

# *Study of Ti (III) solutions in various molten alkali chlorides.*

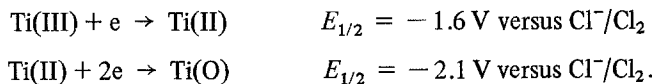
## *I. Chemical and electrochemical investigation*

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The effect of alkali metal cations in molten chloride baths on the behaviour of Ti(III) in these melts has been studied. With caesium chloride the percentage of total dissolved titanium present as Ti(II) after 72 hours at 700°C is 0.1%, whereas in lithium chloride it is 2%. In the presence of excess titanium metal the proportion of Ti(II) is always much higher. In LiCl it depends strongly on the area of titanium exposed and may reach 85%. In CsCl, on the other hand, this factor has no effect since a fine dispersion of powdery titanium appears at the very beginning of the reaction. The amount of Ti(II) remains close to 50%. In all the baths studied, the electrochemical reduction of Ti(III) at 700°C occurs in two steps:



These results are different from those previously obtained in CsCl-LiCl (40-60 mol%) at 400°C, where reduction is a one-step process.

### 1. Introduction

The development of an electrolytic preparation of titanium from its tetrachloride in molten salts has been hindered by many difficulties. These are mainly due to the presence in the baths of several oxidation states of titanium [1, 2]. Since the tetrachloride  $\text{TiCl}_4$  cannot be reduced to metallic titanium in a single step, a diaphragm is necessary to isolate the anode compartment and to avoid unwanted reoxidations. Refractory materials cannot be used for these separators as they are brittle and constitute a source of oxygen contamination; therefore the present trend is to use woven metallic diaphragms of low porosity [3, 4]. Any attempts to improve the energy balance must depend on a better understanding of the equilibria between the different oxidation states of titanium. As a contribution to an improved understanding of the chemical reactions occurring during electrolysis, we have studied the behaviour of the oxidation states II and III of titanium as a function of the bath composition.

Data in the literature, confirmed by the results of our previous work, indicate that in alkali

chloride baths the stability of valence states IV and III of titanium increases with the radius of the cations in the melts, while that of Ti(II) decreases [5, 6]. Moreover, an electrochemical study has shown that in a bath containing alkali metals of extreme radii, i.e. CsCl and LiCl (40-60 mol%), the reduction of Ti(III) at 400°C occurs, as in fluoride melts, in a single step  $\text{Ti(III)} \rightarrow \text{Ti(O)}$ , whereas in KCl/LiCl it occurs in two steps via the intermediate valency Ti(II) [2].

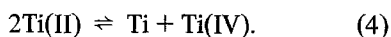
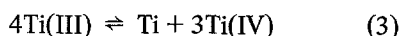
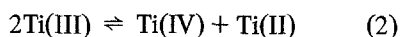
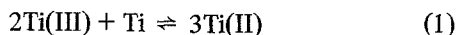
In order to understand this different behaviour we have studied first the equilibria between Ti(III), Ti(II) and Ti(O) in alkali metal chlorides by chemical analysis of the solutions. This work is completed by a study of the electrochemical reduction of Ti(III) in these media and by Raman spectroscopic identification of the titanium complexes present (see Part 2).

### 2. Chemical study of the $\text{Ti(III)} \rightleftharpoons \text{Ti(II)}$ equilibrium

The different oxidation states of titanium are interrelated by four disproportionation reactions:

Table 1. Bath characteristics

Eutectic	Composition (mol%)	Melting point (° C)
LiCl	100	614
LiCl-KCl	60-40	355
KCl-NaCl	50-50	658
KCl-CsCl	35-65	610
CsCl	100	646



These reactions, which occur simultaneously, are heterogeneous: titanium metal is a solid, while Ti(IV) is in the form of gaseous  $\text{TiCl}_4$  in equilibrium with the soluble complex  $\text{TiCl}_6^{2-}$ . As a consequence, the results obtained depend markedly on the experimental conditions: temperature, nature of the atmosphere, surface area and type of titanium exposed.

