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Thermodynamics of Reactions Among Al_2O_3, CaO, SiO_2 and Fe_2O_3 During Roasting Processes

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1. Introduction

The thermodynamic of the chemical reactions among Al_2O_3, CaO, SiO_2 and Fe_2O_3 in the roasting processes was investigated in this chapter. The chemical reactions are classified into SiO_2-Al_2O_3 system, Fe_2O_3-Al_2O_3 system, SiO_2-Fe_2O_3 system, CaO-Al_2O_3 system, SiO_2-CaO system, SiO_2-calcium aluminates system, CaO-Fe_2O_3 system, Al_2O_3-calcium ferrites system and Al_2O_3-CaO-SiO_2-Fe_2O_3 system. When the roasting temperature is over 1100K, $3Al_2O_3 \cdot 2SiO_2$ is preferentially formed in SiO_2-Al_2O_3 system; $FeO \cdot Al_2O_3$ can be formed in Fe_2O_3-Al_2O_3 system; ferric oxide and SiO_2 could not generate iron silicate; $12CaO \cdot 7Al_2O_3$ is preferentially formed in CaO-Al_2O_3 system when one mole Al_2O_3 reacts with CaO; $2CaO \cdot SiO_2$ is preferentially formed in SiO_2-CaO system; except for $CaO \cdot 2Al_2O_3$ and $CaO \cdot Al_2O_3$, the other calcium aluminates can transform into calcium silicate by reacting with SiO_2 in SiO_2-calcium aluminates system; $2CaO \cdot Fe_2O_3$ is preferentially formed in CaO-Fe_2O_3 system; alumina is unable to form $3CaO \cdot Al_2O_3$ with calcium ferrites($2CaO \cdot Fe_2O_3$ and $CaO \cdot Fe_2O_3$), but able to form $12CaO \cdot 7Al_2O_3$ with $2CaO \cdot Fe_2O_3$; when CaO, Fe_2O_3, Al_2O_3, SiO_2 coexist, they are more likely to form ternary compound $2CaO \cdot Al_2O_3 \cdot SiO_2$ and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$.

2. Binary compounds

2.1 Fe_2O_3-Al_2O_3-$CaCO_3$ system

Fe_2O_3 and Al_2O_3 can all react with limestone during roasting to generate corresponding aluminates and ferrites. In Fe_2O_3-Al_2O_3-CaO system, the reaction Fe_2O_3 and Al_2O_3 with $CaCO_3$ coexist, and the reactions equations are as followed:

Reactions	A, J/mol	B, J/K.mol	Temperature, K
$CaCO_3+Al_2O_3=CaO \cdot Al_2O_3+CO_2$	161088.3	-244.1	298~1200
$CaCO_3+Fe_2O_3=CaO \cdot Fe_2O_3+CO_2$	151677.8	-220.9	298~1200

Table 1. The ΔG_T^θ of Fe_2O_3-Al_2O_3-$CaCO_3$ system（$\Delta G_T^\theta = A + BT$, J/mol; P_{CO_2} =30Pa, i.e., the partial pressure of CO_2 in the air）

The relationships between Gibbs free energy (ΔG_T^θ) and temperature (T) are as shown in figure 1.

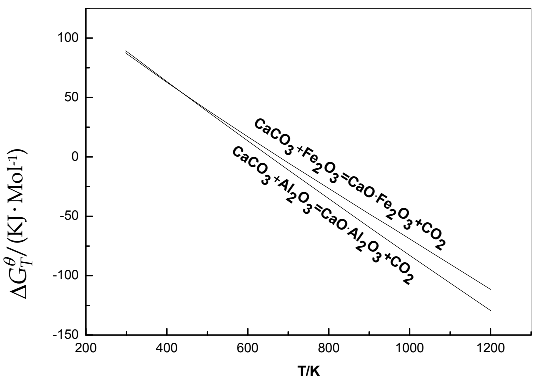

Fig. 1. Relationships between ΔG_T^θ and temperature in Fe_2O_3-Al_2O_3-$CaCO_3$ system

Figure 1 shows that, the Gibbs free energy of reactions on Fe_2O_3 and Al_2O_3 with $CaCO_3$ decreased with the rise of temperature in normal roasting process (due to decomposition of $CaCO_3$ over 1200K, so the curve has no drawing above 1200K), and the reactions all can automatically react to generate the corresponding calcium aluminate and calcium ferrite. The ΔG_T^θ of reaction with Al_2O_3 is more negative than the ΔG_T^θ of reaction with Fe_2O_3 at the same temperature. $CaCO_3$ has actually decomposed at 1473~1673K industrial roasting temperature, therefore, only CaO is taken into account on the following analysis.

2.2 SiO_2-Al_2O_3 system

SiO_2 mainly comes from the ore and coke ash in the roasting process. SiO_2 reacts with Al_2O_3 to form aluminium silicates. The aluminium silicates mainly include $Al_2O_3{\cdot}2SiO_2$(AS_2), $Al_2O_3{\cdot}SiO_2$(AS,andalusite), AS(kyanite), AS(fibrolite), $3Al_2O_3{\cdot}2SiO_2$(A_3S_2). Thermodynamic calculation indicates that, AS_2 can not be formed from the reaction of Al_2O_3 and SiO_2 under the roasting condition. The others equations are shown in table 2.

