Deoxidation Limits of Titanium Alloys during Pressure Electro Slag Remelting

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Abstract. This paper focuses on deoxidation of titanium alloys produced by aluminothermic reduction (ATR) and subsequent homogenizing and alloying by vacuum induction melting (VIM). The main goal of the performed research work is to outline the deoxidation limit during pressure electro slag remelting (PESR) of the described material.

To obtain electrodes for deoxidation, a Ti-24Al-16V masteralloy was produced by ATR and afterwards melted in a 0.5 litre calcium-zirconate (lab scale) or 14 litres high purity calcia (pilot scale) crucibles with continuous addition of Ti-sponge after reaching liquid state in order to obtain a final Ti-6Al-4V alloy. During melting, in both cases evaporation of calcium was noticed. The cast ingots were analysed for oxygen using inert gas fusion method, matrix and alloying elements were analysed by XRF.

Results show oxygen levels between 0.5 and 0.95 wt.-% for the ingots which were melted in calcium-zirconate crucibles and approx. 1 – 1.2 wt.-% for the material produced by utilization of calcia crucibles. The subsequent deoxidation was carried out in lab and pilot scale electroslag remelting furnaces using a commercially pure calcium fluoride slag and metallic calcium as deoxidation agent. It could be shown, that deoxidation of the highly contaminated material is possible applying this method to a certain limit. Pilot scale trials showed a reduction of oxygen contents by 1500 – 3500 ppm. Oxygen levels in lab scale trials showed weaker deoxidation effects.

In order to describe the achieved deoxidation effects in a quantitative way, the analyzed oxygen contents of the obtained ingots are compared with calculated data resulting from a mathematical kinetic model. The modelled datasets are in good agreement with experimental oxygen values.

1. Introduction

Titanium and its alloys combine several attractive properties such as high strength, low density, corrosion resistance and excellent biocompatibility. Despite these characteristics, the wider application of titanium and titanium alloys is limited due to the high manufacturing costs. Therefore, since approximately 10 years the IME, RWTH Aachen University, is working on the application of a new synthesis and recycling process route for titanium alloys with special regard on decreasing the level of oxygen due to its negative influence on the ductility. Detailed investigations on each process step were performed by Lochbichler [1] Stoephasius [2], and Reitz [3]. An important aspect of the process route is to resort to conventional and established metallurgical processes such as Vacuum Induction Melting (VIM), Electroslag Remelting (ESR) or Vacuum Arc Remelting (VAR).
According to the type of material (scrap, raw materials) and the composition, different process steps are combined to achieve the desired product quality. Main principle to control the oxygen level is the introduction of metallic calcium to the liquid slag or melt as a deoxidant. Especially for the material class of $\gamma$-TiAl it could be shown, that deoxidation of these alloys from investment casting scraps during ESR is feasible resulting in final oxygen contents below 500 ppm in the product [3]. The research presented in this paper focuses on an alternative process route for Ti6Al4V alloys with special regard on the PESR deoxidation.

2. Fundamentals

One of the most challenging tasks in the refining process of titanium alloys is the removal of oxygen present in titanium as dissolved TiO. Besides the high stability of TiO ($\Delta G_f = -357 \text{ kj/mol @ 1750°C}$) also the oxygen solubility of up to 33 at% in the system Ti-O indicates that the removal is difficult. The deoxidation by vacuum distillation is not feasible due to the necessary oxygen partial pressure in the furnace atmosphere ($p_o < 10^{-20} \text{ bar for 1000ppm in a cp-Ti melt}$) which is so low, that even present oxygen from the gas phase will be nearly fully dissolved. Thus, the use of deoxidation agents becomes evident.

Regarding the Vacuum Induction Melting of titanium and titanium alloys, the choice of the refractory material is crucial. According to standard Gibbs free energy calculations of oxides, only CaO, Y$_2$O$_3$, and ZrO$_2$ seem to be sufficiently stable against titanium, whereas CaO should be most stable. Tsukihashi et al. [4] investigated the calcium and oxygen uptake in c.p. titanium and TiAl melts in equilibrium with solid CaO. The experiments were conducted in a closed system by using a lid to avoid Ca evaporation. His research shows, that the reaction according to (1) is causal between for the equilibrium between calcium and oxygen in titanium melts, which depends strongly on temperature. [4] [5]

\[
\text{[TiO]}_{\text{Ti}} + \text{[Ca]}_{\text{Ti}} = \text{[CaO]}_{\text{slag}} + \text{Ti} \quad (1)
\]