In order to study the effect of the alkali metal cations in the bath, we used the eutectics listed in Table 1 at a working temperature of  $700^\circ\text{C}$  (at which all these mixtures are molten).

### 2.1. Experimental techniques

The alkali metal chloride or the mixtures are carefully dehydrated before melting under vacuum and then stored in a glove box under pure argon. For each run a given weight of one of these salts is mixed with a known amount of  $\text{TiCl}_3$  or one of the complexes  $\text{K}_3\text{TiCl}_6$  or  $\text{Cs}_3\text{TiCl}_6$ , prepared by reaction of  $\text{TiCl}_3$  with KCl or CsCl in stoichio-

metric proportions at  $750^\circ\text{C}$ . The mixtures are introduced into a silica tube, sealed under vacuum and then kept at  $700^\circ\text{C}$  for 72 hours.

For the runs carried out with an excess of metallic titanium, we introduced a weight of metal ten times that indicated by the stoichiometry of Reaction 1. To study the effect of the area of exposed titanium, a given weight of metal was introduced, sheet rolled either to 0.35 mm or 1 mm thickness. Concentrations of Ti(II) and Ti(III) were measured by chemical analysis on quenched samples. The Ti(II) was determined by measuring the volume of hydrogen evolved after addition of hydrochloric acid [7]. The total Ti(II) + Ti(III) was determined by titration with potassium dichromate in dilute hydrochloric acid using barium diphenylamine sulphonate as the indicator. The initial molar fractions of Ti(III) in the melts are between  $0.3 \times 10^{-2}$  and  $10 \times 10^{-2}$ . In this range the percentage of Ti(II) obtained does not change with the concentrations of the Ti(III) species.

### 2.2. Results

To determine the equilibria obtained under conditions close to the preparation of titanium we first examined the dependence of the stability of  $\text{TiCl}_3$  on the alkali metal cation in the bath. Then we investigated the effect of metallic titanium on these same equilibria. Table 2 shows how the percentage of Ti(II) after equilibration depends on those different factors.

**2.2.1. Behaviour of Ti(III) in the baths.** Ti(III) is very stable in molten caesium chloride at  $700^\circ\text{C}$ . The amount of Ti(II) obtained after 72 hours at this temperature is very low, about 0.1%. However, the titanium balance, calculated according

Table 2. Percentage of Ti(II) relative to total titanium ( $\text{Ti(II)} \times 100 / [\text{Ti(II)} + \text{Ti(III)}]$ ) in the various solutions

	LiCl	LiCl/KCl	KCl/NaCl	KCl/CsCl	CsCl
No titanium	2-2.5	—	—	2.5 <sup>†</sup> 2.5 <sup>‡</sup>	0.1
Titanium added as 1 mm thick foils	50	40	40	40	50
Ti: same weight 0.35 mm thick foils	80-85	—	—	—	50

<sup>†</sup> Ti(III) introduced as  $\text{Cs}_3\text{TiCl}_6$ .

<sup>‡</sup> Ti(III) introduced as  $\text{K}_3\text{TiCl}_6$ .

to Reaction 2 from the Ti(III) introduced initially and the Ti(II) and Ti(III) analysed after reaction, indicates that 35% of the material has been lost. Consequently part of the Ti(II) and/or Ti(III) has decomposed by Reactions 3 and 4. Indeed a small amount of powdery titanium can be observed and part of the  $TiCl_4$  has volatilized.

In lithium chloride, at the same temperature,  $TiCl_3$  is less stable since the amount of Ti(II) is twenty times as great (2–2.5%) and the titanium balance indicates that 45% has been lost. This increased loss arises from a displacement of Reactions 3 and 4 to the right-hand side. The Ti(IV) formed cannot be stabilized as the  $TiCl_6^{2-}$  complex in this bath, as it is partially in caesium chloride. Therefore the gaseous tetrachloride  $TiCl_4$  comes out of the bath and causes a shift in the equilibrium.