Reactions	A, J/mol	B, J/K.mol	Temperature, K
$Al_2O_3+SiO_2=Al_2O_3{\cdot}SiO_2$ (kyanite)	-8469.3	9.0	298~1696
$Al_2O_3+SiO_2=Al_2O_3{\cdot}SiO_2$ (fibrolite)	-4463.8	-0.9	298~1696
$Al_2O_3+SiO_2=Al_2O_3{\cdot}SiO_2$ (andalusite)	-6786.1	0.6	298~1696
$\frac{3}{2}Al_2O_3+SiO_2=(\frac{1}{2})3Al_2O_3\cdot 2SiO_2$	12764.7	-16.7	298~1696

Table 2. The ΔG_T^θ of Al_2O_3-SiO_2 system ($\Delta G_T^\theta = A + BT$, J/mol)

The relationships of ΔG_T^θ and temperature in Al_2O_3-SiO_2 system is shown in figure 2.

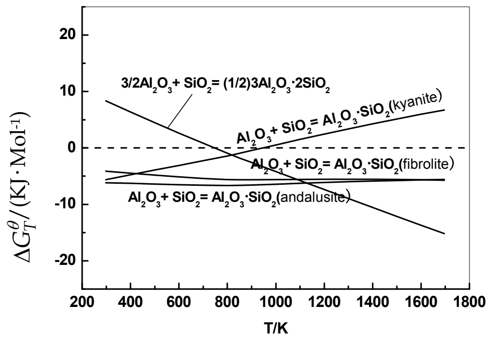

Fig. 2. Relationships of ΔG_T^θ and temperature in Al_2O_3-SiO_2 system

Figure 2 shows that, the ΔG_T^θ of kyanite is greater than zero at 1000~1700K, so the reaction cannot happen; the ΔG_T^θ of andalusite and fibrolite alter little with temperature changes; the ΔG_T^θ of A_3S_2 decreases with the rise of temperature. The thermodynamic order of forming aluminium silicates is A_3S_2, AS(andalusite), AS(fibrolite) at 1100~1700K.

2.3 Fe_2O_3-Al_2O_3 system

Al_2O_3 does not directly react with Fe_2O_3, but Al_2O_3 may react with wustite (FeO) produced during roasting process to form FeO·Al_2O_3. No pure ferrous oxide (FeO) exists in the actual process. The ratio of oxygen atoms to iron atoms is more than one in wustite, which is generally expressed as Fe_xO(x=0.83~0.95), whose crystal structure is absence type crystallology. For convenience, FeO is expressed as wustite in this thesis. Al_2O_3 may react with wustite(FeO) to form FeO·Al_2O_3 in the roasting process. The relationship of ΔG_T^θ and temperature is shown in figure 2, and the chemical reaction of the equation is as followed:

$$Al_2O_3+FeO=FeO\cdot Al_2O_3 \quad \Delta G_T^\theta = -30172.2+9.3T,\ J.mol^{-1} \quad 843\sim1650K \tag{1}$$

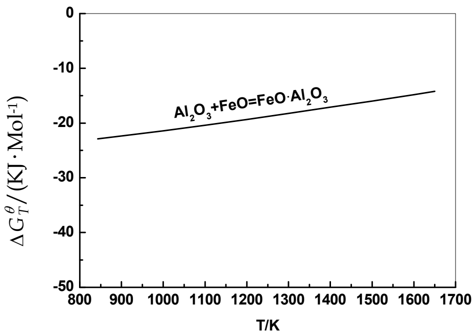

Fig. 3. Relationship of ΔG_T^θ and temperature in Fe_2O_3-Al_2O_3 system

Figure 3 shows that, the ΔG_T^θ is negative at 843~1650K, reaction can happen and generate $FeO \cdot Al_2O_3$; the ΔG_T^θ rises with the temperature, the higher temperature is, the lower thermodynamic reaction trends.

2.4 SiO_2-Fe_2O_3 system

SiO_2 also does not directly react with Fe_2O_3, but Al_2O_3 may react with wustite (FeO) to form $FeO \cdot SiO_2$ (FS) and $2FeO \cdot SiO_2$(F_2S). The relationships of ΔG_T^θ and temperature is shown in figure 4, and the chemical reactions of the equations are shown in table 3.

Reactions	A, J/mol	B, J/K.mol	Temperature, K
$FeO+SiO_2 = FeO \cdot SiO_2$	26524.6	18.8	847~1413
$2FeO+SiO_2 = 2FeO \cdot SiO_2$	-13457.3	30.3	847~1493

Table 3. The ΔG_T^θ of SiO_2- Al_2O_3 system （$\Delta G_T^\theta = A + BT$, J/mol）

Figure 4 shows that, the ΔG_T^θ of SiO_2- Al_2O_3 system are above zero at 847~1500K, so all of the reactions can not happen to form ferrous silicates (FS and F_2S).