Unfortunately, Tsukihashis results do not allow a prediction of the reachable final oxygen contents in the melt during ESR since the distribution coefficient between calcium in the metal and calcium in the slag is not known. Extending Tsukihashis work, Okabe et al. [6] equilibrated Ti melts with CaO and Ca ($a_{\text{Ca}} = a_{\text{CaO}} = 1$) and calculated the activity coefficient $f_{\text{TiO}}$. Based on this work, Stoephasius et al. [5] calculated the deoxidation limits of Ti and TiAl melts with metallic calcium as deoxidant. Since during electroslag remelting, instead of pure CaO a CaF$_2$-(CaO) slag (with metallic Ca as deoxidant) is used, the CaO activity is decreased. Therefore, from a thermodynamic point of view, deoxidation of cp titanium melts below 2000 ppm oxygen should be possible in general. However, major challenge during PESR deoxidation of titanium is to achieve a homogeneous oxygen distribution in the whole ingot. Since the CaO concentration is increasing according to (1) during remelting, the Ca activity has to be continuously increased during the process for compensation. Furthermore, the CaO-activity can be decreased by dilution via addition of CaF$_2$ to the slag. Figure 1 exhibits that the necessary Ca content in the slag to reach specification conform oxygen contents is much higher in cp-Ti melts than in TiAl. Thus, because of the high vapour pressure of Ca, this results into difficult handling of high Ti containing melts.
3. Experimental

3.1. Masteralloy synthesis by Aluminothermic Reduction (ATR)

The feasibility of aluminothermic reduction (ATR) of TiO\textsubscript{2} to produce Ti alloys was shown in previous works [7][8]. The main challenge for the ATR process is to produce Ti alloys with high titanium and low aluminium content. However, the high oxygen solubility of titanium does not allow producing Ti alloys with low aluminium and simultaneous low oxygen contents. Because Al is used as alloying element in many Ti materials, residual Al content in the ATR product can be tolerated. The inverse correlation of Al and O content in titanium materials is reported to be 6 wt.-% Al at >10 wt.-% O and 36.-% Al at 1.4 wt.-% O. [9] The typical oxygen content of aluminothermically produced TiAl material varies between 1.3 and 1.8 wt.-% [7][8]. Therefore, a subsequent deoxidation step has to be performed for ATR Ti in order to meet the specifications of 2000 ppm. It is of particular interest to provide aluminothermic reduced titanium for further titanium based alloy production. By co-reduction of TiO\textsubscript{2} and other oxides of alloying elements such as vanadium the synthesis of a master alloy is possible. In this respective, Ti-6Al-4V, representing the most utilized titanium alloy, gets relevant.. For the present research the composition of the master alloy is chosen as Ti with 60 wt.-%, Al with 24 wt.-% and V 16 wt.-%. For the subsequent processing by VIM titanium sponge has to be charged with a ratio of 3:1.

The reduction of TiO\textsubscript{2} with aluminium requires further heat input to obtain the reaction self-propagated. KClO\textsubscript{4} is added to the reaction mixture with the required amount of aluminium. For synthesis of the master alloy, the combined reduction of oxides of titanium and vanadium is performed. There are different oxides available, such as V\textsubscript{2}O\textsubscript{3}, V\textsubscript{3}O\textsubscript{4}, V\textsubscript{2}O\textsubscript{5} and mixtures of theses oxides whereat V\textsubscript{2}O\textsubscript{5} provides the highest enthalpy input. In order to decrease the KClO\textsubscript{4} amount and hereby decreasing Cl-bearing off-gas V\textsubscript{2}O\textsubscript{3} is used in every experiment. In order to decrease the liquidus temperature of the alumina slag, lime is added to the ATR mixture as flux. All input materials are added in powder form and blended before charging. Experiments on two different scales (20 L ± 6kg of product and 90 L ± 30 kg) are performed in the present work. The initial ignition is carried out by a filament on top of the input mixture in all trials. After reaction, the produced metal ingot is analyzed with respect to total oxygen as well as base elements. The ingot is cleaned from residual slag attached to the surface and crushed for the subsequent processing steps.
The cross sections of the ATR products are shown in Figure 2. It can be seen, that a weak segregation occurred in the small scale trail in the middle of metal ingot wherein the melt solidifies at last. On a macroscopic scale, there are no porosities observed within the metal products.