*2.2.2. Effect of metallic titanium on the behaviour of Ti(III).* In contrast to previous results, the amount of Ti(II) formed in the presence of excess titanium turned out to be important whatever the size of the alkali metal cations in the bath, i.e. whatever the stability of the complexes  $M_3TiCl_6$  and  $M_2TiCl_6$ . Thus, as indicated in Table 2, for a given quantity of titanium with a defined area the amounts of Ti(II) are the same (50%) whether the experiment is carried out in lithium or caesium chloride.

These results must however be examined more closely. In lithium chloride the percentage of Ti(II) in solution increases markedly (80%) when the area for the same mass of metal is tripled (thickness 0.35 mm instead of 1 mm); in caesium chloride this parameter has no effect. Moreover the Ti(III) solutions obtained with LiCl, KCl–LiCl or KCl–NaCl after equilibration with the metal are perfectly clear, whereas with CsCl and KCl–CsCl there is a lot of powdery titanium in suspension. These results are explained by the fact that Reactions 2, 3 and 4 are more or less important, depending on the nature of the bath.

In baths containing small alkali metal cations (ionic radius less than that of potassium), little powdery titanium arises. Reactions 3 and 4 are therefore only slightly shifted to the right and Reactions 1 and 2 are the most important. Now, Ti(IV) is poorly complexed; thus about 25% of the titanium is lost from the LiCl bath. With the

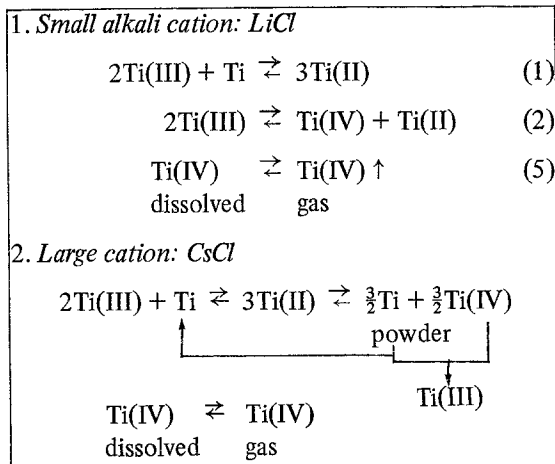


Fig. 1. Effect of the bath composition on the relative importance of the disproportion reactions.

KCl–LiCl eutectic the loss is only 10% since the Ti(IV) is stabilized.

A large amount of powdery titanium appears in baths containing alkali metal cations larger than potassium. The Ti(II) formed by Reaction 1 is not very stable in these media. It disproportionates by Reaction 4 to give, from the very beginning of the experiment, highly reactive, powdery, nascent titanium. This explains why the area of the metal exposed at the start of the run has no effect. The instability of Ti(II) and the presence of powdery titanium tends to shift Reaction 1 towards the right. Furthermore the amount of Ti(IV) dissolved in these baths is relatively large because of the higher stability of the  $TiCl_6^{2-}$  complex. This Ti(IV) reacts with the powdery titanium by Reaction 3 leading to the formation of Ti(III). Thus the quantity of Ti(II) and Ti(III) dissolved in the baths is greater than Reaction 1 would suggest.

The schemes in Fig. 1 summarize the behaviour of  $TiCl_3$  in the presence of titanium in the two extreme cases, LiCl and CsCl. The relative compositions of the solutions of Ti(II) and Ti(III) in equilibrium with titanium at 700° C differ according to the nature of the alkali metal cation. When the cations are larger than potassium, the titanium valencies IV and III are stabilized. In the presence of metal, equivalent concentrations of Ti(II) and Ti(III) are obtained. Because of the instability of Ti(II), powdery titanium appears and high concentrations of Ti(II) cannot be obtained. In contrast, if the alkali metal cations

