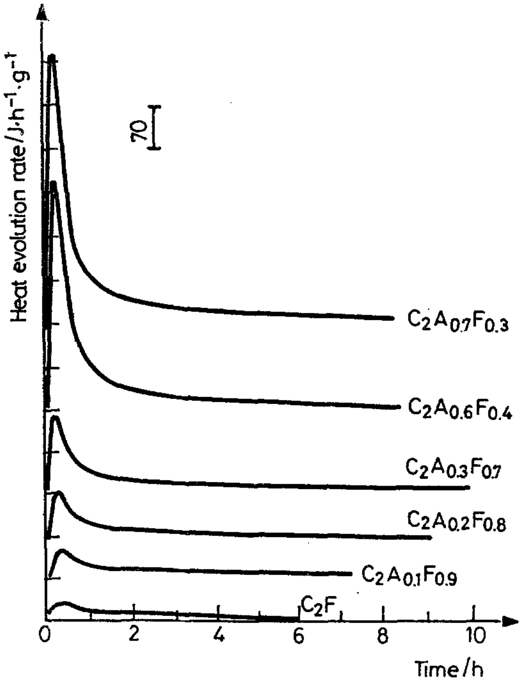

Fig. 4 Heat evolution curves for $C_2A_xF_{(1-x)}$ (water/solid = 0.7, T= 25°C)

corder made in Japan. This instrument has the characteristics of no hysteresis. Figure 4 shows that the heat evolution of C_2F hydration (W/C = 0.7) at room temperature is rather low and with the increase of Al_2O_3 / Fe_2O_3 the rate of heat evolution increases.

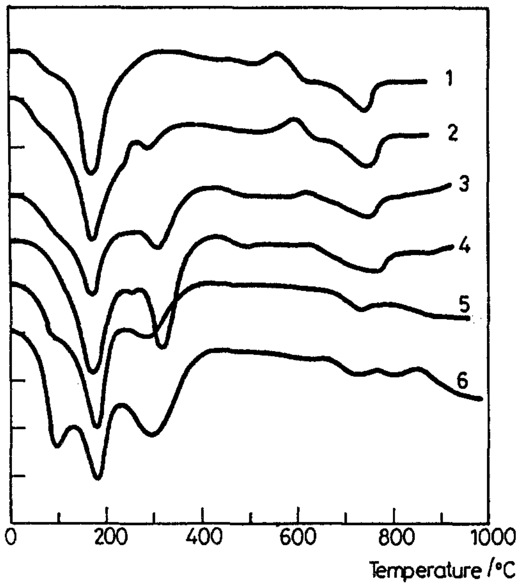

Fig. 5 DTA, DTG curves for $C_2A_xF_{(1-x)}$ hydrated 1 day at 25°C with water/solid ratio of 0.7. 1) C_2F; 2) $C_2F_{0.1}F_{0.9}$; 3) $C_2A_{0.3}F_{0.7}$; 4) $C_2A_{0.5}F_{0.5}$; 5) $C_2A_{0.6}F_{0.4}$; 6) $C_2A_{0.7}F_{0.3}$. Heating rate: 20 deg/min. Sample weight: 20 mg

Figures 5 and 6 are DTA and DTG curves of the products of the same samples as in Fig. 4 after 24 hours hydration. On the thermoanalytical curves of C_2F hydration product, the large endothermal presents C_4FH_{13} dehydration and iron hydrate gel dewatering. The exothermal at 552°C and the endothermal at 612°C are iron hydrate gel crystallizing and dewatering, respectively. In the specimen with Al_2O_3, the dewatering temperature of $C_4(A, F)H_{13}$ is in the range of 170°–180°C. As the Al_2O_3 increases, the crystallization temperature of iron hydrate gel gradually lifts, i.e. at 627°C for $C_2A_{0.5}F_{0.5}$ and at 663°C for $C_2A_{0.7}F_{0.3}$, which means the increase of basicity in the system, and its peak area decreases, which indicates the decrease of its amount. An endothermal at slightly above 100°C and another one at about 300°C are caused by CAH_{10} and $C_3(A, F)H_6$, respectively. Both of them become more and more significant as the Al_2O_3 increases.

