A new Processing Route for Titanium Alloys by Aluminothermic Reduction of Titanium Dioxide and Refining by ESR

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Abstract

In this work a thermodynamic model based on molar Al/TiO_2 ratio, CaO content in slag and energy density was created to describe aluminothermic reduction. The influence of these parameters was theoretically calculated and experimentally proofed. The high solubility of γ-TiAl for oxygen doesn't allow to produce γ-TiAl with low aluminium content and low oxygen content (below 500 ppm) at the same time. Therefore, a second reduction step with Ca is necessary.

Thermodynamic calculations showed that a Ca containing CaF_2 slag is able to decrease oxygen content in γ-TiAl below 100 to 250 ppm depending on the molar slag/metal ratio and Ca content in the slag. A pilot electro slag remelting unit is used to proof these calculations. In opposite to common aluminothermic process the produced liquid metal is directly cast without contact to air into a water cooled copper mould. This eliminates the difficult process step of impacting γ-TiAl pieces to an electrode after the won ingot has been crushed.

1 Introduction

The technical use of Titanium was initiated after developing the Kroll and Hunter Process from about 60 years ago. Since this time the acceptance of titanium increased due to its low density, high thermal stability and corrosion resistance. In the last years γ-TiAl got a high importance due to its corrosions resistance especially at high temperature applications. Increasing pressure to reduce the production costs, brought different alternative processes to the Kroll and Hunter-Process. One of them is the aluminothermic reduction of rutile or titanium oxide pigment, which should reduce production costs of titanium aluminides to 15 $/kg [1].

The reduction of TiO_2 by aluminium was studied by Fletcher [2], Kubaschewski/Dench [3] e. a. It can be expressed simplified by following equation.

$$3\ TiO_2 + 7\ Al\ \rightarrow\ 3\ TiAl + 2\ Al_2O_3 \qquad (1)$$
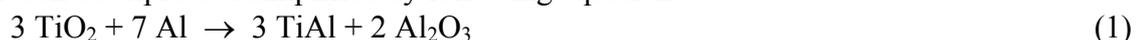
By adjusting molar Al/TiO_2 ratio of feed material, composition and oxygen content can be influenced. For decreasing oxygen content below 1 % Al/TiO_2 ratio must be higher than 2.5 [3]. Further fundamental research projects from M. Maeda et al. [4, 5] dealt with aluminothermic reduction of TiO_2 under a CaF_2-CaO-Al_2O_3 slag. Results showed that minimum oxygen content of 0.42 % can be reached by using a Al/TiO_2 ratio of 2.8. Fletcher proofed this composition.

Benz/Carter [6] and Tsukihashi et al. [7] made basic experiments concerning decreasing of oxygen content. They showed that a metallic Ca containing CaF_2 slag can be used to reduce

oxygen content in titanium aluminides below 0.05 %, which is enough to reach current requirements.

2 Conceptual Process Design of the IME-TiAl-Process

At IME Process Metallurgy and Metal Recycling, department and chair of the Aachen University of Technology, following so-called IME-TiAl-Process was designed. TiO_2, which can be brought in as pigment or possibly as high-grade rutile, is mixed with alloying metal oxides (e. g. Nb_2O_5 or Cr_2O_3) and reduced by aluminium in a metallothermy reaction (fig. 1). Because of the high difference between melting points of Al_2O_3 slag and metal, addition of CaO is necessary to decrease melting point and viscosity of slag. The main reaction (1) doesn't bring in enough energy for the process. Therefore a second booster reaction is needed. Reaction between $KClO_4$ and Al produces Al_2O_3 slag and KCl which evaporates at 1,475 °C and doesn't influences the main reaction. The formed Al_2O_3 must be considered during calculation of CaO addition.

