A self-sustaining reaction for titanium aluminides production via alumino-calciothermic reduction of TiO\textsubscript{2}

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Titanium aluminides can be produced via an alumino-calciothermic reduction of TiO\textsubscript{2} in presence of KClO\textsubscript{4}. This reaction, named KRH process, has been studied in this paper. The results show that after heating of starting materials with rate of 20°C/min, a self-sustaining reaction is ignited at about 550°C which led to the rapid increasing of system temperature to 1950°C during a short time of 192 s with a mean internal heating rate of around 437°C/min.

Keywords: Alumino-calciothermic, TiO\textsubscript{2}, Self-sustaining reaction

Reduction of TiO\textsubscript{2} with a powered reducing agent like Ca\textsuperscript{1,2} or CaH\textsubscript{2,3,4} can be considered as an alternative process for production of titanium. On the other hand, using of Al as a weaker reducing agent can be led to production of titanium aluminides-alumina composite powder\textsuperscript{5,6}. Direct reduction of TiO\textsubscript{2} is an interesting idea, especially due to the removing of chlorination process which is included in conventional Kroll process for production of metallic titanium. Recently, we proposed a process, named KRH process, for production of separated phases of titanium aluminides and slag using both Al and Ca reducing agents. This process is occurred on the basis a variety of reactions between TiO\textsubscript{2}, Al, Ca and KClO\textsubscript{4}\textsuperscript{7} like following reaction\textsuperscript{8}:

\[3\text{TiO}_2 + 11\text{Al} + 2\text{KClO}_4 + 2\text{Ca} = 3\text{TiAl} + 2\text{CaAl}_2\text{O}_4 + 2\text{KCl}\]

... (1)

It has been proved that this reaction is governed by a multi-stage mechanism on the basis of a complicated self-sustaining high temperature synthesis (SHS)\textsuperscript{9}. In SHS processes, after heating of starting materials to ignition temperature, reaction progresses in a self-sustaining state without any need for external energy. Therefore understanding of self-sustaining region of these processes has scientific and technical important. In this paper, self-sustaining state of KRH process was investigated.

Experimental Procedure

Raw materials
The elemental powders of Al (Merck, <100 µm, 99.95%), TiO\textsubscript{2} (Merck, <150 µm, 99.98%), KClO\textsubscript{4} (Merck, <150 µm, 99.99%) and Ca (Merck, granulated, 99.95%) were used as raw materials. The reactions were performed in an Al\textsubscript{2}O\textsubscript{3} crucible (99.95%).

KRH process
The powders of TiO\textsubscript{2}, Al, Ca and KClO\textsubscript{4} as raw materials were combined and mixed by a mixer. The mixed powders were placed in an alumina crucible after which was pounded by a mallet. The crucible then sealed by means of a ceramic bung. The crucible was placed in a flanged steel vessel where the empty space within the vessel was filled with MgO or Al\textsubscript{2}O\textsubscript{3} powder. The presence of MgO or Al\textsubscript{2}O\textsubscript{3} powders is desirable for preventing damage to ceramic crucible which may occur as a result of severe shocking during the reaction. The steel vessel was sealed by means of screwing with a steel bung (Fig. 1) and then was placed into an electric furnace. The heating of the furnace was carried out with the rate of 20°C/min to 1000 °C. A S type thermocouple (JUMO model) was used for measurement of temperature in the reaction vessel (Fig. 1). After 20 min when the reaction was fulfilled, furnace was turned off. After ensuring the cooling of vessel to about room temperature, the vessel was removed.

Analyzing
In order to reaction study, the differential thermal analysis (DTA) with heating rate of 20°C/min was
performed. Different mixtures of raw materials were prepared. About 100 mg of each was placed in DTA analyzer where heated under static argon with high purity. The output materials from DTA analyzer (about 1 g) were characterized by XRD (siemens kristalloflex 810 equipped with a copper anode operated at 40 kV and 30 mA, with a graphite curved monochromator on the diffracted beam).

Results and Discussion

On the basis of reaction (1) TiAl and CaAl$_4$O$_7$ can be produced from TiO$_2$, Al, Ca and KClO$_4$ raw materials: After the reaction, products included two parts that were easily separated by using a hammer (Fig. 2). These two parts were a metallic part consisting of gamma TiAl as major phase and Ti$_3$Al as minor phase and a non-metallic slag part of CaAl$_4$O$_7$ according to XRD analysis.

