INTRINSIC KINETICS OF THE OXIDATION OF Na_2TiF_6 AND Na_3TiF_6

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The intrinsic kinetics, unaffected by diffusional and mass transfer effects, of the air oxidation of Na_2TiF_6 and Na_3TiF_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_3TiOF_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_3TiOF_5 to a mixture of $NaF + TiO_2$ was determined to be 52.4 kJ/mol and 55.3 kJ/mol for Na_2TiF_6 and Na_3TiF_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.
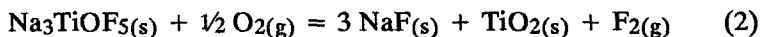
A process to manufacture metallic Ti that would utilize lower-grade titanium ores such as ilmenite, $FeTiO_3$, and involve simpler process steps has long been sought. Early attempts to develop such a process focused on the conversion of ilmenite with fluoride salts as the Ti extraction agent to produce fluorotitanates or Ti fluorides. Kroll [3] discussed the advantages and problems of producing TiF_4 and alkalimetal fluorotitanates such as Na_2TiF_6 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], H_2SiF_6 [7], alkalimetal fluorosilicates [8-9], NH_4F [10], alkalimetal double fluorides [11], CaF_2 with H_2SO_4 [12] and FeF_3 [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 Na_2SiF_6 leads to the formation of Na_2TiF_6, while the hydrothermal treatment of $TiOSO_4$ solutions results in the precipitation of Na_2TiF_6. 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 Na_2TiF_6 and Na_3TiF_6 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 faciltates their treatment prior to the reduction step. We found previously [14] that the air oxidation of Na_2TiF_6 and Na_3TiF_6 proceeds through two-step reactions, with formation of the oxyfluorotitanate, Na_3TiOF_5, as the intermediate. The oxidation of Na_2TiF_6 is presented below:

$$3\ Na_2TiF_{6(s)} + O_{2(g)} = 2\ Na_3TiOF_{5(s)} + TiF_{4(g)} + 2\ F_{2(g)} \quad (1)$$

$$Na_3TiOF_{5(s)} + \tfrac{1}{2}\ O_{2(g)} = 3\ NaF_{(s)} + TiO_{2(s)} + F_{2(g)} \quad (2)$$

The formation of Na_3TiOF_5 from Na_3TiF_6 in air is given by the reaction

$$Na_3TiF_{6(s)} + \tfrac{1}{2}\ O_{2(g)} = Na_3TiOF_{5(s)} + \tfrac{1}{2}\ F_{2(g)} \quad (3)$$
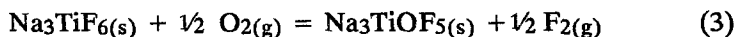
The further oxidation of Na_3TiOF_5 proceeds according to reaction (2).

This means that the kinetic parameters, i.e. the activation energy and the preexponential factor for the oxidation of oxyfluorotitanate, Na_3TiOF_5, in the second step for both fluorotitanates, should be characterized by similar values. The air oxidation of Na_2TiF_6 started at about $320°$. For comparison, the oxidation of Na_3TiF_6 started at a slightly lower temperature, $260°$. In both cases, the oxidation proceeded through two distinguishable steps, the weight losses in these steps corresponding closely to the stoichiometry of the above reactions.

The fractional oxidation conversion was calculated separately for each step according to the above reactions. At the end of the first step, both sodium fluorotitanates were oxidized completely to Na_3TiOF_5. In the present paper, we have determined the kinetic parameters for the formation of Na_3TiOF_5 (overall reaction (1) and (3)) and for the further oxidation of Na_3TiOF_5 (overall reaction (2)) for both sodium fluorotitanates.

As mentioned above, we used a nonisothermal technique to find the kinetic parameters for these reactions. In this technique, temperature is increased linearly with time during a run. Thus

$$T = T_0 + at \qquad (4)$$

and in this case k is not a constant, but

$$k = A \exp\left(\frac{-E}{RT}\right) \qquad (5)$$

Combining Eqs (4) and (5) with the general form of the rate expression for a gas - solid reaction (6):

$$\frac{dX}{dt} = k * f_1(p_{02}) * f_2(X) \qquad (6)$$

and integrating, we obtain

$$\int_0^x \frac{dx}{f_2(X)} = g(X) = \frac{Af_1(p_{02})}{a} \int_0^T e^{-E/RT} dT \qquad (7)$$

where X is the fractional oxidation conversion of the given sodium fluorotitanate, $f_1(p_{O_2})$ is the dependence of the rate on the O_2 concentration

in the inlet gas $f_2(X)$ is the dependence of the rate on the fraction of unconverted fluorotitanate, and a is the heating rate (deg/s); A is the preexponential factor $(s \cdot kPa)^{-1}$ and E is the activation energy (J/mol).

We used the following examples for $g(X)$:
for a shrinking-core scheme:

$$g(X) = 1 - (1-X)^{1/F} \quad F = 3 \tag{8}$$

for a first-order reaction:

$$g(X) = -\ln (1-X) \tag{9}$$

for reactions of order 1.5 and 2:

$$g(X) = (1-X)^{-m} - 1 \quad m = 1/2; 1 \tag{10}$$

We assumed that the integral on the right-hand side of Eq. (7) up to the initial temperature is negligible, as is most usually the case in experiments of this type.