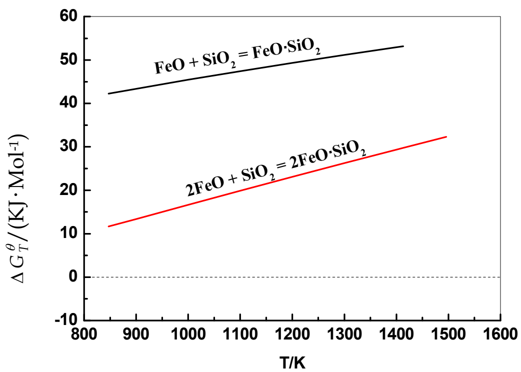

Fig. 4. Relationships of ΔG_T^θ and temperature in SiO_2-Fe_2O_3 system

2.5 CaO-Al_2O_3 system

Al_2O_3 can react with CaO to form calcium aluminates such as $3CaO \cdot Al_2O_3$(C_3A), $12CaO \cdot 7Al_2O_3$($C_{12}A_7$), $CaO \cdot Al_2O_3$(CA) and $CaO \cdot 2Al_2O_3$ (CA_2). As regard as the calcium aluminates only $C_{12}A_7$ can be totally soluble in soda solution, C_3A and CA dissolve with a slow speed, and the other calcium aluminates such as CA_2 are completely insoluble. Equations that Al_2O_3 reacted with CaO to form C_3A, $C_{12}A_7$, CA and CA_2 are presented in table 4.

Figure 5 shows that, the ΔG_T^θ of reactions of Al_2O_3 with CaO decreases with the rise of temperature; all reactions automatically proceed to generate the corresponding calcium aluminates at normal roasting temperature (1473~1673K, same as follows); At the same roasting temperature, the thermodynamic order that one mole Al_2O_3 reacts with CaO to generate calcium aluminates such as $C_{12}A_7$, C_3A, CA, CA_2.

Reactions	A, J/mol	B, J/K.mol	Temperature, K
$3CaO+ Al_2O_3=3CaO\cdot Al_2O_3$	-9.9	-28.4	298~1808
$\frac{12}{7}CaO+Al_2O_3=(\frac{1}{7})12CaO\cdot 7Al_2O_3$	318.3	-44.5	298~1800
$CaO+ Al_2O_3=CaO\cdot Al_2O_3$	-15871.5	-18.1	298~1878
$\frac{1}{2}CaO+Al_2O_3=(\frac{1}{2})CaO\cdot 2Al_2O_3$	-6667.2	-13.8	298~2023

Table 4. The ΔG_T^θ of Al_2O_3-CaO system（$\Delta G_T^\theta = A + BT$, J/mol）

The relationships between ΔG_T^θ and temperature (T) are shown in figure 5.

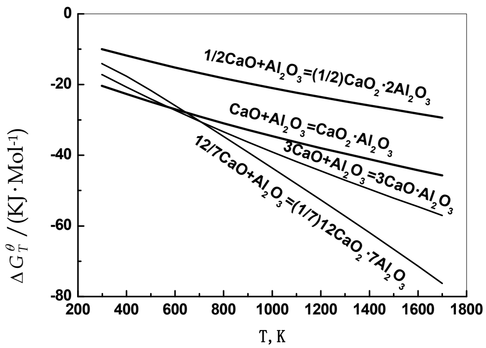

Fig. 5. Relationships between ΔG_T^θ and temperature in Al_2O_3-CaO system

Reactions	A, J/mol	B, J/K.mol	Temperature, K
$(\frac{4}{3})3CaO\cdot Al_2O_3+Al_2O_3=(\frac{1}{3})12CaO\cdot 7Al_2O_3$	13939.7	-65.8	298~1800
$(\frac{1}{2})3CaO\cdot Al_2O_3+Al_2O_3=(\frac{3}{2})CaO\cdot Al_2O_3$	-18843.8	-13.0	298~1878
$(\frac{1}{5})3CaO\cdot Al_2O_3+Al_2O_3=(\frac{3}{5})CaO\cdot 2Al_2O_3$	-6011.2	-10.9	298~2023
$(\frac{1}{5})12CaO\cdot 7Al_2O_3+Al_2O_3=(\frac{12}{5})CaO\cdot Al_2O_3$	-38544.8	18.8	298~1878
$(\frac{1}{17})12CaO\cdot 7Al_2O_3+Al_2O_3=(\frac{12}{17})CaO\cdot 2Al_2O_3$	-9541.1	-1.2	298~2023
$CaO\cdot Al_2O_3+ Al_2O_3=CaO\cdot 2Al_2O_3$	2543.8	-9.5	298~2023

Table 5. The ΔG_T^θ of Al_2O_3-calcium aluminates system（$\Delta G_T^\theta = A + BT$, J/mol）

When CaO is insufficient, redundant Al_2O_3 may promote the newly generated high calcium-to-aluminum ratio (CaO to Al_2O_3 mole ratio) calcium aluminates to transform into lower calcium-to-aluminum ratio calcium aluminates. The reactions of the equations are presented in table 5:

The relationships between ΔG_T^θ of reactions of Al_2O_3-calcium aluminates system and temperature (T) are shown in figure 6.

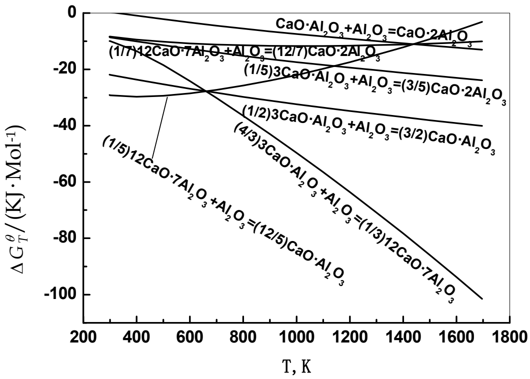

Fig. 6. Relationships between ΔG_T^θ of reactions Al_2O_3-calcium aluminates system and temperature

Figure 6 shows that, Gibbs free energy of the reaction of Al_2O_3-calcium aluminates system are negative at 400~1700K, and all the reactions automatically proceed to generate the corresponding low calcium-to-aluminum ratio calcium aluminates; Except for the reaction of Al_2O_3-$C_{12}A_7$, the ΔG_T^θ of the rest reactions decreases with the rise of temperature and becomes more negative. Comparing figure 4 with figure 5, it can be found that Al_2O_3 reacts with CaO easily to generate $C_{12}A_7$.

