



# Modelling the Oxygen Content of Titanium during Deoxidation in the Pressure Electroslag Remelting (PESR) Process

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## Abstract

Due to the combination of high strength, low density and good corrosion resistance, titanium alloys are the material of choice in the aeronautics and medical industry. However, the use of titanium and its alloys is limited to high performance applications as a result of the high production costs.

Therefore, a new production route for titanium alloys is under investigation at IME, RWTH Aachen University. Main idea is the synthesis of a TiAlV master alloy by aluminothermic reduction (ATR) of rutile ore. This alloy is then mixed with Ti-sponge in order to obtain a Ti-6Al-4V ratio and subsequently processed in a pressure electroslag remelting (PESR) furnace. In this PESR step, metallic calcium is added to the flux as a deoxidant to decrease the oxygen level of the remelted material. Since strict specifications regarding chemical homogeneity must be met the deoxidation step has to be controlled carefully in order to achieve a constant oxygen level and hence uniform mechanical properties. Since on-line measurements of the slag and metal phase are not feasible, a theoretical approach is made in order to describe the reaction rates in the PESR process. This paper presents a model for the kinetic aspects of deoxidation at the metal-slag interfaces. The calculated rate of deoxidation is presented and contrasted with results of experimental trials.

## Introduction

The electroslag remelting process is a refining method used mainly in the steel- and superalloy industry. Main goal is the inclusion removal, desulphurization and the adjustment of a uniform microstructure. The fundamentals of this process are described elsewhere [1] and are not further outlined in this paper. The potentials of the application of ESR for the remelting of pure titanium using CaF<sub>2</sub>-based fluxes have been investigated by various researchers [2][3][4] with promising results concerning the possibility to produce slab-shaped ingots and improvements regarding material yield and energy consumption in comparison to Vacuum Arc Remelting (VAR). Results also show interesting possibilities to reduce segregation effects due to lower possible melt rates compared to VAR. Mechanical properties of electroslag remelted c.p. titanium are reported to be comparable to vacu-



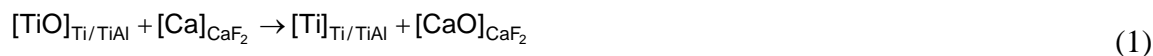
um arc remelted titanium [4], despite an ongoing discussion about possible solution of fluorine in the metal.

Since approximately 10 years the IME, RWTH Aachen University is working on the application of this refining process on titanium and titanium alloys with the goal of decreasing the level of oxygen because of its negative influence on the ductility. Main principle is the introduction of metallic calcium to the liquid slag as a deoxidant during the process. It could be shown that an oxygen decrease below 500 ppm is possible [5].

## Thermodynamics of Deoxidation

For deoxidation by PESR, slags based on  $\text{CaF}_2$  offer the best combination of thermochemical stability, stable processing conditions, availability and final ingot quality [6]. Thermochemical calculations in the system Ca-CaO- $\text{CaF}_2$  have shown that even the deoxidation of pure titanium should be possible by ESR using “reactive slags” where metallic calcium is added to the flux as a deoxidation agent [7]. Ca is chosen as a reactant, because of its high oxygen affinity, good solubility in the slag and available experimental data for the equilibrium of Ca and O in titanium melts.

The main principle of deoxidation by Ca is based on the reaction between oxygen dissolved in the metal phase as TiO with calcium dissolved in the slag which results in precipitation of CaO according to (1):



$[\text{A}]_{\text{B}}$  – Element or compound A dissolved in molten phase B

Thus, with increasing CaO concentration the Ca activity has to be continuously increased during the process for compensation. Additionally the CaO-activity can be decreased by dilution via addition of virgin  $\text{CaF}_2$ . In order to sync both measures of interaction with the metal-slag system, modelling of the activity coefficients of Ca and CaO in the chosen slag system as a function of Ca and CaO concentration and temperature was conducted [7].

