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Thermodynamics of Reactions Among Al$_2$O$_3$, CaO, SiO$_2$ and Fe$_2$O$_3$ During Roasting Processes

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1. Introduction

The thermodynamic of the chemical reactions among Al$_2$O$_3$, CaO, SiO$_2$ and Fe$_2$O$_3$ in the roasting processes was investigated in this chapter. The chemical reactions are classified into SiO$_2$-Al$_2$O$_3$ system, Fe$_2$O$_3$-Al$_2$O$_3$ system, SiO$_2$-Fe$_2$O$_3$ system, CaO-Al$_2$O$_3$ system, SiO$_2$-CaO system, SiO$_2$-calcium aluminates system, CaO-Fe$_2$O$_3$ system, Al$_2$O$_3$-calcium ferrites system and Al$_2$O$_3$-CaO-SiO$_2$-Fe$_2$O$_3$ system. When the roasting temperature is over 1100K, 3Al$_2$O$_3\cdot$2SiO$_2$ is preferentially formed in SiO$_2$-Al$_2$O$_3$ system; FeO$\cdot$Al$_2$O$_3$ can be formed in Fe$_2$O$_3$-Al$_2$O$_3$ system; ferric oxide and SiO$_2$ could not generate iron silicate; 12CaO$\cdot$7Al$_2$O$_3$ is preferentially formed in CaO-Al$_2$O$_3$ system when one mole Al$_2$O$_3$ reacts with CaO; 2CaO$\cdot$SiO$_2$ is preferentially formed in SiO$_2$-CaO system; except for CaO$\cdot$2Al$_2$O$_3$ and CaO$\cdot$Al$_2$O$_3$, the other calcium aluminates can transform into calcium silicate by reacting with SiO$_2$ in SiO$_2$-calcium aluminates system; 2CaO$\cdot$Fe$_2$O$_3$ is preferentially formed in CaO-Fe$_2$O$_3$ system; alumina is unable to form 3CaO$\cdot$Al$_2$O$_3$ with calcium ferrites(2CaO$\cdot$Fe$_2$O$_3$ and CaO$\cdot$Fe$_2$O$_3$), but able to form 12CaO$\cdot$7Al$_2$O$_3$ with 2CaO$\cdot$Fe$_2$O$_3$; when CaO, Fe$_2$O$_3$, Al$_2$O$_3$, SiO$_2$ coexist, they are more likely to form ternary compound 2CaO$\cdot$Al$_2$O$_3\cdot$SiO$_2$ and 4CaO$\cdot$Al$_2$O$_3\cdot$Fe$_2$O$_3$.

2. Binary compounds

2.1 Fe$_2$O$_3$-Al$_2$O$_3$-CaCO$_3$ system

Fe$_2$O$_3$ and Al$_2$O$_3$ can all react with limestone during roasting to generate corresponding aluminates and ferrites. In Fe$_2$O$_3$-Al$_2$O$_3$-CaO system, the reaction Fe$_2$O$_3$ and Al$_2$O$_3$ with CaCO$_3$ coexist, and the reactions equations are as followed:

Reactions	A, J/mol	B, J/K.mol	Temperature, K
CaCO$_3$+Al$_2$O$_3$=CaO$\cdot$Al$_2$O$_3$+CO$_2$	161088.3	-244.1	298~1200
CaCO$_3$+Fe$_2$O$_3$=CaO$\cdot$Fe$_2$O$_3$+CO$_2$	151677.8	-220.9	298~1200