$$3\ KClO_4 + 8\ Al\ \rightarrow\ 3\ KCl + 4\ Al_2O_3 \tag{2}$$
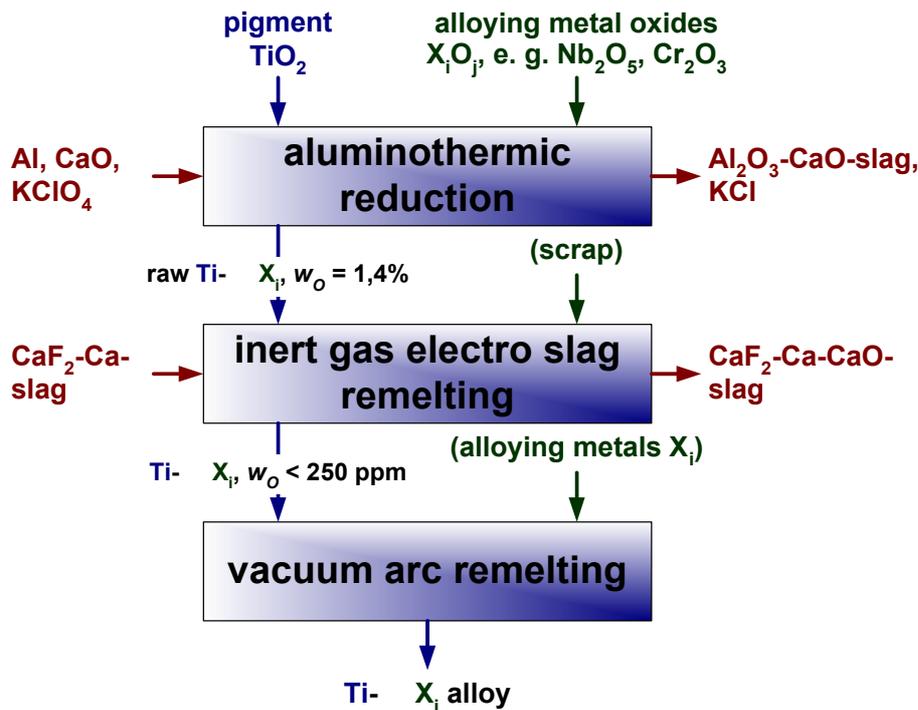
Figure 1: IME-TiAl-process flow of aluminothermic Ti-Al-X production

Beside a flue dust, which mainly consists of KCl and slag drops, and the slag, which contains small amounts of titanium oxide, a raw Ti-Al-X alloy is formed. Because of the high oxygen content and small inclusions of slag, this alloy has to be refined in a second process step. The high brittleness of γ-TiAl doesn't allow conventional treatment of aluminothermic won ingot, i.e. crushing and compacting to an electrode that is remelted in ESR furnace. Therefore a water-cooled mould is mounted below aluminothermic reaction chamber, shut with a Ti surrounded Al sheet and filled with inert gas. As soon as reaction front reaches the

Al-sheet, it melts and metal can fill the mould without any contact with air atmosphere. The Ti surrounding prevents a too strong cooling down of the melt above the Al sheet.

The won Ti-Al-X electrodes are remelted in ESR furnace under an active (i.e. Ca containing) CaF$_2$ slag. Ca has stronger oxygen affinity than Al and is able to reduce the oxygen content below 100 ppm. It is necessary that the Ca content in ESR slag is lower than a few percent, because otherwise the risk of a Ca enrichment in Ti-Al-X increases. Therefore during the process Ca has to be brought in continuously using a recharging unit. The CaO enrichment of slag, which can't be prevented, limits reduction capacity of ESR slag and leads to growing oxygen content in Ti-Al-X ingot up to 250 ppm during the process, if the Ca content remains constant.

If the homogeneity of Ti-Al-X ingot is not sufficient for application, a third process step is executed, in which the ingot is remelted in a vacuum arc furnace. During ESR and VAR process it's possible to add alloying elements to adjust the final composition.

