

## Electrochemical deoxidation of yttrium–oxygen solid solutions

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### Abstract

Oxygen was removed from yttrium by an electrochemical method in which the metal is made the cathode in a cell consisting of a carbon anode and molten  $\text{CaCl}_2$  electrolyte. At 1223 K yttrium containing 5700 ppm oxygen was deoxidized down to less than 100 ppm. The method can be used to deoxidize other highly reactive metals. Furthermore, in principle it should be possible to remove other impurities besides oxygen.

*Keywords:* Yttrium; Purification; Deoxidation; Refining; Titanium

### 1. Introduction

In recent years 99.9999% yttrium (excluding carbon and gaseous elements) has been produced commercially for use in electronics [1]. The major impurity in this material is oxygen, present in the amount 0.1 to 0.5% (5000 ppm by mass). Oxygen removal from yttrium metal is extremely difficult owing to a combination of two factors: yttrium has a very strong affinity for oxygen (see Fig. 1 [2]) and dissolves oxygen in large concentrations (see Fig. 2 [3,6]). In the present study a new electrochemical cell was used to deoxidize yttrium down to below 100 ppm. The method can be used to deoxidize other highly reactive metals, for example the lanthanides, to meet the growing demand for oxygen-free material for electronics applications [4,5].

The purification of yttrium metal has been investigated by numerous researchers [1,7–10]. Most of the metallic impurities were eliminated by conventional methods, such as molten salt electrolysis [1]. In contrast, oxygen removal from the metal was found to be very difficult. Carlson et al. [7] showed that solid state electrotransport (SSE) is effective in removing inter-

stitial impurities in yttrium. By passing a large current through a yttrium rod for 190 h at 1175 K, yttrium metal containing about 90 mass ppm oxygen was obtained. Volkov et al. [9] succeeded in reducing oxygen below the 40 mass ppm level using SSE by passing several hundred amperes through a high-purity yttrium rod for 500 h. Although SSE is one of the most effective methods of removing impurities from a reactive metal, there are limitations on the initial impurity level and sample geometry.

By utilizing oxyhalide formation, Corbett et al. [10] reduced the oxygen concentration in yttrium to about 0.19 at.% (about 340 mass ppm) by reaction with yttrium trichloride at about 1000 K for 14 days. Although this method is effective, it suffers from poor production efficiency due to the necessity of long reaction time and the need for a highly controlled atmosphere.

In recent years, the authors have developed a calcium–halide flux deoxidation method to reduce the oxygen concentration in titanium [11,12] and in titanium aluminide [13] to levels below 50 mass ppm. The thrust of the present investigation was to enhance the effectiveness of this method by combining it with electrochemical polarization to remove oxygen to concentrations below the detection limit of conventional gas analysis [14]. This new method is not specific to yttrium and in principle can be generalized for the removal of oxygen from a variety of reactive metals.

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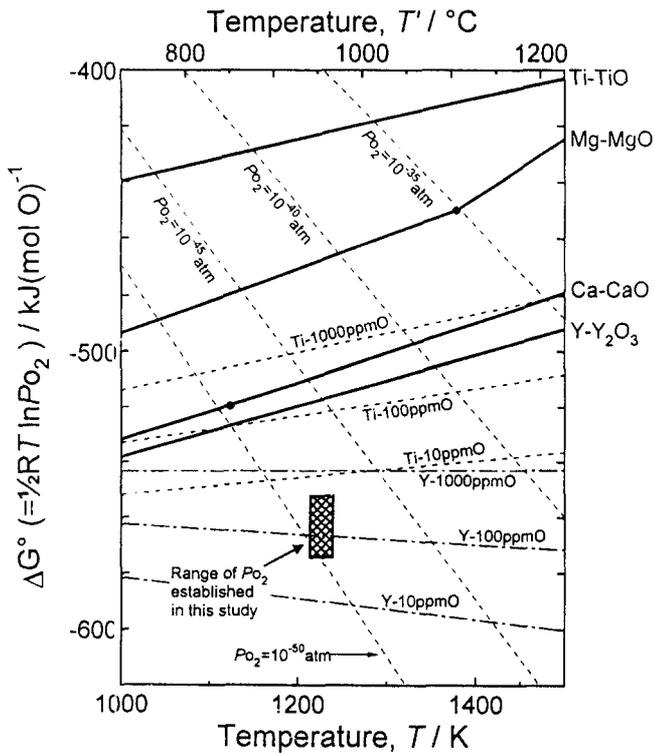