Table 1. The ΔG_T^θ of Fe$_2$O$_3$-Al$_2$O$_3$-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.
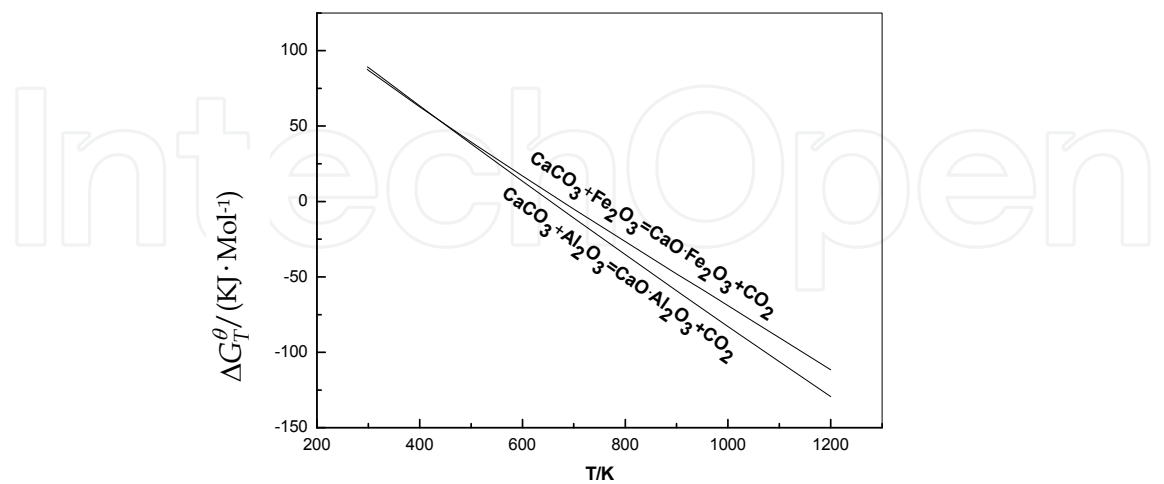

Fig. 1. Relationships between ΔG_T^θ and temperature in Fe_2O_3-Al_2O_3-$CaCO_3$ system

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 SiO₂-Al₂O₃ 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）

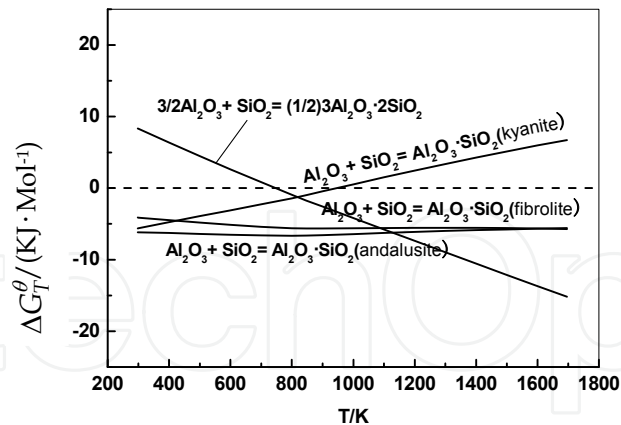The relationships of ΔG_T^θ and temperature in Al_2O_3-SiO_2 system is shown in figure 2.

Fig. 2. Relationships of ΔG_T^{θ} and temperature in Al$_2$O$_3$-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$_3$S$_2$ decreases with the rise of temperature. The thermodynamic order of forming aluminium silicates is A$_3$S$_2$, AS(andalusite), AS(fibrolite) at 1100~1700K.

2.3 Fe$_2$O$_3$-Al$_2$O$_3$ system

Al$_2$O$_3$ does not directly react with Fe$_2$O$_3$, but Al$_2$O$_3$ may react with wustite (FeO) produced during roasting process to form FeO·Al$_2$O$_3$. 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$_x$O(x=0.83~0.95), whose crystal structure is absence type crystallology. For convenience, FeO is expressed as wustite in this thesis. Al$_2$O$_3$ may react with wustite(FeO) to form FeO·Al$_2$O$_3$ 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:
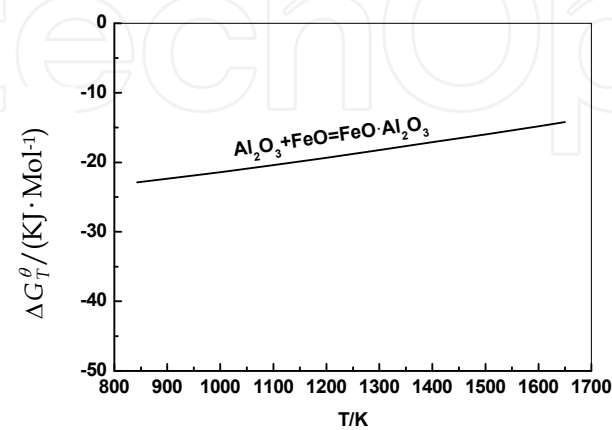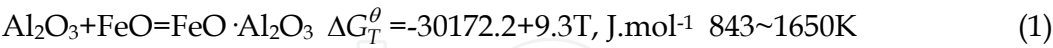
$$Al_2O_3+FeO=FeO \cdot Al_2O_3 \quad \Delta G_T^{\theta} =-30172.2+9.3T, \ J.mol^{-1} \quad 843~1650K \quad (1)$$