3.2. Electrode production by Vacuum Induction Melting (VIM)

Consolidation, alloying and electrode production were carried out in a 40kW and 150kW vacuum induction furnace at IME. The crucibles used for melting were made of CaZrO$_3$ (lab scale) or CaO (pilot scale) refractory material. Properties of the CaZrO$_3$ crucibles are described elsewhere [10]. At the beginning of each vacuum induction only the ATR material is charged into the crucible. Titanium sponge (ratio 3 Ti: 1 ATR) is added subsequently using a charging system after obtaining a melt in order to keep the titanium activity as low as possible at any time to minimize crucible-melt reactions. During melting, strong evaporation of calcium can be noticed. The melt is hold at a temperature of 1750 °C for 10 min to obtain a good homogenization. Afterwards, the melt is tapped in a water cooled copper mould with a diameter of 50mm and 100mm respectively.

After cooling and stripping, the cast ingot is analyzed for oxygen using inert gas fusion method, matrix and alloying elements were analyzed by XRF. Figure 3 shows the cast electrodes.
3.3. Final Deoxidation by (Pressure) Electroslag Remelting (PESR)

3.3.1. Lab Scale

Remelting of the lab scale electrodes was performed in a chamber electroslag furnace (ChESR) at Donetsk National Technical University (DonNTU), Ukraine with a maximum operating power of 724kW. The furnace is equipped with a water cooled copper crucible (70 mm diameter, 425 length) and a Chamber for operating under shield gas at slight overpressure. Before remelting, the crucible is filled with 700 g technically pure CaF₂ and calcium granules for deoxidation, which were pressed to a tablet. The calcium content varies from 4 to 8 wt.-% of the total slag mass depending on the trial. After this, the chamber is evacuated and backfilled with Argon (99.987%). Starting of the process is performed by arcing between the electrode and calcium tablet. Process control is done by manual adjustment of the current, which is kept by approx. 3 kA. During remelting, the gas pressure in the chamber is maintained at 0.3 -0.4 atm. above atmosphere. The process time varies from 130 to 250 s depending on the electrode length. After cooling, the ingot (Figure 4) is analyzed by OES for metals and inert gas fusion for dissolved oxygen.

Figure 4: Obtained ingots after electroslag remelting before (left) and after (right) slag skin removal

3.3.2. Pilot Scale

The experiments for pilot scale deoxidation were performed in the IME pressure electroslag remelting furnace. The furnace is equipped with a charging system, which allows the continuous feeding of additives into the melt during the process at all operating pressures and with adjustable speed. Before the furnace is closed, the electrode is connected to the electrode rod with a titanium stub. A starting plate made of Ti-50Al sputter targets is placed on the crucible bottom to ensure electrical contact during the starting phase of the process. Afterwards, the crucible is filled with 4-4.5 kg of preheated (15 h @ 650 °C) process slag that consists of the technically pure CaF₂ slag Wacker Electroflux 2052 (> 97 wt.-% CaF₂) as well as 225-300 g of metallic calcium depending on the trial. The bunkers of the feeding system are filled with a CaF₂-Ca mixture (ratio 2:1). The furnace is closed and, in order to avoid reactions with oxygen from ambient air, the vessel is evacuated to a pressure of 10⁻¹ mbar. Consecutively, the vessel is backfilled with Ar gas to the desired process pressure of 20 bar to avoid excessive Ca evaporation. During remelting, constant feeding of the CaF₂-Ca mixture was performed in order to compensate Ca-losses and to reduce the CaO activity. After
remelting and cooling for several hours, the ingot is stripped, the cap-slag and slag skin are removed, the ingot is sectioned and analyzed by IGF for oxygen.

4. Results and Discussion

4.1. Masteralloy synthesis

EDX-analyses exhibit that present inclusions are mainly alumina based oxide particles, spinel type particles of alumina and calcia were detected as well. The EDX-results indicate locally strong variations of the metal composition. The titanium content varies between 51 and 62 wt.-%, Al between 21 and 26 wt.-% and vanadium between 13.6% and 22.4 %. However, the average values for aluminium and titanium match with the results of the ICP-analysis. The metal product of the small scale trial results in lower titanium yields and effects hereby a higher amount of aluminium because not consumed for TiO₂ reduction.