The DTG curves are quite identical with the DTA ones: peak of $C_4(A, F)H_{13}$ at 140°–160°C, and $C_3(A, F)H_6$ at 270°–300°C.

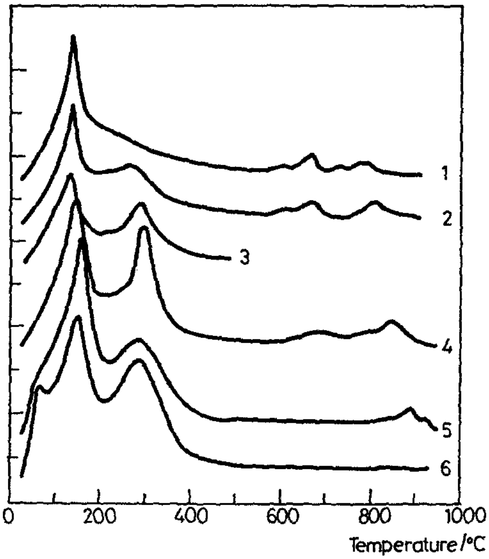

Fig. 6 DTA, DTG curves for $C_2A_xF_{(1-x)}$ hydrated 1 day at 25°C with water/solid ratio of 0.7. 1) C_2F; 2) $C_2F_{0.1}F_{0.9}$; 3) $C_2A_{0.3}F_{0.7}$; 4) $C_2A_{0.5}F_{0.5}$; 5) $C_2A_{0.6}F_{0.4}$; 6) $C_2A_{0.7}F_{0.3}$. Heating rate: 20 deg/min. Sample weight: 20 mg

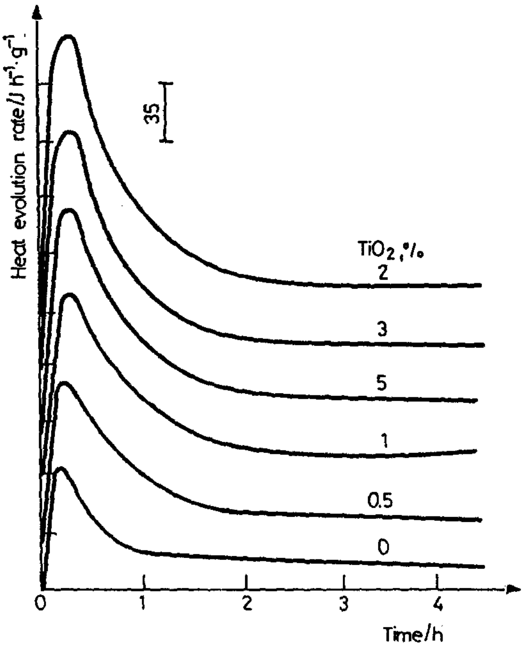

Fig. 7 Heat evolution curves of C_6AF_2 with TiO_2 (water/solid = 0.8, T = 20°C)

Influence of impurities soluted on the heat evolution of C_6AF_2 *hydration*

Figures 7 and 8 give the heat evolution curves of the hydration of C_6AF_2 with small amount of MgO and TiO_2, respectively. It is clear that the heat evolution enhances with the rise of MgO amount up to 5%. In the case of TiO_2 the highest value is reached when TiO_2 added is 2%. this difference may be caused by the different location of the impurities at C_6AF_2 lattice.