For relatively large values of E/RT, the integral on the right-hand side can be replaced by an approximate solution which is known in the literature [15] by using the substitution $U = E/RT$:

$$g(X) = \frac{Af_1(pO_2)}{a} \frac{RT^2}{E} \left(1 - \frac{2RT}{E} + \ldots\right) \exp\left(\frac{-E}{RT}\right) \tag{11}$$

Taking Eq. (11) into account, it is apparent that a linear plot of $\ln[g(X)/T^2]$ as a function of $1/T$ would yield the activation energy E and the preexponential factor A if the ratio RT/E is small, which is a valid approximation for this work. The value of E is rather insensitive to the magnitude of RT/E as long as the latter is relatively small compared with unity. This is because the right-hand side of Eq. (11) is dominated by the exponential term. The value of RT/E does effect the computed value of A. The best value of A is obtained by using the value of T at $X = 0.5$ in the term $(1-2RT/E)$; this is equivalent to forcing a fit between the experimental data and the conversion *vs.* temperature equation at 50% conversion.

The determination of intrinsic kinetics requires the complete elimination of any diffusional and mass transfer effects. This is achieved by using samples of small dimensions and a rapid air flow. In this work, we used shal-

low layers of fine particles of Na_2TiF_6 or Na_3TiF_6. The advantage of the nonisothermal technique lies in the fact that the activation energy and the preexponential factor can be obtained from a single run, whereas the isothermal method requires many runs to obtain the same parameters.

Experimental

The oxidation of the sodium fluorotitanates was followed by using a standard thermogravimetric apparatus. The holder was made of a thin platinum sheet. The temperature close to the sample was monitored with Pt-Pt/Rh thermocouples.

Na_2TiF_6 was obtained according to the procedure described by Hunter [2]. For the preparation of Na_3TiF_6, we have used a procedure based on the following reaction:

$$3\ Na_2TiF_6 + Ti + 6\ NaF = 4\ Na_3TiF_6 \qquad (12)$$
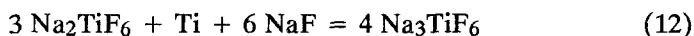
Accurately calculated and weighed amounts of previously obtained Na_2TiF_6 and NaF and Ti powders were ground together thoroughly in a mortar under absolute alcohol, and dried. The mixture was compacted into pellets and was then heated in evacuated and sealed silica tubes at $680°$ for several days until X-ray diffraction analysis of the quenched sample showed only the presence of Na_3TiF_6. The obtained sodium fluorotitanates were ground and screened into two size fractions: -150 mesh +200 mesh, and -200 mesh. Samples of both fluorotitanates were kept in a desiccator.

For oxidation experiments, the sample of Na_2TiF_6 or Na_3TiF_6 was placed in the reactor and was heated in air at a constant heating rate. The weight loss of the sample was continuously recorded. The mass transfer and diffusional effects were eliminated by using a sufficiently high flow rate of air and a small amount of solid particles spread thinly on the sample pan. The minimum value of the flow rate of air at which the effect of external mass transfer becomes negligible was determined by continuously increasing the flow rate of air until the conversion vs. time relationship no longer changed. A flow rate of 0.2 dm^3 per minute was found to be sufficiently large in our system and was therefore used in subsequent runs for both fluorotitanates. It was also found that a sample weight of 100 mg was within the range where diffusional effects within the interstitial space were negligible.

Results and discussion

Four rate expressions were tested to find the expression which gives the best fit of the experimental data. Values of the correlation coefficients for various rate expressions are shown in Table 1. The first-order rate expression gave the best correlation for both fluorotitanates for each oxidation step. Thus:

$$g(X) = -\ln (1-X) \ \text{ and } f_2 (X) = 1 - X \tag{13}$$

The values of these correlation coefficients obtained by means of Eq. (13) indicate that this rate expression applied separately to two oxidation steps for both fluorotitanates adequately describes the oxidation rate.

The kinetic parameters determined for the air oxidation of Na_2TiF_6 and Na_3TiF_6 are given in Figs 1 and 2, respectively. The samples of -150 + 200 mesh size were used. The heating rate was 0.185 deg per second. In these Figures, the experimental data are plotted according to

$$\ln \left[-\ln (1 - x) / T^2 \right] = \ln \left[\frac{A f_1 (p_{O_2})^R}{aE} \left(1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \tag{14}$$

which is obtained by combining Eqs (9) and (11).

Here, T represents the temperature at $X = 0.5$

As can be seen in the Figures, there is only a small difference in the values of the activation energy within the experimental uncertainty for the second steps of oxidation for both fluorotitanates.