Assuming that thermochemical equilibrium is only achieved at the phase boundary itself, it consequently has to be considered that diffusion of Ca and CaO through a finite layer in the slag and O through a layer on the metal side respectively could be rate limiting factors. To complicate things further we have to consider that in PESR, three distinguished local zones for metal-slag interaction can be identified as illustrated in Figure 1:

- Zone 1: Reaction between to top-side of the slag and the liquid film below the electrode. This zone is characterised by continuous surface renewal by release of droplets and a temperature close to the metal liquidus.
- Zone 2: Reaction between the bulk slag and the droplet falling through the slag. This zone is characterized by increasing heat-transfer to the droplet, a certain superheat can be assumed.



- Zone 3: Reaction between the upper surface of metal pool and the lower surface of the slag. In this phase, the metal temperature equilibrates with the slag temperature and superheat can be in the range of 100K.

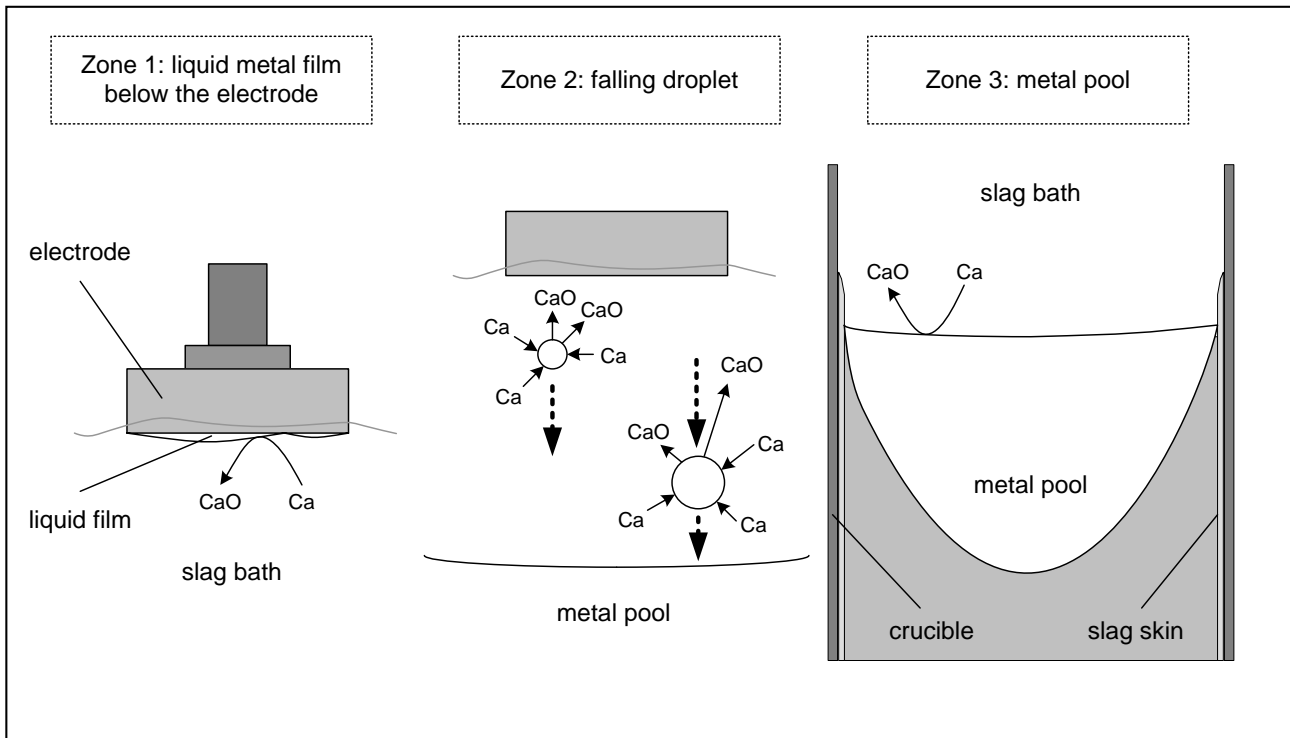


Figure 1: Possible zones of slag metal interaction in ESR [8]

## Kinetic model

It would be beyond the framework of this paper to develop and experimentally examine our full own understanding of reaction kinetics for all three sites. However Fraser [9] investigated various mass transfer aspects of AC ESR of steels (slagging of Mn and desulphurisation) in a very comprehensive thesis work and the findings of his work can be adapted to the conditions for the presented case.