To understand the process steps, the starting materials according to reaction (1) as well as all supposed sub-reactions were heated in a DTA analyzer. Then, the product obtained from heating of starting materials up to different temperatures analyzed by a XRD analyzer. The results are shown in Fig. 3. Any present peak in reaction between 3TiO$_2$+11Al+2KClO$_4$+2Ca starting materials can be described using consideration of DTA curves of other reactions. According to Fig. 3, during heating of 3TiO$_2$+11Al+2KClO$_4$+2Ca starting materials, there was an endothermic peak at 349°C, which is related to phase transformation of KClO$_4$ from rhombic to cubic structure, according to Lee et al.$^{10}$. Second endothermic peak at 472°C was related to phase transformation of Ca from fcc to bcc that has been reported to occurrence at 476°C$^{11}$. Third peak at 534°C was related to reaction between Ca and KClO$_4$ which led to production of KCl and CaO. Remaining of KClO$_4$ starting material reacted with Al at same temperature, due to instability of remaining KClO$_4$ high energy material after ignition of process. There were two exothermic peaks at 584 and 600°C which were related to a two-stage mechanism for production of TiAl product according to following reactions$^9$:

$$3\text{TiO}_2+5\text{Al} = \text{Ti}_3\text{Al}+2\text{Al}_2\text{O}_3 \quad \ldots (2)$$

$$\text{Ti}_3\text{Al}+2\text{Al} = 3\text{TiAl} \quad \ldots (3)$$

On the other hand, the endothermic peak at 613°C was related to reaction between Al$_2$O$_3$ and CaO that led to formation of CaAl$_4$O$_7$ according to following reaction on the basis of Al$_2$O$_3$-CaO phase diagram$^{12}$:

$$\text{CaO} + 2\text{Al}_2\text{O}_3 = \text{CaAl}_4\text{O}_7 (\Delta H_{880}= + 232 \text{ kcal}) \quad \ldots (4)$$

The last peak at 737°C was related to the KCl melting. It should be noted that the conditions during the DTA analysis are different from these during reactions in the experimental vessel (Fig. 1). The experimental vessel is a closed container that the heat lose is very smaller than the DTA analyzer. This leads to formation of an extra phase (CaAl$_{12}$O$_{19}$) in addition of γ-TiAl, Ti$_3$Al and CaAl$_4$O$_7$ in DTA analysis.

For determining of the self-sustaining region of reaction, DTA analysis of 3TiO$_2$+11Al+2KClO$_4$+2Ca starting materials as well as results of XRD analysis from obtained product after heating of starting materials up to different temperatures is shown in Fig. 4. According to this figure, after occurrence of
the first exothermic peak at 524°C, the same results from XRD analyses of product were obtained. On the other hand, obtained product after heating of starting materials at all temperatures more than 524°C were TiAl, Ti₃Al, Ca₃Al₂O₇ and CaAl₁₂O₁₉. It means that the stopping of the materials heating had not any effect after occurrence of the first exothermic peak and reaction progress was in a self-sustaining state.

Temperature versus time curve in reaction vessel (Fig. 1) during the reaction as well as DTA cures of reaction on the basis of reaction time were shown in Fig. 5. According to the Fig. 5a, ignition and combustion temperatures of reaction in reaction vessel is 505°C and 1950°C respectively and time interval between occurrence of reaction ignition and obtaining of the highest temperature was 192 s. In this time period, system is in a self-sustaining state. On the other hand, time interval between occurrences of the first and third exothermic peaks in DTA curve was 228 s (Fig. 5b). There is a good agreement between two mentioned interval temperatures. Therefore, during the first to third peaks in DTA curve(Fig. 5b), in temperature interval of 505-1950°C and time interval of 2552-2744
s after starting of reaction in reaction vessel, the reaction was in a self-sustaining state. According to Fig. 5, in ignition temperature, external heating with a rate of 20°C/min was replaced by an internal self-sustaining heating with a rate of around 437°C/min.

Conclusions

Heating of TiO$_2$, Al, Ca and KClO$_4$ starting materials can be led to the ignition of a self-sustaining high temperature process (SHS) and production of separated phases of titanium aluminides and slag. After heating of starting materials up to 550°C, reaction went to a self-sustaining manner for 192 s, which led to increasing of system temperature to a high amount of 1950°C. At ignition temperature, the external heating of materials with a rate of 20°C/min was replaced by an internal heating with a rate of around 437°C/min.

References