2.6 SiO_2- CaO system

SiO_2 can react with CaO to form CaO·SiO_2 (CS), 3CaO·2SiO_2 (C_3S_2), 2CaO·SiO_2 (C_2S) and 3CaO·SiO_2(C_3S) in roasting process. The reactions are shown in table 6, and the relationships between △G^0 of the reactions of SiO_2 with CaO and temperature are shown in figure 7.

Reactions	A, J/mol	B, J/K.mol	Temperature, K
CaO+SiO_2 = CaO·SiO_2(pseud-wollastonite)	-83453.0	-3.4	298~1817
CaO+SiO_2 = CaO·SiO_2(wollastonite)	-89822.9	-0.3	298~1817
$\frac{3}{2}CaO+SiO_2=(\frac{1}{2})\ 3CaO\cdot 2SiO_2$	-108146.6	-3.1	298~1700
3CaO+SiO_2 = 3CaO·SiO_2	-111011.9	-11.3	298~1800
2CaO+SiO_2 = 2CaO·SiO_2(β)	-125875.1	-6.7	298~2403
2CaO+SiO_2 = 2CaO·SiO_2(γ)	-137890.1	3.7	298~1100

Table 6. The ΔG_T^θ of SiO_2-CaO system($\Delta G_T^\theta = A + BT$, J/mol)

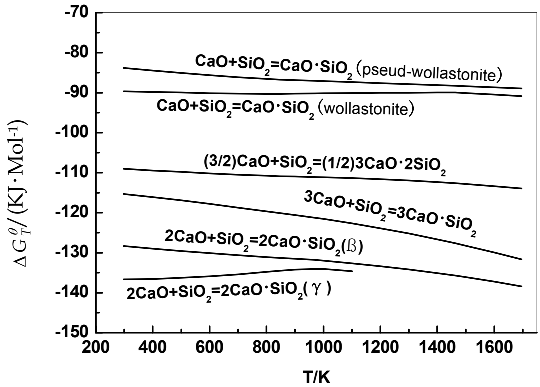

Fig. 7. Relationships between ΔG_T^{θ} and temperature

Figure7 shows that, SiO_2 reacts with CaO to form γ-C_2S when temperature below 1100K, but β-C_2S comes into being when the temperature above 1100K. At normal roasting temperature, the thermodynamic order of forming calcium silicate is C_2S, C_3S, C_3S_2, CS.
Figure 5 ~ figure 7 show that, CaO reacts with SiO_2 and Al_2O_3 firstly to form C_2S, and then $C_{12}A_7$. Therefore, it is less likely to form aluminium silicates in roasting process.

2.7 SiO_2- calcium aluminates system

In the CaO-Al_2O_3 system, if there exists some SiO_2, the newly formed calcium aluminates are likely to react with SiO_2 to transform to calcium silicates and Al_2O_3 because SiO_2 is more acidity than that of Al_2O_3. The reaction equations are presented in table 7, the relationships between ΔG_T^{θ} and temperature are shown in figure 8.

Figure 8 shows that, the ΔG_T^{θ} of all the reactions increases with the temperature increases; the reaction ($3CA_2+SiO_2=C_3S+6Al_2O_3$) can not happen when the roasting temperature is above 900K , i.e., the lowest calcium-to-aluminum ratio calcium aluminates cannot transform to the highest calcium-to-silicon ratio (CaO to SiO_2 molecular ratio) calcium silicate; when the temperature is above 1500K, the ΔG_T^{θ} of reaction($3CA+ SiO_2=C_3S+3Al_2O_3$) is also more than zero; but the other calcium aluminates all can react with SiO_2 to generate calcium silicates at 800~1700K. The thermodynamic sequence of calcium aluminates reaction with SiO_2 is firstly C_3A, and then $C_{12}A_7$, CA, CA_2.