Table 1 shows the oxygen contents of the obtained master alloys. With respect to the lower titanium content and higher aluminium content, the lower oxygen amount in the small scale trial is evident and corresponds with literature data. For further processing, the 6kg batch was used for lab scale VIM trials (VIM1a-3a), the 30kg batch for pilot scale (VIM1b-3b) melts.

| Trial       | Ti   | Al  | V   | Fe  | Si  | O    |
|------------|------|-----|-----|-----|-----|------|
| 6 kg batch | bal. | 31.7| 12.6| 2.40| 0.28| 0.78 |
| 30 kg batch| bal. | 22.4| 14.4| 1.95| 0.73| 0.92 |

*a – lab scale, b – pilot scale

4.2. Vacuum Induction Melting

Table 2 show the concentration of the major elements in the obtained electrodes from lab and pilot scale tests. Since one lab scale ingot consists of two castings, an oxygen concentration gradient from top to bottom can be measured. In general, the oxygen pickup when using CaZrO₃ crucibles is lower, which indicate their stability. On the contrary, a Zr enrichment in the metal can be measured. A detailed description of the CaZrO₃-Ti-interaction is given by [10]. Melting in pure lime crucibles leads to an oxygen increase to approx. 1-1.2 wt.-%. All cast electrodes are further processed in the electroslag remelting process.

Table 2. Chemical composition of obtained lab- and pilot scale electrodes (all elements in wt.-%)

| Trial       | Ti   | Al  | V   | Zr  | Fe  | Si  | O top/bottom |
|------------|------|-----|-----|-----|-----|-----|--------------|
| VIM 1a     | 89.77| 5.69| 2.38| 1.36| 0.24| 0.14| 0.70/0.93    |
| VIM 2a     | 90.97| 5.32| 2.12| 0.87| 0.24| 0.11| 0.62/0.72    |
| VIM 3a     | 90.51| 4.87| 2.47| 1.43| 0.25| 0.12| 0.74/0.94    |
| VIM 1b     | 85.53| 9.05| 4.61| -   | 0.36| 0.20| 1.05         |
| VIM 2b     | 87.00| 8.20| 3.91| -   | 0.32| 0.26| 1.04         |
| VIM 3b     | 85.82| 8.60| 4.48| -   | 0.36| 0.20| 1.24         |

*a – lab scale, b – pilot scale
4.3. Electroslag deoxidation

Table 3 summarizes the main (P)ESR process parameters, final ingot oxygen concentrations as well as the deoxidation efficiency. The trial number refers to the VIM electrode used (see Table 2). Regarding the lab scale trials, the oxygen analyses were performed again in the top and bottom section of the ingot. As results show, deoxidation could be achieved for each ingot in the bottom part. On the contrary, the oxygen content in the top part is equal to or higher than in the initial electrode. An oxygen gradient can be explained by CaO enrichment and Ca loss in the slag. An additional oxygen uptake cannot be explained entirely by considering only dilution effects between top and bottom. Here, more trials are necessary. In respect to the pilot scale tests, a clear deoxidation effect for all Calcium containing trials can be observed. Figure 5 shows the oxygen change after remelting for all pilot scale tests in detail. The oxygen level is significantly decreased, especially trial number PESR number 1b shows a clear tendency which indicates a rising Ca activity in the slag during the melt. Unfortunately, an on-line measurement of the Ca content in the slag is not possible. The reference melt without Ca-addition shows an oxygen uptake during the whole process which can be explained by dilution of CaO residues in the slag, as well as the dilution of remaining oxide residues from the electrode. In general, a clear tendency between the added Calcium/ingot mass ratio could not be verified and has to be investigated in further trials.