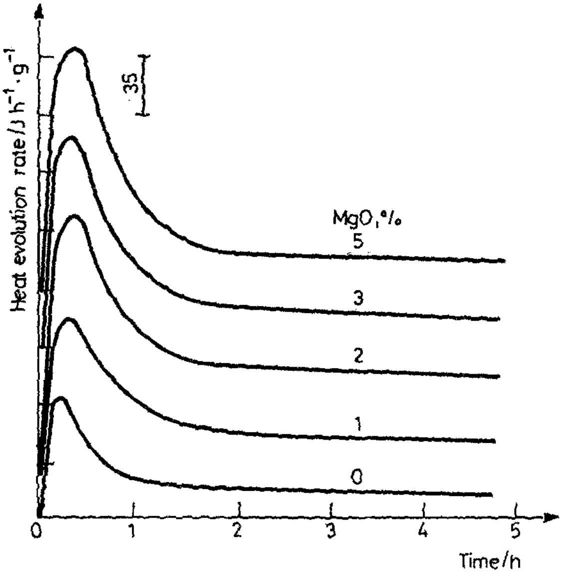

Fig. 8 Heat evolution curves of C_6AF_2 with MgO (water/solid = 0.8, T = 20°C)

Conclusion

Calorimetry and thermal analysis, such as DTA and TG/DTG, are useful and effective in the research on the formation and hydration of calcium aluminoferrite.

By DTA it can be deduced that the liquids appearing during heating are main factors accelerating the formation of calcium aluminoferrite. As $Al_2O_3/(Al_2O_3 + Fe_2O_3) < 1/3$ the eutectic of $CaO-Fe_2O_3$ and/or the melt of CF below 1240°C are sufficient for total formation of calcium aluminoferrite. When $Al_2O_3 / (Al_2O_3 + Fe_2O_3)$ increases up to $2/3$ the eutectic between aluminates at 1360°C can make it be synthesized. The addition of $\beta-C_2S$ and MgO will lower the temperature by producing an extra eutectic point.

The heat evolution of calcium aluminoferrite hydration lifts with the increase of Al_2O_3, in the phase and that of C_6AF_2 is lifted by the addition of MgO up to 5% and reaches the highest when TiO_2 added is 2%. The hydration product of calcium aluminoferrite contains $C_4(A, F)H_{13}$, $C_3(A, F)H_6$, CAH_{10} and the iron hydrate gel.

Among them $C_3(A, F)H_6$ and CAH_{10} increase and iron hydrate gel decreases with the rise of Al_2O_3 / Fe_2O_3.

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This project is supported by National Natural Science Fundation of China and by the National Science and Technology Developing Fundation in Building Materials Field.

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Zusammenfassung — Mittels DTA wurde die Bildung von Calciumaluminoferrit aus CaO, Al_2O_3 und Fe_2O_3 im Verhältnis 2:x:1-x (mit x=0-3/4) sowie der Einfluß von C_4A_3S, $C_{11}A_7CaF_2$, ß-C_2S und MgO auf diesen Prozeß untersucht. Die Bildung wird durch die Schmelze von CF und das Eutektikum von CaO-Fe_2O_3, CA-$C_{12}A_7$, CA-C_3A, $C_{12}A_7$-C_3A und CA-$C_2A_xF_{(1-x)}$ begünstigt. Durch Gegenwart von ß-C_2S und MgO wird die Bildungstemperatur durch ein zusätzliches Eutektikum herabgesetzt, während C_4A_3S und $C_{11}A_7CaF_2$ dies nicht bewirken.
Mit Hilfe eines von uns hergestellten Konduktions-Kalorimeters wurde die frühe Wärmeentwicklung während der Hydratation von $C_2A_xF_{(1-x)}$ gemessen und die Produkte nach einer 1-tägigen Hydratation mittels TG und DTA untersucht. Die Ergebnisse zeigten, daß mit einem steigenden Wert für x die Peaks der Wärmeentwicklung größer werden, die Menge des Hydratationsproduktes Eisenhydratgel abnimmt und CAH_{10} und $C_3(A,F)H6$ ebenfalls mehr werden.Je mehr MgO (bis zu 5 %) in C_6AF_2 gelöst ist, umso höher ist die Hydratationswärme für diesen Mischkristall. Wird in C_6AF_2 2 % TiO_2 gelöst, erreicht die Hydratationswärme ihr Maximum für dieses System.