3   Thermodynamic Calculations and Experimental Work

3.1   Theoretical Oxygen Content in TiAl after Aluminothermic Reduction

Based on data of ternary Al-Ti-O system from Lee and Saunders [8] and FACT-SLAG from FACT database [9] calculations of theoretical oxygen content were made [10]. For this purpose the following parameters where used to describe the equilibrium composition of aluminothermy. The equilibrium temperature is estimated with 1 400 °C marginally below the melting point of TiAl, because of the very high cooling rate in the water-cooled mould.

$$\varphi \equiv \frac{n_{Al}}{n_{TiO_2}} \tag{3}$$

(φ = molar Al to TiO$_2$ ratio [-], n_{Al} = amount of Al [mol], n_{TiO2} = amount of TiO$_2$ [mol])

$$\psi \equiv \frac{n_{CaO}}{n_{Al_2O_3}} \tag{4}$$

(ψ = molar CaO to Al$_2$O$_3$ ratio [-], n_{CaO} = amount of CaO [mol], n_{Al2O3} = amount of Al$_2$O$_3$ [mol])

For equilibrium calculation the main reaction (eq. 1) is extended to eq. 5. The molar O to Ti ratio in metal x is changed from 0 to 0.5. For each x the free Gibbs energy is calculated. Minimizing free Gibbs energy leads to the equilibrium state where oxygen content can be calculated.

$$TiO_2 + \varphi\, Al + \tfrac{2-x}{3}\psi\, CaO \;\rightarrow\; TiAl_{\varphi-2\left(\frac{2-x}{3}\right)}O_x + \tfrac{2-x}{3}\left[Al_2O_3 \cdot (CaO)_\psi\right] \tag{5}$$
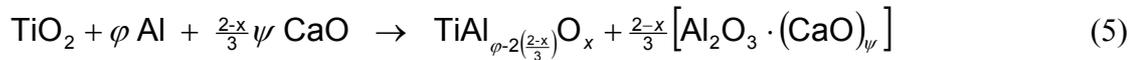
(x = molar O to Ti ratio in metal [-])

The equilibrium calculations show the strong dependency of the oxygen content on molar Al to TiO$_2$ ratio. Rising amounts of aluminium and a lower equilibrium temperature (i.e. slower cooling rate) reduce the oxygen content of the ingot. Beside these both well-known effects also the CaO content in slag has a significant influence. A reason for this is that CaO lowers the activity of Al$_2$O$_3$ in slag by forming ceramic complexes like (Al$_2$O$_3$)$_6$ · CaO or (Al$_2$O$_3$)$_2$ · CaO. This shifts the equilibrium in the metal phase to lower oxygen contents (fig. 2).
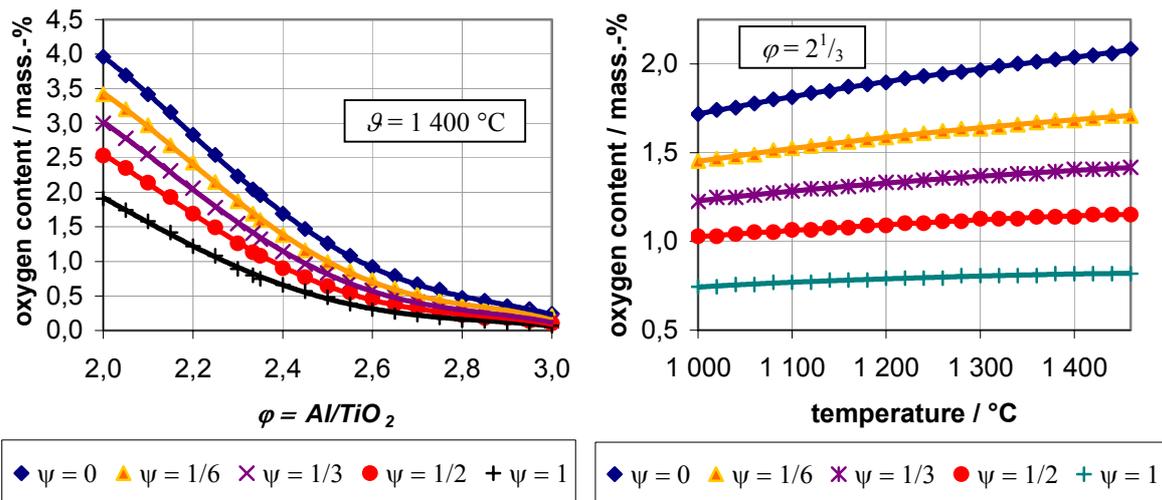
Figure 2: Dependency of the oxygen content in TiAl on φ (left) and temperature (right)