Reactions	A, J/mol	B, J/K.mol	Temperature, K
$(3)CaO\cdot 2Al_2O_3+SiO_2=3CaO\cdot SiO_2+6Al_2O_3$	-69807.8	70.8	298~1800
$(3)CaO\cdot Al_2O_3+SiO_2=3CaO\cdot SiO_2+3Al_2O_3$	-62678.8	42.6	298~1800
$(\frac{1}{4})12CaO\cdot 7Al_2O_3+SiO_2=3CaO\cdot SiO_2+\frac{7}{4}Al_2O_3$	-111820.6	66.7	298~1800
$(2)CaO\cdot 2Al_2O_3+SiO_2=2CaO\cdot SiO_2+4Al_2O_3$	-98418.8	48.1	298~1710
$(\frac{3}{2})CaO\cdot 2Al_2O_3+SiO_2=(\frac{1}{2})3CaO\cdot 2SiO_2+3Al_2O_3$	-87585.9	38.0	298~1700
$CaO\cdot 2Al_2O_3+SiO_2=CaO\cdot SiO_2+2Al_2O_3$	-76146.6	27.1	298~1817
$CaO\cdot Al_2O_3+SiO_2=CaO\cdot SiO_2+Al_2O_3$	-73770.2	17.7	298~1817
$(\frac{3}{2})CaO\cdot Al_2O_3+SiO_2=(\frac{1}{2})3CaO\cdot 2SiO_2+\frac{3}{2}Al_2O_3$	-84021.4	23.8	298~1700
$(2)CaO\cdot Al_2O_3+SiO_2=2CaO\cdot SiO_2+2Al_2O_3$	-93666.1	29.2	298~1710
$(\frac{1}{12})12CaO\cdot 7Al_2O_3+SiO_2=CaO\cdot SiO_2+\frac{7}{12}Al_2O_3$	-90150.8	25.7	298~1800
$(\frac{1}{8})12CaO\cdot 7Al_2O_3+SiO_2=(\frac{1}{2})3CaO\cdot 2SiO_2+\frac{7}{8}Al_2O_3$	-108592.3	35.9	298~1700
$(\frac{1}{6})12CaO\cdot 7Al_2O_3+SiO_2=2CaO\cdot SiO_2+\frac{7}{6}Al_2O_3$	-126427.4	45.3	298~1710
$(\frac{1}{3})3CaO\cdot Al_2O_3+SiO_2=CaO\cdot SiO_2+\frac{1}{3}Al_2O_3$	-86654.2	9.4	298~1808
$3CaO\cdot Al_2O_3+SiO_2=3CaO\cdot SiO_2+Al_2O_3$	-100774.6	16.9	298~1808
$(\frac{1}{2})3CaO\cdot Al_2O_3+SiO_2=(\frac{1}{2})3CaO\cdot 2SiO_2+\frac{1}{2}Al_2O_3$	-103069.3	11.0	298~1700
$(\frac{2}{3})3CaO\cdot Al_2O_3+SiO_2=2CaO\cdot SiO_2+\frac{2}{3}Al_2O_3$	-119063.3	12.1	298~1710

Table 7. The ΔG_T^{θ} of the reactions SiO_2 with calcium aluminates($\Delta G_T^{\theta}=A+BT$, J/mol)

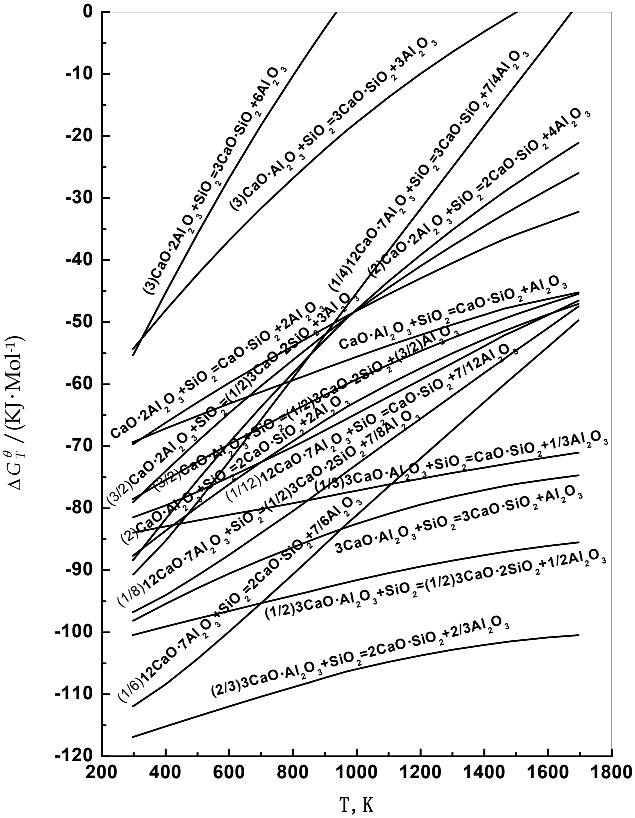

Fig. 8. Relationships between ΔG_T^θ and temperature in SiO_2-calcium aluminates system

2.8 CaO- Fe_2O_3 system

Fe_2O_3 can react with CaO to form CaO·Fe_2O_3(CF) and 2CaO·Fe_2O_3(C_2F). When Fe_2O_3 is used up, the newly formed C_2F can react with Fe_2O_3 to form CF. The reaction equations are shown in table 8, and the relationships between △G^0 and temperature are shown in figure 9.

Figure 9 shows that, Fe_2O_3 reacts with CaO much easily to form C_2F; CF is not from the reaction of C_2F and Fe_2O_3, but from the directly reaction of Fe_2O_3 with CaO. When Fe_2O_3 is excess, C_2F can react with Fe_2O_3 to form CF.

Reactions	A, J/mol	B, J/K.mol	Temperature, K
CaO+Fe_2O_3=CaO·Fe_2O_3	-19179.9	-11.1	298~1489
2CaO+Fe_2O_3=2CaO·Fe_2O_3	-40866.7	-9.3	298~1723
2CaO·Fe_2O_3+Fe_2O_3=(2)CaO·Fe_2O_3	2340.8	-12.6	298~1489

Table 8. The ΔG_T^θ of Fe_2O_3-CaO system($\Delta G_T^\theta = A + BT$, J/mol)

