Phase formation in the process of iron and titanium oxides metallothermic reduction

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Abstract. Phase formation in the alloys obtained during process of collective Ti and Fe oxides reduction by Al has been investigated. Thermodynamic computer simulation of the process (based on the system free energy minimizing principle) has indicated a range of possible reactions with various metallic compounds formation. Differential-thermal (DT), X-ray diffraction (XRD) methods and melting of reaction mixtures at 1773-1973 K have been carried out to confirm the thermodynamic predictions. The DT experiments showed that the process began after Al melting at 943 K and was accompanied by large exothermic effects. The intermetallic phases of alloys with various content of Ti, Fe and Al have been observed by the XRD analysis.

1. Introduction
Joint Fe and Ti aluminothermy reduction from oxide compounds is described by many possible reactions such as following:

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\begin{align*}
\text{Fe}_2\text{O}_3 + 2\text{Al} &= 2\text{Fe} + \text{Al}_2\text{O}_3 \\
3\text{Fe}_2\text{O}_3 + 2\text{Al} &= 6\text{FeO} + \text{Al}_2\text{O}_3 \\
3\text{FeO} + 2\text{Al} &= 3\text{Fe} + \text{Al}_2\text{O}_3 \\
3\text{TiO}_2 + 4\text{Al} &= 3\text{Ti} + 2\text{Al}_2\text{O}_3 \\
3\text{TiO}_2 + 2\text{Al} &= 3\text{TiO} + \text{Al}_2\text{O}_3 \\
3\text{TiO} + 2\text{Al} &= 3\text{Ti} + \text{Al}_2\text{O}_3 \\
3\text{TiO} + 5\text{Al} &= 3\text{AlTi} + \text{Al}_2\text{O}_3 \\
3\text{TiO} + 3\text{FeO} + 4\text{Al} &= 3\text{FeTi} + 2\text{Al}_2\text{O}_3 \\
2\text{TiO} + \text{FeO} + 3\text{Al} &= \text{FeTi} + \text{AlTi} + \text{Al}_2\text{O}_3 \\
\text{FeTiO}_3 + 2\text{Al} &= \text{FeTi} + \text{Al}_2\text{O}_3
\end{align*}
\]

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FeTi + Al = AlTi + Fe  \hspace{1cm} (11)

It is difficult to find out the dominant reactions because of the high temperatures and rates of processes. Information of the intermetallic compounds which form in the alloys could serve to increase metals reduction.

The purpose of the present work was to consider iron-titanium alloys formation in the aluminothermy reduction of iron and titanium oxides. Thermodynamic simulation method and its experimental testing results are presented.

2. Experimental

Computer thermodynamic simulation based on the free energy minimizing principle of the closed system was carried out. Perfect solutions Raoult law was obeyed supposedly by all investigated melts and activities factors were taken as unities. On this basis the equilibrium distribution of the components between metal and oxide phases was determined.

The experiments were carried out in vertical tube resistance furnace. Mixture of 100-150 g mass was charged in alumina crucible preheated with furnace to 1773 K. After melting and 15-20 min exposition at the 1873-1923 K the crucible with melt was extracted from the furnace and cooled in the air. The formed products were subjected to chemical and X-ray diffraction (XRD) analysis. Additional information was obtained also from differential-thermal (DT) analysis.

3. Results and Discussion

Thermodynamic simulation using only (1-4) reactions of interaction between aluminum and the composition ((kmol) 0.03Fe$_2$O$_3$ - 0.097FeTiO$_3$ - 0.35TiO$_2$) have shown that heating weakly affects the reduction percentage. The most effect gives a factor of reductant quantity. Upon the consumption of 0.073 kmol Al, the iron and titanium reduction degree (the ratio of component quantity in the metal phase to its initial value in oxide phase) was close to 1.

Taking into account a titanium monoxide (reaction 5) formation resulted in a fall of titanium reduction degree (figure 1a). Moreover, at temperature more than 1073 K the reaction (6) is not possible in principle. The reduction of Ti from oxide compounds to the metal form (at the condition of TiO appearance) becomes possible with the FeTi and AlTi intermetallic compounds formation. The most preferable are temperatures 1873-2023 K. However negative values of Gibbs energy for reactions (7-10) decrease with temperature increasing and consequently equilibrium constants of these reactions are reduced as well as its completeness (figure 1b). Calculations at 1873 K have shown (figure 2) that completeness of the reactions (7-10) can be increased with the iron and aluminum quantity increase in the metal phase. Besides, AlTi intermetallic compound formation is more preferable according to reactions (11).

DT analysis of the TiO$_2$ + CaO + CaF$_2$ + Al and TiO$_2$ + CaO + CaF$_2$ + Fe$_2$O$_3$ + Al mixtures indicated that titanium oxides reduction in the presence (figure 4) as well as absence (figure 3) of iron oxides enters the very active stage right after liquid aluminum appearance (943-1073 K).

The melting experiments at 1873-1923 K for the Fe$_2$O$_3$ - FeTiO$_3$ - TiO$_2$ mixtures with aluminum and CaO, CaF$_2$ additives have showed good agreement with thermodynamic calculations. Experiments have revealed presence of Fe$_5$Ti, AlFeTi, Al$_3$Fe$_4$, AlTi$_3$, Ti$_9$Al$_3$ intermetallic compounds in formed alloys. The titanium reduction degree reached 0.85. This is an obvious evidence that TiO is an unstable compound. Its formation and existence could be affected by temperature and other components concentration in oxide phase.

4. Conclusions

Joint iron and titanium aluminothermic reduction from oxides is characterized by TiO as well as Fe-Ti, Al-Ti, Al-Fe-Ti intermetallic compounds formation. This process depends on existence conditions of these compounds.
Figure 1. Temperature dependence of components composition in oxide (a) and metal (b) phases in mixture (kmol) 0.03Fe$_2$O$_3$ + 0.097FeTiO$_3$ + 0.35TiO$_2$ + 0.073 Al.

Figure 2. Components composition dependence in metal phase on Al content in mixture (kmol) 0.03Fe$_2$O$_3$ + 0.097FeTiO$_3$ + 0.35TiO$_2$ + 0.073 Al at 1873 K.
Figure 3. Differential-thermal analysis of interaction between aluminum and mixture TiO$_2$ + CaO + CaF$_2$.

Figure 4. Differential-thermal analysis of interaction between aluminum and mixture TiO$_2$ + CaO + CaF$_2$ + Fe$_2$O$_3$. 