Fig. 3. Relationship of ΔG_T^{θ} and temperature in Fe$_2$O$_3$-Al$_2$O$_3$ 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 SiO₂-Fe₂O₃ 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 F₂S).
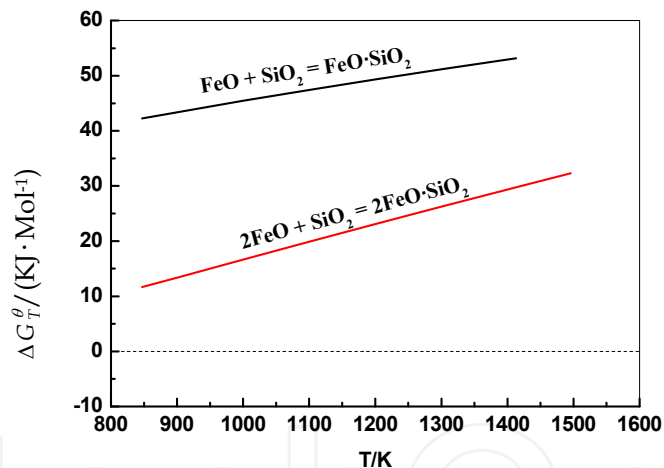

Fig. 4. Relationships of ΔG_T^θ and temperature in SiO_2-Fe_2O_3 system

2.5 CaO-Al₂O₃ 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 $CaO \cdot 2Al_2O_3$ (CA₂). As regard as the calcium aluminates only $C_{12}A_7$ can be totally soluble in soda solution, C₃A and CA dissolve with a slow speed, and the other calcium aluminates such as CA₂ are completely insoluble. Equations that Al_2O_3 reacted with CaO to form C₃A, C₁₂A₇, CA and CA₂ 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）

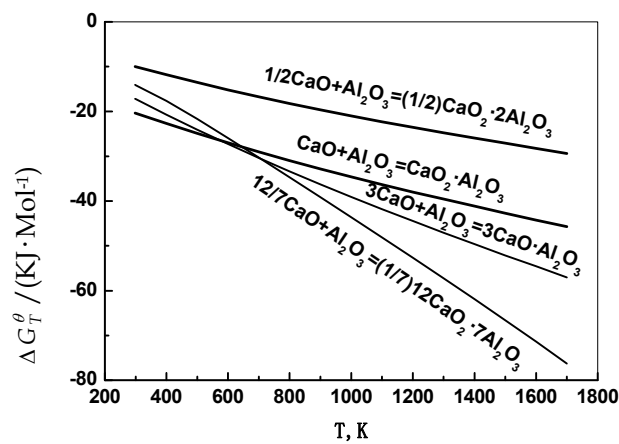The relationships between ΔG_T^θ and temperature (T) are shown in figure 5.

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.
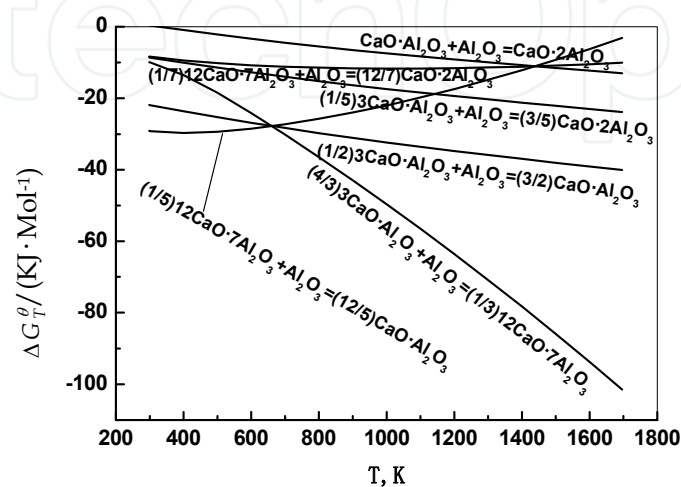