This difference between $E_2 = 52.4$ kJ/mol and $E_4 = 55.3$ kJ/mol can also be related to different reactivities of the Na_3TiF_5 formed according to reactions (1) and (3) from different reactants. The calculated values of the preexponential factors for both air oxidation reactions of Na_3TiOF_5 also gave similar values, i.e. $A_2 = 0.9 \ [(s \cdot kPa)^{-1}]$ for reaction (2) and $A_4 = 0.7 \ [(s \cdot kPa)^{-1}]$ for reaction (4).

The final oxidation products for both fluorotitanates, i.e. a mixture of $NaF + TiO_2$, cannot coexist at high temperature. We noted that above $800°$ there is a weight loss step which corresponds to the reaction of NaF and TiO_2 with the formation of sodium titanates. Thus, $800°$ was the upper temperature limit in our experiments.

The dependence of the rate on the partial pressure of oxygen was determined for both fluorotitanates with the samples of $-150 +200$ mesh. The
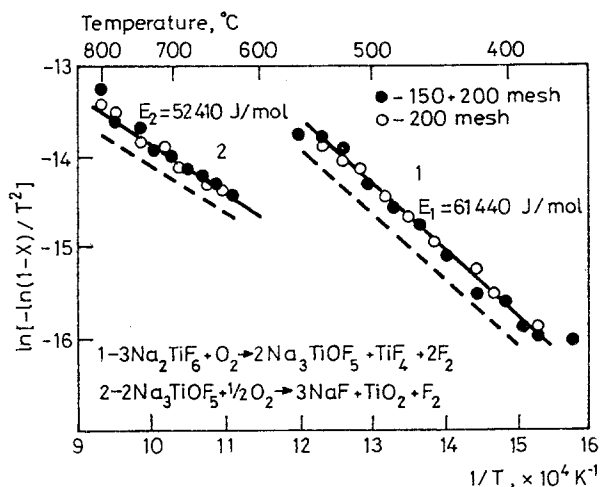
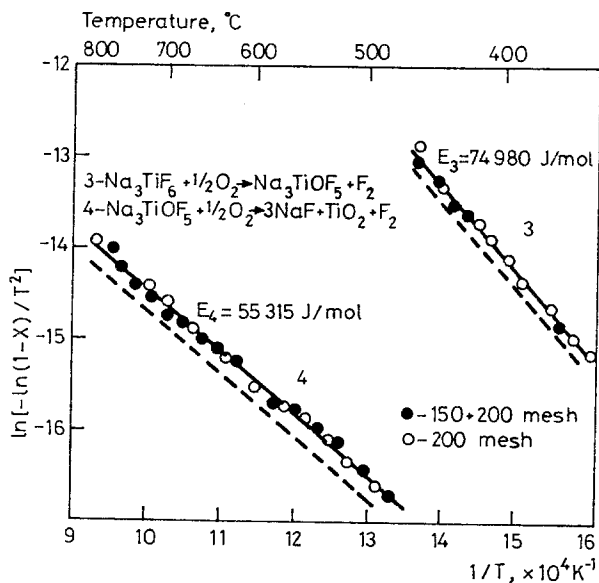Fig. 1 Determination of the rate parameters for the oxidation of Na₂TiF₆

Fig. 2 Determination of the rate parameters for the oxidation of Na₃TiF₆

oxygen partial pressure was changed to 10 mol% of O_2 by diluting air with nitrogen. For comparison, plots of the data in 10 mol% O_2 according to Eq. (14) are given in Figs 1 and 2 with dashed lines. It can be seen that the lines have almost the same slopes, indicating the same activation energy. We

noted that the runs with -200 mesh samples gave the same results as for the
-150 +200 mesh grains for both fluorotitanates.

The results indicate that the oxidation of fluorotitanates is of first order
with respect to the amount of unreacted solids for each of the two-step reac-
tions. It is likely that these reactions are also of first order with respect to
oxygen partial pressure. In order to confirm this suggestion, it is necessary
to conduct a third oxidation run to obtain a linear plot of $Af_1(p_{O_2})$ as a func-
tion of p_{O_2}. The kinetic parameters obtained are the intrinsic values, because
care was taken to eliminate diffusional and mass transfer effects. These
results cannot be compared, since there are no other published data.

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Zusammenfassung — Mittels eines nichtisothermen Verfahrens wurde die eigentliche,
durch Diffusion und Massentransport nicht beeinflußte Kinetik der Oxidation von Na_2TiF_6
und Na_3TiF_6 an Luft untersucht. Die Oxidation dieser Natriumfluorotitanate verläuft über
eine Zweischrittereaktion unter Bildung von Oxidfluorotitanat Na_3TiOF_5 als Zwi-
schenprodukt. Bei beiden Fluorotitanaten zeigt die Reaktionsgeschwindigkeit in beiden
Reaktionsschritten bezüglich der Menge unreagierten Feststoffes eine Abhängigkeit erster
Ordnung. Für die Aktivierungsenergie der weiteren Oxidation von Na_3TiOF_5 zu einem
Gemisch aus NaF und TiO_2 wurden für Na_2TiF_6 und Na_3TiF_6 als Reaktanden Werte von
52.4 kJ/mol bzw. 55.3 kJ/mol gefunden.