INTRINSIC KINETICS OF THE OXIDATION OF Na$_2$TiF$_6$ AND Na$_3$TiF$_6$

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The intrinsic kinetics, unaffected by diffusional and mass transfer effects, of the air oxidation of Na$_2$TiF$_6$ and Na$_3$TiF$_6$ were determined by using a nonisothermal technique. The oxidation of these sodium fluorotitanates proceeds through two-step reactions involving the formation of oxyfluorotitanate, i.e. Na$_3$TiOF$_5$, as the intermediate. The oxidation rate shows a first-order dependence on the amount of the unreacted solids for each of the two-step reactions for both fluorotitanates. The activation energy for the further oxidation of Na$_3$TiOF$_5$ to a mixture of NaF + TiO$_2$ was determined to be 52.4 kJ/mol and 55.3 kJ/mol for Na$_2$TiF$_6$ and Na$_3$TiF$_6$ as reactants, respectively.

Titanium is currently made mostly by the Kroll process [1], but some is also made by the Hunter process [2]. Both the Kroll and the Hunter process use natural or synthetic rutile, Richards Bay titania slag or upgraded sand ilmenite as the raw material. In lengthy separation and purification steps, rutile is chlorinated to produce TiCl$_4$ and other impurity chlorides, followed by distillation to separate TiCl$_4$ from the other chlorides; the TiCl$_4$ is then reduced with liquid Mg (Kroll), or liquid Na (Hunter) or by means of two-step electrolysis in the recently developed Ginatta process. TiCl$_4$ and most of the impurity chlorides are hygroscopic and must be protected from contact with the atmosphere to prevent the formation of oxides and oxychlorides, which would lead to oxygen contamination of the metal. Closed containers with an argon atmosphere are used throughout. Neither the Kroll nor the Hunter process is continuous. Expensive raw materials, many processing steps, and a high energy consumption are all disadvantages of the Kroll and Hunter processes.
A process to manufacture metallic Ti that would utilize lower-grade titanium ores such as ilmenite, FeTiO₃, and involve simpler process steps has long been sought. Early attempts to develop such a process focused on the conversion of ilmenite with fluoride salts as the Ti extraction agent to produce fluorotitanates or Ti fluorides. Kroll [3] discussed the advantages and problems of producing TiF₄ and alkalimetal fluorotitanates such as Na₂TiF₆ as alternatives to the chloride route to Ti. The distinct advantage emphasized by Kroll[4] is that oxygen does not displace fluoride from Ti as does chloride, making the fluorotitanates somewhat easier to handle.

Despite a number of investigations on the extraction of Ti from ores with fluoride compounds such as HF [5-6], H₂SiF₆ [7], alkalimetal fluorosilicates [8-9], NH₄F [10], alkalimetal double fluorides [11], CaF₂ with H₂SO₄ [12] and FeF₃ [13], the stability of the sodium fluorotitanates in air with increasing temperature has not been reported in the literature. The high-temperature reaction of titaniferous ores with Na₂SiF₆ leads to the formation of Na₂TiF₆, while the hydrothermal treatment of TiOSO₄ solutions results in the precipitation of Na₂TiF₆. After separation and purification, both fluorotitanates can be reduced to Ti metal with reactive metals, e.g. Na or Al, or by electrolysis of the molten salts.

In the present study, the intrinsic kinetics of the oxidation of Na₂TiF₆ and Na₃TiF₆ was determined in air. A nonisothermal technique was used which yields the temperature dependence of the rate constant from a single run.

**Theoretical consideration**

The high stability of fluorotitanates in air facilitates their treatment prior to the reduction step. We found previously [14] that the air oxidation of Na₂TiF₆ and Na₃TiF₆ proceeds through two-step reactions, with formation of the oxyfluorotitanate, Na₃TiOF₅, as the intermediate. The oxidation of Na₂TiF₆ is presented below:

\[
3 \text{Na}_2\text{TiF}_6(s) + \text{O}_2(g) = 2 \text{Na}_3\text{TiOF}_5(s) + \text{TiF}_4(g) + 2\text{F}_2(g) \quad (1)
\]

\[
\text{Na}_3\text{TiOF}_5(s) + \frac{1}{2}\text{O}_2(g) = 3\text{NaF}(s) + \text{TiO}_2(s) + \text{F}_2(g) \quad (2)
\]

The formation of Na₃TiOF₅ from Na₂TiF₆ in air is given by the reaction

\[
\text{Na}_3\text{TiF}_6(s) + \frac{1}{2}\text{O}_2(g) = \text{Na}_3\text{TiOF}_5(s) + \frac{1}{2}\text{F}_2(g) \quad (3)
\]

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