Fig. 6. Relationships between ΔG_T^θ of reactions Al_2O_3-calcium aluminates system and temperature

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 SiO₂- CaO system

SiO_2 can react with CaO to form $CaO \cdot SiO_2$ (CS), $3CaO \cdot 2SiO_2$ (C_3S_2), $2CaO \cdot SiO_2$ (C_2S) and $3CaO \cdot SiO_2$(C_3S) in roasting process. The reactions are shown in table 6, and the relationships between $\triangle G^0$ 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
$CaO+SiO_2 = CaO \cdot SiO_2$(pseud-wollastonite)	-83453.0	-3.4	298~1817
$CaO+SiO_2 = CaO \cdot SiO_2$(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
$3CaO+SiO_2 = 3CaO \cdot SiO_2$	-111011.9	-11.3	298~1800
$2CaO+SiO_2 = 2CaO \cdot SiO_2(\beta)$	-125875.1	-6.7	298~2403
$2CaO+SiO_2 = 2CaO \cdot SiO_2(\gamma)$	-137890.1	3.7	298~1100

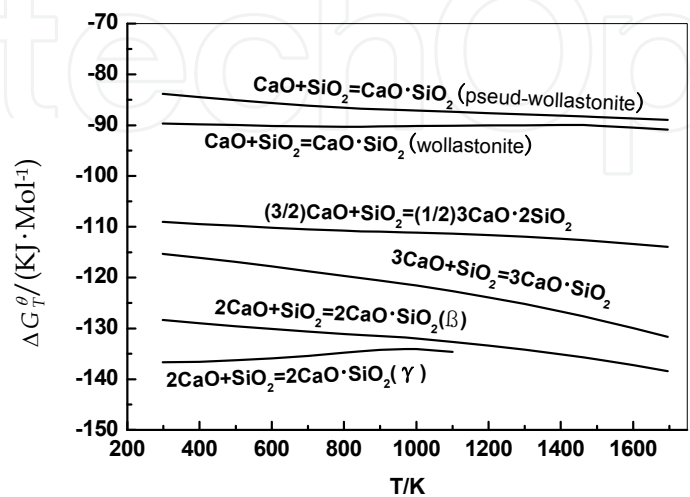Table 6. The ΔG_T^θ of SiO_2-CaO system($\Delta G_T^\theta = A + BT$, J/mol)

Fig. 7. Relationships between ΔG_T^θ and temperature

Figure7 shows that, SiO$_2$ reacts with CaO to form γ-C$_2$S when temperature below 1100K, but β-C$_2$S comes into being when the temperature above 1100K. At normal roasting temperature, the thermodynamic order of forming calcium silicate is C$_2$S, C$_3$S, C$_3$S$_2$, CS.