Fig. 1. Ellingham diagram of selected oxides [2] and solid solutions of Ti–O and Y–O [15]. The range of oxygen potential established in this study is depicted by cross hatching.

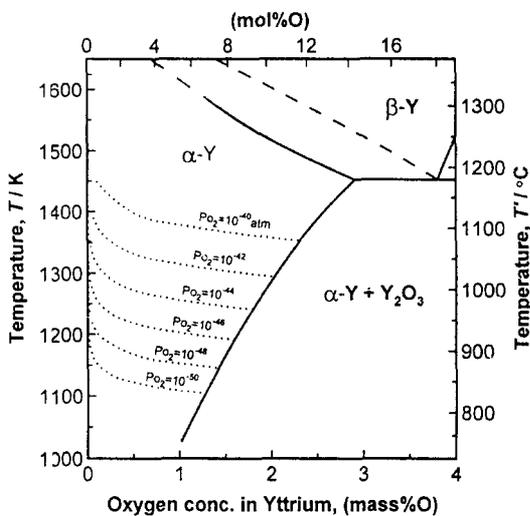


Fig. 2. Phase diagram of the yttrium-rich end of the Y–O system [3,6] and calculated iso-oxygen potential lines in the  $\alpha$ -yttrium solid solution phase field [15].

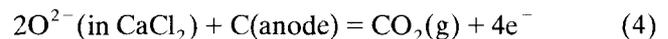
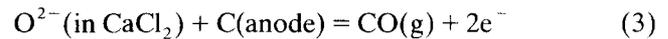
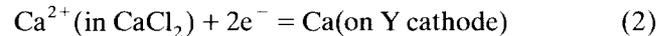
## 2. Theory

Since the principles of the electrochemical deoxidation method have been reported in detail elsewhere [14], only a brief outline will be given here.

The electrochemical deoxidation method used in this study is a modification of the calcium–halide flux

deoxidation method [11,12]. The main features are the production of calcium metal deoxidizer by electrolysis of the  $\text{CaCl}_2$  flux and the dissolution of CaO deoxidation product into the flux for the subsequent electrolysis.

In this method, as expressed by Eq. (1), yttrium, which is made the cathode, is deoxidized by calcium produced electrochemically according to Eq. (2). At the carbon anode  $\text{O}^{2-}$  ions are removed as CO (or  $\text{CO}_2$ ) gas by reactions expressed in Eqs. (3) and (4).



At 1223 K, where carbon is oxidized in a conventional gas–solid reaction, the formation of CO is thermodynamically favored. However, in the oxidation of carbon immersed in a molten salt bath, kinetic limitations may promote the production of  $\text{CO}_2$ , as for example in the Hall cell electrolysis of aluminum.

In contrast to the calcium–halide flux deoxidation process [11,12], the present method offers a number of advantages. First, the addition of metallic calcium as a deoxidant is not required since the activity of calcium near the cathode can be electrochemically increased, even as high as unity, by controlling the applied voltage between the yttrium cathode and carbon anode. In some cases, elemental calcium can even be precipitated on the cathode when the applied voltage is high enough (in situ generation). Second, the product CaO is also soluble in molten  $\text{CaCl}_2$ , and this facilitates continuous electrochemical removal of CaO ( $\text{Ca}^{2+}$  is discharged at the cathode and  $\text{O}^{2-}$  at the anode). Therefore, the activity of the CaO in the melt is kept at a very low level and does not increase during the process. Third, in situ generation of calcium by electrolysis produces a deoxidant free of impurities that otherwise could contaminate the yttrium.