Table 3. Experimental parameter and results of lab- and pilot scale deoxidation trials

| Trial   | $M_{\text{Ingot}}$/kg | melt rate/kg/min | $m_{\text{CaF}_2}$/kg | $\text{Ca}_{\text{start}}$/wt.-% | $m_{\text{Ca}}/m_{\text{Met}}$/g/kg | $O_{\text{top/bottom}}$/wt.-% | $\Delta O_{\text{O}}$/wt.-% |
|---------|----------------------|------------------|------------------------|----------------------------------|----------------------------------|-------------------------------|-----------------------------|
| ESR 1a  | 1.38                 | 0.6              | 700                    | 8.14                             | 44.93                            | 0.7/0.78                      | 0.00/-0.15                  |
| ESR 2a  | 1.57                 | 0.5              | 700                    | 9.20                             | 50.96                            | 0.78/0.58                     | +0.16/-0.15                 |
| ESR 3a  | 2.73                 | 0.7              | 700                    | 8.50                             | 23.81                            | 0.86/0.75                     | +0.12/-0.19                 |
| PESR 1b | 27.0                 | 0.6              | 4500                   | 4.76                             | 14.81                            | 0.73                         | -0.32                       |
| PESR 2b | 29.6                 | 0.6              | 4000                   | 6.98                             | 22.64                            | 0.79                         | -0.25                       |
| PESR 3b | 30.6                 | 0.6              | 4500                   | 0                                | 1.47                             | 1.26                         | +0.02                       |

*a – lab scale, b – pilot scale (20 bar pressure),

Figure 5: Deoxidation efficiency in PESR pilot scale tests
5. Kinetic Model

Fraser [11] investigated various mass transfer aspects of AC ESR of steels (slagging of Mn and desulphurisation) in a very comprehensive thesis work. The findings of his work can be adapted to the conditions for the presented case. General assumption for describing the reaction kinetics during ESR is, that thermochemical equilibrium is only achieved at the metal-slag phase boundary itself, thus 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.

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 [12].

All necessary thermochemical and physical data for calculating the transport coefficients and solving the differential equation was collected from literature or calculated by using different approaches. For a detailed description please refer to [12]. With the necessary data determined, all parameters were put together in MS Excel™ 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 can be modelled in discrete time steps by recursive recalculation of the oxygen concentration.

Figure 6 shows the modelling results of trial PESR 1b. The solid line represents the calculated oxygen content in the melt during the process, the individual data points are oxygen contents in the ingot determined by chemical analysis. Based on the melt rate, for each process time, a corresponding ingot height was allocated. In general, the model is in good agreement with the experimental values and thus indicates a kinetic limit for a deoxidation effect.

![Figure 6: Modelled and experimental oxygen concentrations in the Ti-Al-V ingot (PESR 1b)](image_url)

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![Figure 6: Modelled and experimental oxygen concentrations in the Ti-Al-V ingot (PESR 1b)](image_url)
In a previous study [13], the authors presented the deoxidation behavior of a standard Ti-6Al-4V alloy with 2000 ppm oxygen. Idea was to enforce a quick drop of the oxygen concentration by rapid Ca-addition to the slag during remelting. Figure 7 shows the obtained results, which predict an oxygen level increase at the beginning of the process. This can be explained by the CaO in a technically pure CaF₂ slag, which dissolves in the metal to a level according to the equilibrium constant K of the deoxidation reaction. The further oxygen level trend 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 7, right). The rapid 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. Furthermore, the trials show that PESR deoxidation of Ti6Al4V is possible to values below 1000 ppm.

![Figure 7: Deoxidation behavior of a standard Ti-6Al-4V alloy with 2000 ppm oxygen](image)

6. Conclusions

- Ti-Al-V electrodes containing oxygen contents above specifications were successfully produced by ATR masteralloy synthesis and subsequent alloying via VIM in lab scale (CaZrO₃ refractory) and pilot scale (pure CaO refractory) to test the deoxidation limits in the following ESR process
- Deoxidation trials in chamber and pressure ESR units were performed under varying Ca-contents in the slag
- Deoxidation effects vary significantly over the ingot height in lab scale and cannot be explained entirely. Since only slight overpressure (+0.4 bar) was set, Ca losses due to evaporation are possible, since the operating temperature is above the Ca boiling point
- Oxygen levels in PESR trials (20 bars) can be reduced by max. 3500 ppm
- A clear tendency between the calcium/ingot mass ratio could not be verified. Thus, the process chain needs more trials for validation and ensuring reproducibility
- A kinetic model is presented which predicts the oxygen concentration as a function of process time. Modelled and experimental values are in good agreement
- The main challenge remains achieving a homogeneous oxygen level in the whole ingot

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