Figure 5 ~ figure 7 show that, CaO reacts with SiO$_2$ and Al$_2$O$_3$ firstly to form C$_2$S, 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$_2$O$_3$ 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$_2$O$_3$ because SiO$_2$ is more acidity than that of Al$_2$O$_3$. 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$_3$S+6Al$_2$O$_3$) 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$_3$S+3Al$_2$O$_3$) 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$_3$A, 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)
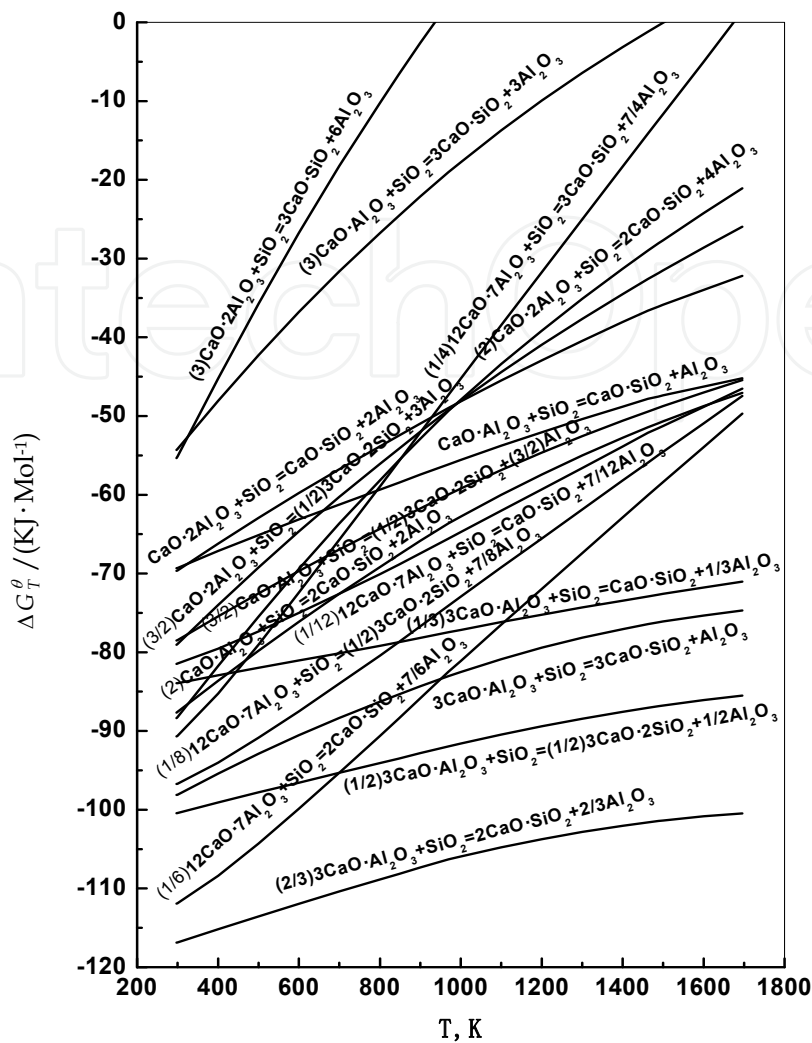
Fig. 8. Relationships between ΔG_T^θ and temperature in SiO$_2$-calcium aluminates system

2.8 CaO- Fe$_2$O$_3$ system

Fe$_2$O$_3$ can react with CaO to form CaO·Fe$_2$O$_3$(CF) and 2CaO·Fe$_2$O$_3$(C$_2$F). When Fe$_2$O$_3$ is used up, the newly formed C$_2$F can react with Fe$_2$O$_3$ to form CF. The reaction equations are shown in table 8, and the relationships between $\triangle$G^0 and temperature are shown in figure 9.

Figure 9 shows that, Fe$_2$O$_3$ reacts with CaO much easily to form C$_2$F; CF is not from the reaction of C$_2$F and Fe$_2$O$_3$, but from the directly reaction of Fe$_2$O$_3$ with CaO. When Fe$_2$O$_3$ is excess, C$_2$F can react with Fe$_2$O$_3$ to form CF.

Reactions	A, J/mol	B, J/K.mol	Temperature, K
CaO+Fe$_2$O$_3$=CaO·Fe$_2$O$_3$	-19179.9	-11.1	298~1489
2CaO+Fe$_2$O$_3$=2CaO·Fe$_2$O$_3$	-40866.7	-9.3	298~1723
2CaO·Fe$_2$O$_3$+Fe$_2$O$_3$=(2)CaO·Fe$_2$O$_3$	2340.8	-12.6	298~1489

Table 8. The ΔG_T^θ of Fe$_2$O$_3$-CaO system($\Delta G_T^\theta = A + BT$, J/mol)
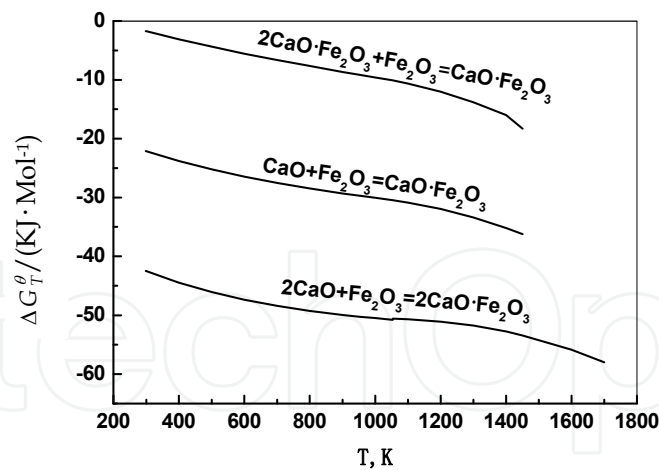
Fig. 9. Relationships between ΔG_T^{θ} and temperature in Fe_2O_3-CaO system