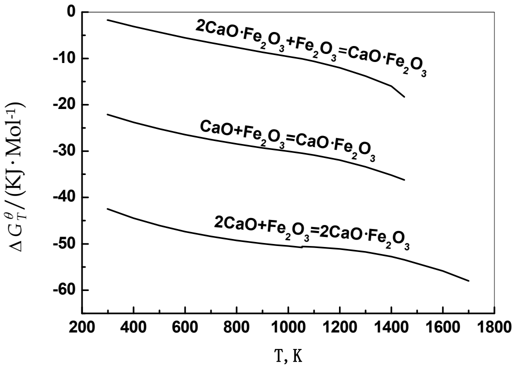

Fig. 9. Relationships between ΔG_T^θ and temperature in Fe_2O_3-CaO system

2.9 Al_2O_3- calcium ferrites system

Figure 1 shows that, the ΔG_T^θ of the reaction of Al_2O_3 with $CaCO_3$ is more negative than that of Fe_2O_3 with $CaCO_3$, therefore, the reaction of Fe_2O_3 with $CaCO_3$ occurs after the reaction of Al_2O_3 with $CaCO_3$ under the conditions of excess $CaCO_3$. The new generated calcium ferrites are likely to transform into calcium aluminates when $CaCO_3$ is insufficient, the reactions are as followed:

Reactions	A, J/mol	B, J/K.mol	Temperature, K
(3)$CaO•Fe_2O_3+ Al_2O_3 = 3CaO•Al_2O_3+3Fe_2O_3$	47922.7	4.5	298~1489
$(\frac{3}{2})2CaO\cdot Fe_2O_3 + Al_2O_3 = 3CaO\cdot Al_2O_3 + \frac{3}{2}Fe_2O_3$	49.6	-1.2×10^{-2}	298~1723
$(\frac{12}{7})CaO\cdot Fe_2O_3 + Al_2O_3 = (\frac{1}{7})12CaO\cdot 7Al_2O_3 + \frac{12}{7}Fe_2O_3$	32685.1	-24.5	298~1489
$(\frac{6}{7})2CaO\cdot Fe_2O_3 + Al_2O_3 = (\frac{1}{7})12CaO\cdot 7Al_2O_3 + \frac{6}{7}Fe_2O_3$	34514.4	-35.0	298~1723
$CaO•Fe_2O_3+ Al_2O_3 =CaO•Al_2O_3+Fe_2O_3$	3626.6	-7.5	298~1489
$(\frac{1}{2})CaO\cdot Fe_2O_3 + Al_2O_3 = (\frac{1}{2})CaO\cdot 2Al_2O_3 + \frac{1}{2}Fe_2O_3$	3215.1	-8.8	298~1489
$(\frac{1}{4})2CaO\cdot Fe_2O_3 + Al_2O_3 = (\frac{1}{2})CaO\cdot 2Al_2O_3 + \frac{1}{4}Fe_2O_3$	3168.6	-11.0	298~1723
$(\frac{1}{2})2CaO\cdot Fe_2O_3 + Al_2O_3 = CaO\cdot Al_2O_3 + \frac{1}{2}Fe_2O_3$	4009.5	-12.8	298~1723

Table 9. The ΔG_T^θ of the reaction Al_2O_3 with calcium ferrites($\Delta G_T^\theta = A + BT$, J/mol)

The relationships between ΔG_T^θ and temperature (T) are shown in figure 10. Figure 10 shows that, Al_2O_3 cannot replace the Fe_2O_3 in calcium ferrites to generate C_3A, and also cannot replace the Fe_2O_3 in $CaO•Fe_2O_3$(CF) to generate $C_{12}A_7$, but it can replace the Fe_2O_3 in $2CaO•Fe_2O_3$(C_2F) to generate $C_{12}A_7$ when the temperature is above 1000K, the higher temperature is, the more negative Gibbs free energy is; Al_2O_3 can react with CF and C_2F to form CA or CA_2, the higher temperature, more negative ΔG_T^θ. Because Fe_2O_3 reacts with CaO more easily to generate C_2F (Fig.9), therefore, $C_{12}A_7$ is the reaction product at normal roasting temperature(1073~1673K) under the conditions that CaO is sufficent in batching and the ternary compounds are not considered.

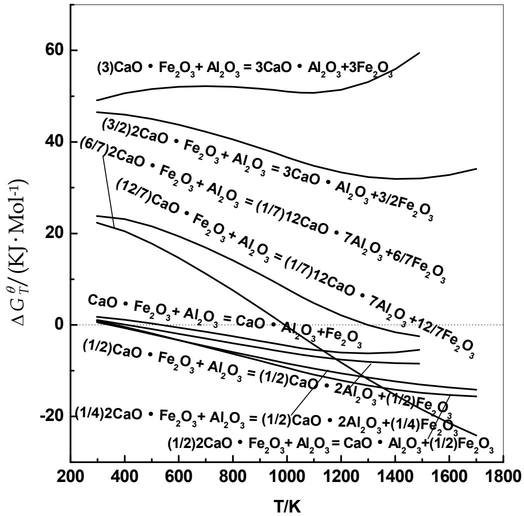

Fig. 10. Relationship between ΔG_T^θ and temperature in Al_2O_3- calcium ferrites system

3. Ternary compounds in Al_2O_3-CaO-SiO_2-Fe_2O_3 system

The ternary compounds formed by CaO, Al_2O_3 and SiO_2 in roasting process are mainly $2CaO\cdot Al_2O_3\cdot SiO_2$($C_2AS$), $CaO\cdot Al_2O_3\cdot 2SiO_2$($CAS_2$), $CaO\cdot Al_2O_3\cdot SiO_2$(CAS) and $3CaO\cdot Al_2O_3\cdot 3SiO_2$($C_3AS_3$). In addition, ternary compound $4CaO\cdot Al_2O_3\cdot Fe_2O_3$($C_4AF$) is formed form CaO, Al_2O_3 and Fe_2O_3. The equations are shown in table 10:

Reactions	A, J/mol	B, J/K.mol	Temperature, K
$CaO\cdot SiO_2 + CaO\cdot Al_2O_3 = 2CaO\cdot Al_2O_3\cdot SiO_2$	-30809.41	0.60	298~1600
$\frac{1}{2}Al_2O_3 + \frac{1}{2}CaO + SiO_2 = (\frac{1}{2})CaO\cdot Al_2O_3\cdot 2SiO_2$	-47997.55	-7.34	298~1826
$Al_2O_3 + 2CaO + SiO_2 = 2CaO\cdot Al_2O_3\cdot SiO_2$	-50305.83	-9.33	298~1600
$Al_2O_3 + CaO + SiO_2 = CaO\cdot Al_2O_3\cdot SiO_2$	-72975.54	-9.49	298~1700
$\frac{1}{3}Al_2O_3 + CaO + SiO_2 = (\frac{1}{3})3CaO\cdot Al_2O_3\cdot 3SiO_2$	-112354.51	20.86	298~1700
$4CaO + Al_2O_3 + Fe_2O_3 = 4CaO\cdot Al_2O_3\cdot Fe_2O_3$	-66826.92	-62.5	298~2000
$Al_2O_3 + 2CaO + SiO_2 = 2CaO\cdot Al_2O_3\cdot SiO_2$ (cacoclasite)	-136733.59	-17.59	298~1863

Table 10. The ΔG_T^θ of forming ternary compounds ($\Delta G_T^\theta = A + BT$, J/mol)

The relationships between ΔG_T^θ and temperature (T) are shown in figure 11. Figure 11 shows that, except for C_3AS_3(Hessonite), all the ΔG_T^θ of the reactions get more negative with the temperature increasing; the thermodynamic order of generating ternary compounds at sintering temperature of 1473K is: C_2AS(cacoclasite) , C_4AF, CAS, C_3AS_3, C_2AS, CAS_2.
C_2AS may also be formed by the reaction of CA and CS, the curve is presented in figure 11. Figure 11 shows that, the ΔG_T^θ of reaction (Al_2O_3+CaO+SiO_2) is lower than that of reaction of CA and CS to generate C_2AS. So C_2AS does not form from the binary compounds CA and CS, but from the direct combination among Al_2O_3, CaO, SiO_2. Qiusheng Zhou thinks that, C_4AF is not formed by mutual reaction of calcium ferrites and sodium aluminates, but from the direct reaction of CaO, Al_2O_3 and Fe_2O_3. Thermodynamic analysis of figure 1~figure11 shows that, reactions of Al_2O_3, Fe_2O_3, SiO_2 and CaO are much easier to form C_2AS and C_4AF, as shown in figure 12.

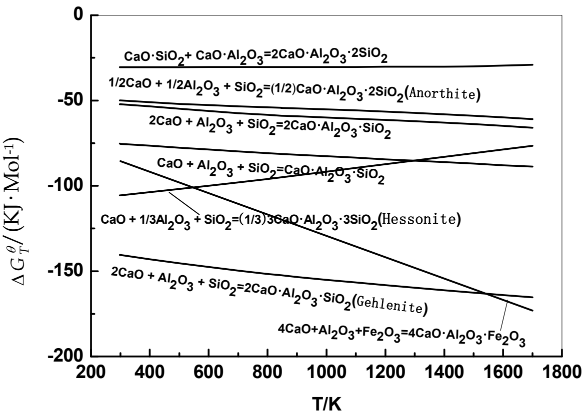

Fig. 11. Relationships between ΔG_T^θ of ternary compounds and temperature

Figure 12 shows that, in thermodynamics, C_2AS and C_4AF are firstly formed when Al_2O_3, Fe_2O_3, SiO_2 and CaO coexist, and then calcium silicates, calcium aluminates and calcium ferrites are generated.

4. Summary

1) When Al_2O_3 and Fe_2O_3 simultaneously react with CaO, calcium silicates are firstly formed, and then calcium ferrites. In thermodynamics, when one mole Al_2O_3 reacts with CaO, the sequence of generating calcium aluminates are $12CaO·7Al_2O_3$, $3CaO·Al_2O_3$, $CaO·Al_2O_3$, $CaO·2Al_2O_3$. When CaO is insufficient, redundant Al_2O_3 may promote the newly generated high calcium-to-aluminum ratio calcium aluminates to transform to lower calcium-to-aluminum ratio calcium aluminates. Fe_2O_3 reacts with CaO easily to form$2CaO·Fe_2O_3$, and $CaO·Fe_2O_3$ is not from the reaction of $2CaO·Fe_2O_3$ and Fe_2O_3 but form the directly combination of Fe_2O_3 with CaO. Al_2O_3 cannot replace the Fe_2O_3 in calcium ferrites to generate $3CaO·Al_2O_3$, and also cannot replace the Fe_2O_3 in $CaO•Fe_2O_3$ to generate $12CaO·7Al_2O_3$, but can replace the Fe_2O_3 in $2CaO•Fe_2O_3$ to generate $12CaO·7Al_2O_3$ when the temperature is above 1000K; Al_2O_3 can react with calcium ferrites to form $CaO·Al_2O_3$ or $CaO·2Al_2O_3$.