In Fraser's model Mn is transported in the metal phase to the phase boundary, is being oxidized by  $Fe^{2+}$  ions from the slag and leaves the reaction zone as  $Mn^{2+}$  in the slag. The author solves a set of four mass-transfer equations in order to obtain a differential equation for the rate of change of Mn-concentration as a function of interfacial area, phase volume, bulk concentration, interfacial concentration at equilibrium, the equilibrium constant  $K$  and all transport coefficients  $k_i$  in the metal and slag diffusion layer. The adaption of this set of equations to the change rate of oxygen concentration in a titanium melt is presented in equation 2.

$$\frac{dc(O)}{dt} = \frac{-A}{V_M} k_{O,M} \left\{ c(O)_M - \left[ \frac{-b \pm (b^2 + 4c)^{1/2}}{2} \right] \right\}$$



$$\text{with } b = \frac{k_{Ca,S}}{\Omega k_{CaO,S}} + \frac{k_{Ca,S}}{k_{O,M}} c(Ca)_S - c(O)_M$$

$$\text{and } c = \frac{k_{Ca,M}}{\Omega} \left\{ \frac{c(O)_M}{k_{CaO,S}} + \frac{c(CaO)_S}{k_{O,S}} \right\}$$

$$\text{and } \Omega = K \cdot \frac{\gamma_{Ca,M} \cdot \gamma_{O,M} \cdot \bar{M}_M \cdot \rho_M}{\gamma_{CaO,S}} \tag{2}$$

$c(x)_{M/S}$  – bulk concentrations in metal (M) and slag (S) /g m<sup>-3</sup>,  $k_{X,P}$  – diffusion transport coefficient of species X in phase P /m s<sup>-1</sup>,  $\Omega$  - ratio of concentrations at the interface,  $\gamma_{i,P}$  – activity coefficient of Element i in phase P (M – metal, S – slag),  $\rho_M$  – density the of metal /kgm<sup>-3</sup>,  $\bar{M}$  – mean molar mass of constituents of the melt /kg mol<sup>-1</sup>,  $A$  – surface of slag-metal interface /m<sup>2</sup>,  $V$  – volume of the metal phase /m<sup>3</sup>

All necessary thermochemical and physical data for calculating the transport coefficients and solving the above mentioned differential equation was collected from literature or calculated by using different approaches. For a detailed description please refer to [8].

Table 1 sums up the calculated transport coefficients for the various reaction zones in the case of a Ti6Al4V alloy. It can be observed that rate constants differ from reaction zone to reaction zone mainly due to largely different calculated boundary layer thicknesses (e.g. falling droplet vs. bulk metal pool) and residence times. It can be observed that the liquid film below the electrode (zone 1) exhibits the largest area to volume ratio i.e. a strong impact of mass transport on volumetric concentration, while the metal pool maintains an aspect ratio two orders of magnitudes lower but at a significantly larger residence time. The impact of the falling droplet, regarded by many authors as the main center of mass transfer in ESR because of the fast counter-current speeds at the metal-slag interface can be nearly neglected as displayed below in the results of the model: A/V is lower than at the electrode film and residence times are calculated to be extremely short.

Table 1: Calculated transport coefficients for the three reactions zones. Most intensive exchange reactions can be expected for high A/V, long residence times and large transport coefficients.