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
$(3)CaO \cdot Fe_2O_3 + Al_2O_3 = 3CaO \cdot Al_2O_3 + 3Fe_2O_3$	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
$CaO \cdot Fe_2O_3 + Al_2O_3 = CaO \cdot Al_2O_3 + Fe_2O_3$	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 $CaO \cdot Fe_2O_3$(CF) to generate $C_{12}A_7$, but it can replace the Fe_2O_3 in $2CaO \cdot Fe_2O_3$(C$_2$F) 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 CA₂, 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 suffcient in batching and the ternary compounds are not considered.
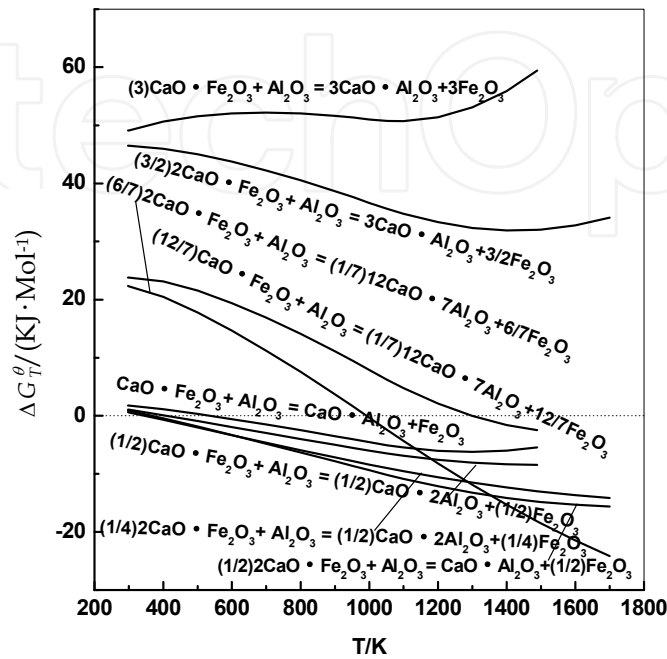

Fig. 10. Relationship between ΔG_T^{θ} and temperature in Al₂O₃- calcium ferrites system

3. Ternary compounds in Al₂O₃-CaO-SiO₂-Fe₂O₃ system

The ternary compounds formed by CaO, Al₂O₃ and SiO₂ 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, Al₂O₃ and Fe₂O₃. 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$_3$AS$_3$(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$_2$AS(cacoclasite) , C$_4$AF, CAS, C$_3$AS$_3$, C$_2$AS, CAS$_2$.

C$_2$AS 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$_2$O$_3$+CaO+SiO$_2$) is lower than that of reaction of CA and CS to generate C$_2$AS. So C$_2$AS does not form from the binary compounds CA and CS, but from the direct combination among Al$_2$O$_3$, CaO, SiO$_2$. Qiusheng Zhou thinks that, C$_4$AF is not formed by mutual reaction of calcium ferrites and sodium aluminates, but from the direct reaction of CaO, Al$_2$O$_3$ and Fe$_2$O$_3$. Thermodynamic analysis of figure 1~figure11 shows that, reactions of Al$_2$O$_3$, Fe$_2$O$_3$, SiO$_2$ and CaO are much easier to form C$_2$AS and C$_4$AF, as shown in figure 12.
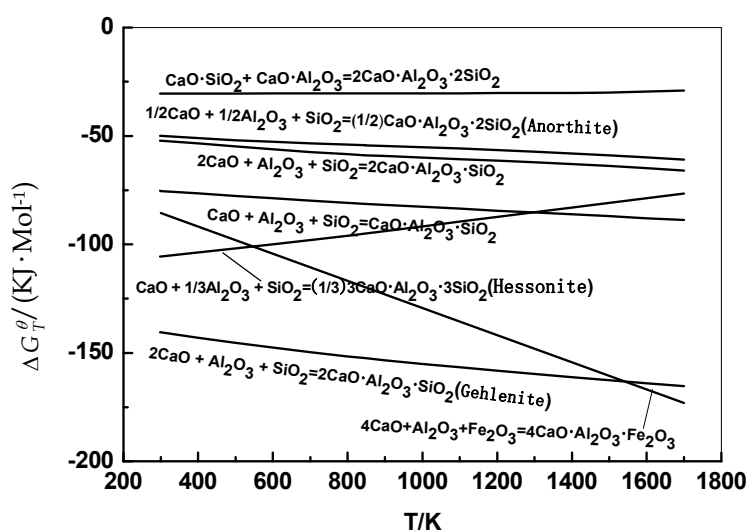