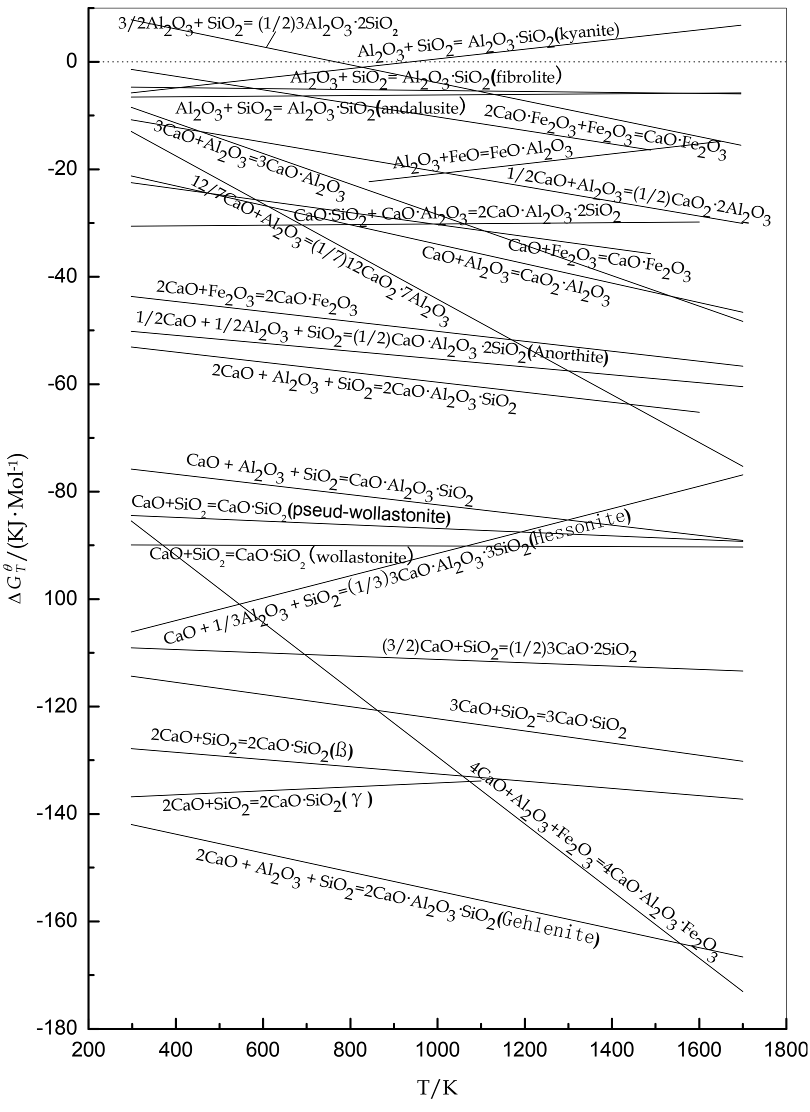

Fig. 12. Relationships between ΔG_T^θ and temperature in Al_2O_3-CaO-SiO_2-Fe_2O_3 system

2) One mole SiO_2 reacts with Al_2O_3 much easily to generate $3Al_2O_3 \cdot 2SiO_2$, Fe_2O_3 can not react with SiO_2 in the roasting process in the air. Al_2O_3 can not directly react with Fe_2O_3, but can react with wustite (FeO) to form $FeO \cdot Al_2O_3$.

3) In thermodynamics, the sequence of one mole SiO_2 reacts with CaO to form calcium silicates is $2CaO \cdot SiO_2$, $3CaO \cdot SiO_2$, $3CaO \cdot 2SiO_2$ and $CaO \cdot SiO_2$. Calcium aluminates can react with SiO_2 to transform to calcium silicates and Al_2O_3. $CaO \cdot 2Al_2O_3$ can not transform to $3CaO \cdot SiO_2$ when the roasting temperature is above 900K; when the temperature is above

1500K, $3CaO \cdot Al_2O_3$ can not transform to $3CaO \cdot SiO_2$; but the other calcium aluminates all can all react with SiO_2 to generate calcium silicates at 800~1700K.

4) Reactions among Al_2O_3, Fe_2O_3, SiO_2 and CaO easily form $2CaO \cdot Al_2O_3 \cdot SiO_2$ and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$. $2CaO \cdot Al_2O_3 \cdot SiO_2$ does not form from the reaction of $CaO \cdot Al_2O_3$ and $CaO \cdot SiO_2$, but from the direct reaction among Al_2O_3, CaO, SiO_2. And $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ is also not formed via mutual reaction of calcium ferrites and sodium aluminates, but from the direct reaction of CaO, Al_2O_3 and Fe_2O_3. In thermodynamics, when Al_2O_3, Fe_2O_3, SiO_2 and CaO coexist, $2CaO \cdot Al_2O_3 \cdot SiO_2$ and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ are firstly formed, and then calcium silicates, calcium aluminates and calcium ferrites.

5. Symbols used

Thermodynamic temperature: T, K
Thermal unit: J
Amount of substance: mole
Standard Gibbs free energy: ΔG_T^{θ} ,J

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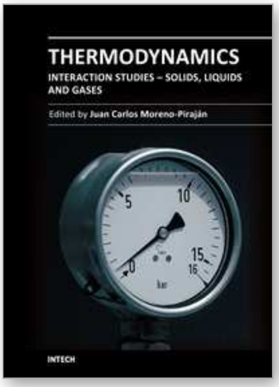

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