## 3. Experimental

As shown in Table 1, yttrium and titanium of various shapes, small pieces and wires (about 0.1–3 g each), were used as starting materials. Reagent-grade anhydrous  $\text{CaCl}_2$  (99.9%) in powder form was dried at 800 K for more than 200 ks (2 days).

A schematic illustration of the apparatus is shown in Fig. 3.  $\text{CaCl}_2$  flux, which had been dehydrated beforehand, was contained in a titanium crucible (72 mm diameter, 160 mm height) and set in a stainless steel reaction tube. The cathode basket, containing

Table 1  
Some analytical values of yttrium and titanium samples used in this study

Sample	Purity <sup>a</sup>	Oxygen concentration (mass ppm)	Nitrogen concentration (mass ppm)	Configuration
Yttrium-2 <sup>b</sup>	99.9%	5700	160	0.5–3 g small pieces
Titanium-2 <sup>c</sup>	99.9%	1100	50	1.2 mm diameter wire
Titanium-2 <sup>c</sup>	99.9%	1400	20	2.0 mm diameter wire

<sup>a</sup> Excluding gaseous elements.

<sup>b</sup> Electron beam-melted commercial yttrium.

<sup>c</sup> Commercial grade.

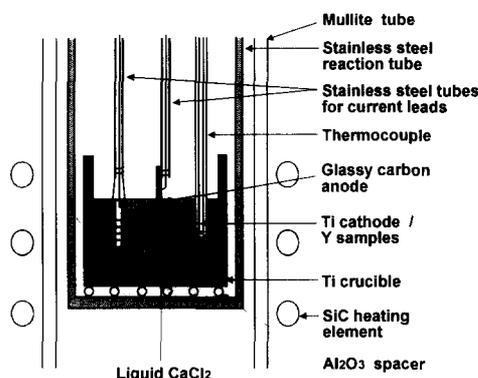


Fig. 3. Schematic illustration of the reaction cell used for electrochemical deoxidation of yttrium metal.

about 3 g of yttrium, was comprised of several strands of titanium wire, about 50 mm long. High purity (99.9%) glassy carbon was used as the anode (100 mm length, 5.9 mm diameter). The anode, the cathode connector, as well as the thermocouple tubing, were inserted into the reaction tube through a gas-tight water-cooled stainless head.

After the assembled cell was evacuated, it was checked for gas-tightness and then heated to about 600 K to render the contents moisture-free. Argon was then introduced into the reaction tube, and the temperature was increased to 1223 K. After  $\text{CaCl}_2$  had melted, the glassy carbon anode was lowered into the molten salt and pre-electrolysis was conducted using the titanium crucible as cathode. About 1.5 V was applied between the titanium crucible and the carbon anode for about 2 ks for the purpose of eliminating residual gaseous impurities in the molten salt. The temperature of the molten salt was directly measured using a chromel–alumel thermocouple protected by a nickel sheath. After pre-electrolysis, the titanium cathode basket containing the yttrium samples was lowered into the melt to a position about 30 mm from the anode, and the deoxidation experiment was performed under conditions of controlled potential electrolysis. In most cases, deoxidation of the yttrium cathode was achieved by applying a voltage of 3.2 to 3.8 V at 1223 K for about 18 ks (5 h).

After reaction, the electrodes were removed from the melt and the cell was allowed to cool in a stream

of argon gas. In some cases it was possible to reheat the same anode and melt to deoxidize subsequent yttrium cathode specimens. The fused salt adhering to the surface of the yttrium samples was removed mechanically. The samples were then carefully file-polished and subjected to gas analysis.

Oxygen and nitrogen concentrations were determined by an inert gas fusion infrared absorption method (LECO TC-336 analyzer). Preceding the oxygen and nitrogen analyses, the yttrium samples were again mechanically polished, while the titanium samples were chemically etched with a 1:4:10 mixture of  $\text{HF}:\text{HNO}_3:\text{H}_2\text{O}$ . For oxygen and nitrogen extraction, a sample weighing 0.1 g enclosed in 1 g of platinum foil was dropped into a graphite crucible and heated to a temperature above 2500 K. The average blank values of oxygen and nitrogen (mainly due to absorption on the platinum) were  $3.6 \pm 1.0 \mu\text{g}$  and  $0.2 \pm 0.1 \mu\text{g}$  respectively.