Fig. 11. Relationships between ΔG_T^θ of ternary compounds and temperature

Figure 12 shows that, in thermodynamics, C$_2$AS and C$_4$AF are firstly formed when Al$_2$O$_3$, Fe$_2$O$_3$, SiO$_2$ and CaO coexist, and then calcium silicates, calcium aluminates and calcium ferrites are generated.

4. Summary

1) When Al$_2$O$_3$ and Fe$_2$O$_3$ simultaneously react with CaO, calcium silicates are firstly formed, and then calcium ferrites. In thermodynamics, when one mole Al$_2$O$_3$ reacts with CaO, the sequence of generating calcium aluminates are 12CaO$\cdot$7Al$_2$O$_3$, 3CaO$\cdot$Al$_2$O$_3$, CaO$\cdot$Al$_2$O$_3$, CaO$\cdot$2Al$_2$O$_3$. When CaO is insufficient, redundant Al$_2$O$_3$ may promote the newly generated high calcium-to-aluminum ratio calcium aluminates to transform to lower calcium-to-aluminum ratio calcium aluminates. Fe$_2$O$_3$ reacts with CaO easily to form2CaO$\cdot$Fe$_2$O$_3$, and CaO$\cdot$Fe$_2$O$_3$ is not from the reaction of 2CaO$\cdot$Fe$_2$O$_3$ and Fe$_2$O$_3$ but form the directly combination of Fe$_2$O$_3$ with CaO. Al$_2$O$_3$ cannot replace the Fe$_2$O$_3$ in calcium ferrites to generate 3CaO$\cdot$Al$_2$O$_3$, and also cannot replace the Fe$_2$O$_3$ in CaO•Fe$_2$O$_3$ to generate 12CaO$\cdot$7Al$_2$O$_3$, but can replace the Fe$_2$O$_3$ in 2CaO•Fe$_2$O$_3$ to generate 12CaO$\cdot$7Al$_2$O$_3$ when the temperature is above 1000K; Al$_2$O$_3$ can react with calcium ferrites to form CaO$\cdot$Al$_2$O$_3$ or CaO$\cdot$2Al$_2$O$_3$.
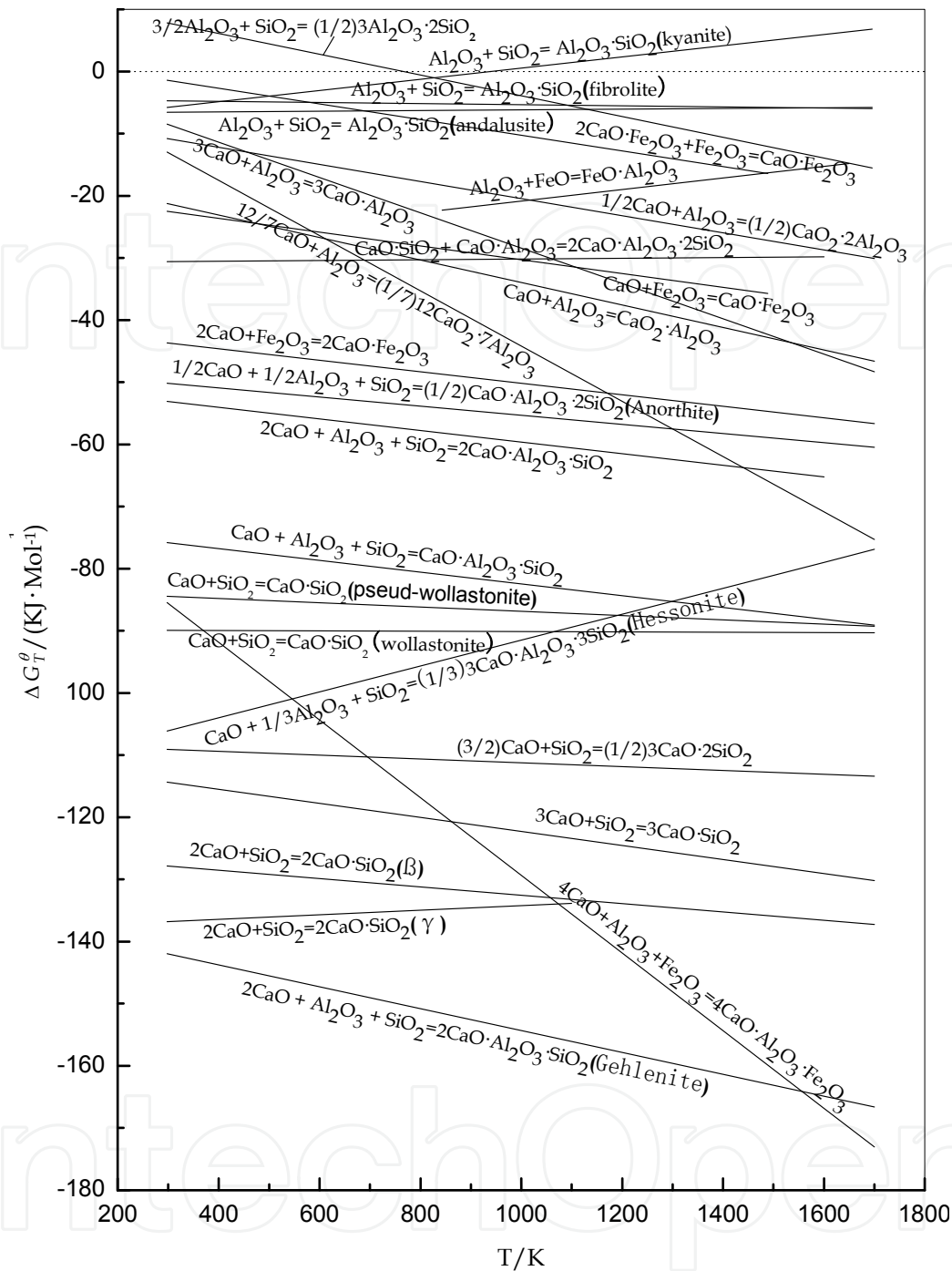
Fig. 12. Relationships between ΔG_T^θ and temperature in Al$_2$O$_3$-CaO-SiO$_2$-Fe$_2$O$_3$ system