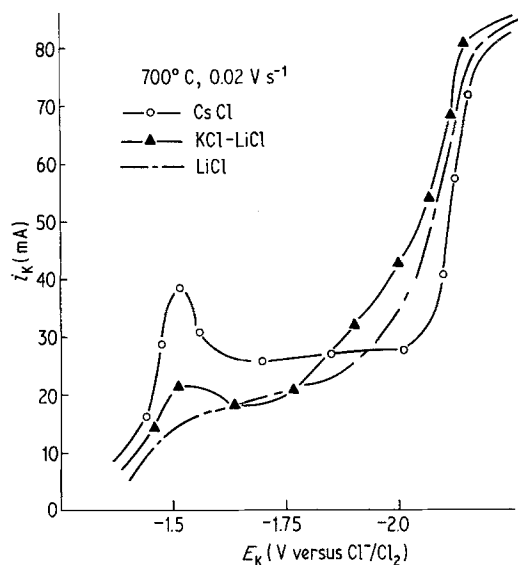


Fig. 2. Reduction curves of Ti(III) dissolved in CsCl, KCl-LiCl and LiCl. Scan speed:  $0.01 \text{ V s}^{-1}$ , temperature:  $700^\circ \text{C}$ , electrode area:  $2 \text{ cm}^2$ ,  $[\text{Ti(III)}] = 10^{-1}$  mole fraction.

are smaller than potassium, when a large area of titanium is exposed, clear solutions rich in Ti(II) are produced. Nevertheless the titanium balance indicates in this case significant losses related to the low stability of Ti(IV) in these baths.

### 3. Electrochemical reduction of trivalent titanium

We have studied the electrochemical reduction of Ti(III) in three of the preceding baths: the two extremes, LiCl and CsCl, and an intermediate one, KCl-LiCl. The temperature was kept at  $700^\circ \text{C}$  as for the study of the equilibria. Voltammetric curves (Fig. 2) were recorded at speeds from  $0.003 \text{ V s}^{-1}$  to  $0.1 \text{ V s}^{-1}$ . The experimental device has already been described [1]. The reference electrode is a classical silver/silver chloride electrode, the auxiliary electrode a 6 mm diameter graphite rod and the working electrode a 3 mm diameter nickel wire.

In all three baths the reduction occurs in two steps:



The half-wave potentials (measured with respect to  $\text{Cl}^-/\text{Cl}_2$ ) of these reactions vary little with the bath.

In agreement with the observations of the previous paragraph, the Ti(III) solutions in caesium chloride are more stable than in the other baths. In lithium chloride the trichloride tends to disproportionate rapidly to Ti(II) and Ti(IV) which is swept away by the argon flow. As a consequence, when introducing the same amount of  $\text{TiCl}_3$  to each bath the first reduction step is more pronounced in caesium chloride. On the other hand, the step  $\text{II} \rightarrow \text{O}$  is smaller. In this case it is necessary to add a little metallic titanium to increase the Ti(II) concentration in the bath and thus to allow the metal to be deposited. Moreover, LiCl, and to a lesser extent the KCl-LiCl mixture, are very hygroscopic and if care is not taken to prevent air getting into the cell additional waves, probably associated with the reduction of oxychlorides, appear.

Comparison of these results with those of previous studies indicates that the temperature has an important bearing upon the electrochemical behaviour of Ti(III) [2]. At a lower temperature ( $400^\circ \text{C}$ ) and in a CsCl-LiCl eutectic the reduction of Ti(III) to Ti(O) occurs in a single step as in fluoride melts [8]. We might expect an analogous result for the reduction of Ti(III) in pure caesium chloride. However the stability of the  $\text{Cs}_2\text{TiCl}_6$  and  $\text{Cs}_3\text{TiCl}_6$  complexes decreases rapidly as the temperature rises. Since the melting point of pure caesium chloride is high ( $646^\circ \text{C}$ ) we carried out this reduction at  $700^\circ \text{C}$ ; the low stability of the titanium complexes at this temperature leads to the appearance of the intermediate step  $\text{Ti(III)} \rightarrow \text{Ti(II)}$ .

This variation in the stability and the electrochemical behaviour of the complex anion formed by Ti(III) in solution with the temperature and the nature of the alkali metal cations in the eutectic led us to attempt to characterize the co-ordination of this ion by Raman spectroscopy [9].

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