The concentration of calcium in yttrium was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Nippon-Jarrell-Ash: ICAP-575II).

#### 4. Results and discussion

Some representative analytical results for oxygen concentration in yttrium and titanium before and after deoxidation are given in Table 2. Titanium was used as a reference material in order to facilitate the determination of the value of the partial pressure of oxygen at the cathode. The details of the technique are described in a previous publication [15].

As indicated by the results of experiments T5 and T4, yttrium could be deoxidized to below 100 mass ppm level. In these specimens, however, the carbon concentration increased to about 70–250 mass ppm. This could be prevented to some extent by separating the anolyte and catholyte with a bored titanium plate [14]. Nitrogen concentration was unchanged or increased by about 10 mass ppm. Calcium concentration in yttrium rose from 80 to 100 mass ppm after deoxidation.

These results indicate that electrochemical deoxida-

Table 2  
Experimental details and chemical analyses of titanium samples before and after electrochemical deoxidation at 1223 K

Experiment no.	Experimental conditions	Oxygen concentration (mass ppm)			
		Yttrium		Titanium	
		Initial	After experiment	Initial	After experiment
T6 <sup>a</sup>	3.8 V 31 ks (8.5 h)	5700	120	1100 1400	≤10, 10 80, 80
T5	3.8 V 29 ks (8.0 h)	5700	50, 70, 100	1100 1400	≤10, 10, 70 70, 90
T4 <sup>a</sup>	3.8 V 31 ks (8.5 h)	5700	70, 80	1100 1400	≤10, 10 40, 80
T3	3.4 V 29 ks (8.0 h)	5700	560	1100 1400	30 80
E11	3.4 V 22 ks (6 h)	5700	530, 750	1100 1400	30 70
T1	3.2 V 20 ks (5.5 h)	5700	1200	1100	850

<sup>a</sup> Pre-electrolysis not performed.

tion is effective for oxygen removal from yttrium metal. In the experiment in which yttrium samples were deoxidized to below 100 mass ppm, under the same conditions titanium samples were deoxidized to below the detection limit of analysis ( $\leq 10$  ppm). However, on the basis of the technique described previously [15], one can estimate that the oxygen level of titanium in the sample is of the order of the 0.1 to 1 ppm level, as the distribution coefficient for the oxygen between yttrium and titanium at 1223 K is about 70.

From the value of the residual oxygen concentration in yttrium, one can determine by the technique described previously [15] that the oxygen potential at the surface of the cathode is approximately  $10^{-49}$  atm. at 1223 K. Furthermore, it can be estimated that the activity of CaO on the surface of the yttrium cathode was lower than 0.002 during the deoxidation.

The oxygen potentials established in this study are indicated in Fig. 1 for reference. One can see that these oxygen potentials are far below that of the Y–Y<sub>2</sub>O<sub>3</sub> equilibrium which is one of the lowest oxygen potentials produced by metal/metal-oxide equilibrium. Thus, it is clear that such ultra-low oxygen potentials can be used in deoxidizing a variety of metals.

## 5. Conclusion

Removal of oxygen from yttrium using an electrochemical technique was examined at temperatures around 1223 K. By applying more than 3.2 V between yttrium and carbon electrodes immersed in molten CaCl<sub>2</sub>, yttrium samples containing 5700 mass ppm oxygen were deoxidized to less than 100 mass ppm. These results indicate that oxygen potentials of about

$10^{-49}$  atm. at 1223 K were achieved by this electrochemical method.

This method is not specific to yttrium and in principle can be generalized for the removal of oxygen from a variety of reactive metals. Furthermore, in principle it should be possible to remove other impurities besides oxygen.

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