2) One mole SiO$_2$ reacts with Al$_2$O$_3$ much easily to generate 3Al$_2$O$_3$·2SiO$_2$, Fe$_2$O$_3$ can not react with SiO$_2$ in the roasting process in the air. Al$_2$O$_3$ can not directly react with Fe$_2$O$_3$, but can react with wustite (FeO) to form FeO·Al$_2$O$_3$.

3) In thermodynamics, the sequence of one mole SiO$_2$ reacts with CaO to form calcium silicates is 2CaO·SiO$_2$, 3CaO·SiO$_2$, 3CaO·2SiO$_2$ and CaO·SiO$_2$. Calcium aluminates can react with SiO$_2$ to transform to calcium silicates and Al$_2$O$_3$. CaO·2Al$_2$O$_3$ can not transform to 3CaO·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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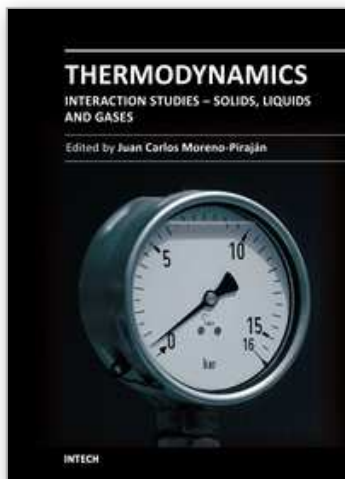
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