	<b>Zone 1</b>	<b>Zone 2</b>	<b>Zone 3</b>
<b>k, O, m /m sec-1</b>	6,83E-05	1,03E-03	2,58E-05
<b>k, Ca, sl /m sec-1</b>	1,21E-04	2,56E-04	1,04E-04
<b>k, CaO, sl /m sec-1</b>	2,67E-04	5,72E-04	2,34E-04
<b>A/V /m^-1</b>	5764,10	2492,59	44,44
<b>residence time /s</b>	1,42	0,015	198,25



With the necessary data determined, all parameters were put together in MS Excel<sup>TM</sup> spreadsheets to allow for easy scale up scenario calculations of furnace parameters (e.g. ingot diameter, melt rate), slag and metal composition. The parameters b, c and the differential equation in (2) were numerically solved independently for the three reaction zones at the respective boundary conditions and then merged together in order to calculate the change of the slag composition and the oxygen concentration of the solidifying metal. Based on this principle the whole remelting process was modelled in discrete time steps by recursive recalculation of the oxygen concentration.

## Experimental validation

In order to validate the model, experimental trials in the IME PESR furnace (300kW, 50 bar max. pressure) were conducted. Therefore, Ti6Al4V electrodes (900mm length, 110 mm diameter, 2000 ppm oxygen) were remelted under a CaF<sub>2</sub> (1,5 wt-% CaO) flux with an abrupt addition of metallic calcium in order to enforce a step response in form of a chemical net reaction between the metal and slag phase. After remelting the ingots were sampled according to Figure 1. Oxygen was determined by inert gas fusion on a Ströhlein ON-Mat 8500.

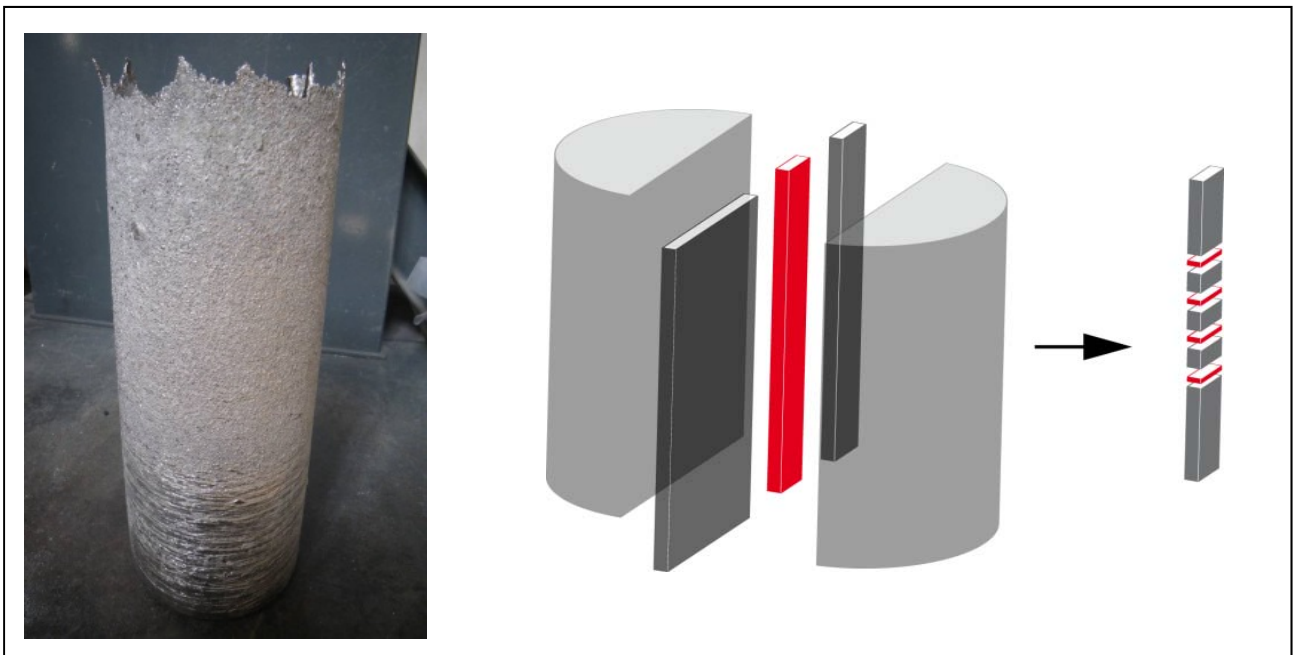


Figure 1: Remelted ingot (left) and sampling methodology for oxygen analysis (right)

## Results

Obtained results of the chemical analysis were plotted as single data points against the process time as shown in Figure 3. The continuous lines in the same diagrams present the predicted oxygen concentration of the metal by the kinetic model. The moment of calcium-addition to the slag is indicated with the vertical lines.



As the results show, oxygen level increases at the beginning of the process. This can be explained by the CaO in the slag which dissolves in the metal to a level according to the equilibrium constant  $K$  of the deoxidation reaction. The further oxygen level in the metal calculated by the model can be explained as follows: As the oxygen concentration in the slag reaches its equilibrium state, a dilution of the solidifying metal takes place as drops from the electrode tip enter the liquid metal pool. This leads to a continuous decrease of the oxygen level towards the initial value of 2000ppm (Figure 3, right). The addition of metallic calcium leads to a sharp decrease of oxygen down to 1000 – 1500 ppm. As both figures show, the predicted oxygen trend is mostly confirmed by the experimental trials.

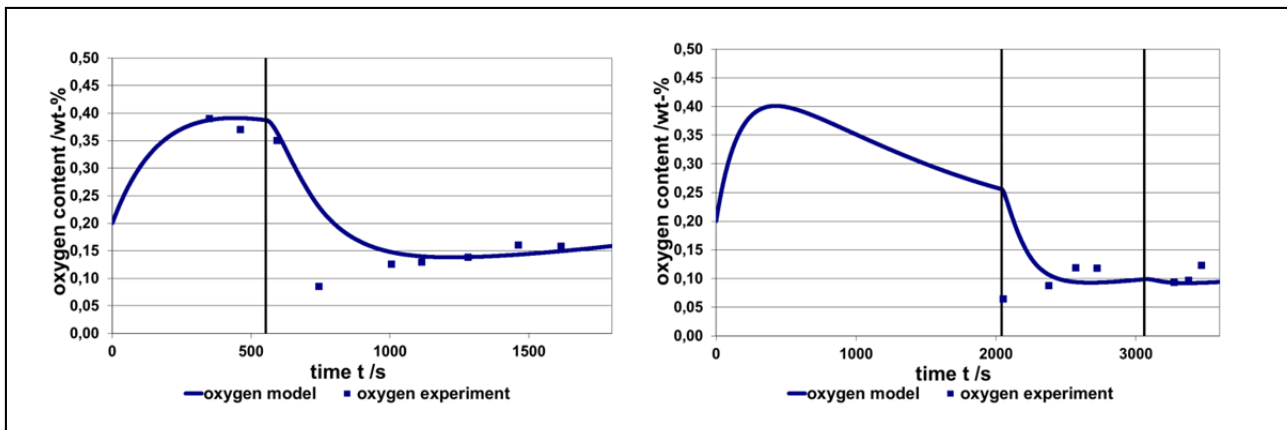


Figure 3: Comparison between calculated and experimental results shows good agreement

## Summary and Outlook

A kinetic model was set up in order to predict the oxygen concentration during deoxidation of titanium alloys in the PESR process. On the basis of Frasers [9] work it could be shown that the rates of deoxidation in the three reaction zones electrode tip, metal droplet and liquid pool differ from each other due to different speed constants, residence times and A/V ratios. By merging the reaction rates for all zones and implementing the calculations into a MS Excel<sup>TM</sup> spreadsheet, the whole re-melting process could be simulated in terms of the oxygen concentration in the metal. Theoretical results were contrasted by experimental trials with using the “step response” method by rapid addition of calcium to the slag.

The kinetic model shows good agreement with the experimental values, especially in terms of the qualitative trend. Further trials are needed to validate the model. If successful, this kinetic model can be used as a tool to calculate the needed calcium addition to the process in order to obtain a homogeneous product.

This work is based on results published by Reitz [8].



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