3.2 Experimental Validation of the Aluminothermic Process Model

As mentioned in chapter 2 the aluminothermic TiAl must be solidified directly after reaction without any contact to air in order to prevent the formation of titanium aluminium nitrides. The experimental set up is illustrated in fig. 3. 20 kg of input mixture are ignited in the reaction chamber after the mould has been filled with argon gas. After a few seconds the reaction front reaches the aluminium sheet, which melts, and the metal flows into the mould. The dimensions of the aluminium sheet are mathematically calculated, because the melt mustn't freeze over the sheet before it melts, and on the other hand the delay must be long enough to allow a good metal/slag separation. Two dimensional numerical heat transfer calculations inside the system melt-sheet-border-shutter piece allowed a rough estimation of the sheet dimensions.
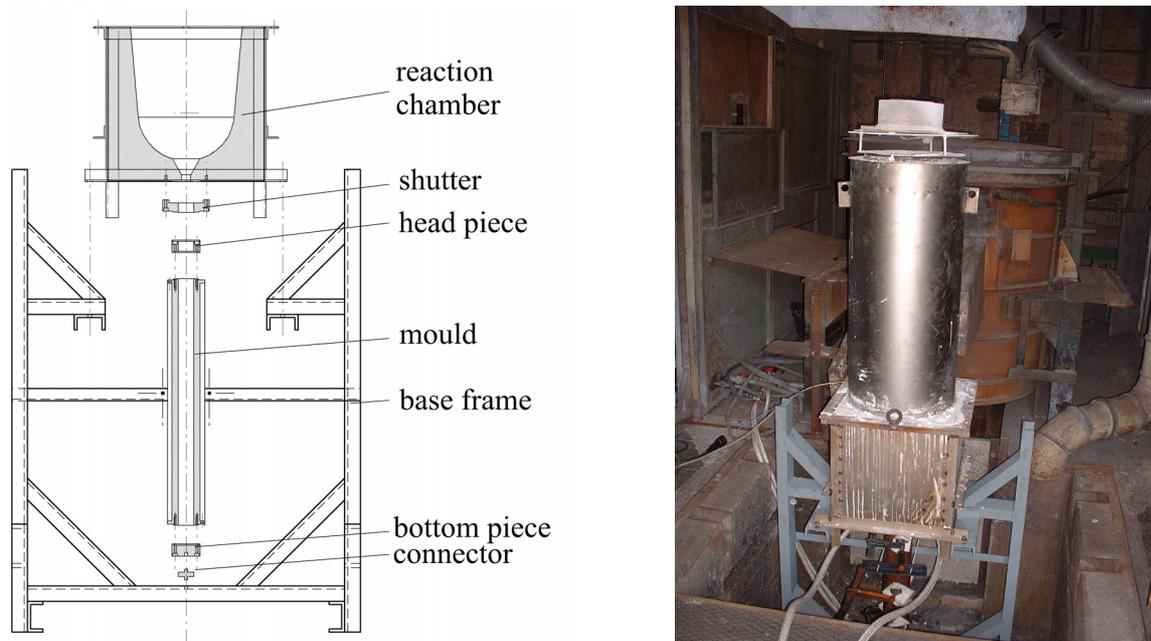
Figure 3: Experimental set up of the inline electrode production process (aluminothermic TiO2-reduction)

Two test series were conducted to proof the electrode production principle. The first series dealt with optimising the shutter mechanism and the dimensions of the shutter sheet. The experiments showed that good results can be reached by using a thin aluminium sheet of about 1.5 mm thickness and a diameter not much larger than the diameter of the tap hole, which is 30 mm in this series. The aluminium sheet is fixed to reaction chamber with a 1 mm titanium sheet which is a good thermal isolator compared to aluminium and copper. This arrangement allows nearly linear increase of temperature in aluminium sheet and therefore a well controllable melting time. In opposite to former expectations the first test series proofed that a short melting time of less than 1 second of the aluminium sheet is enough to allow separation of metal and slag.

The target of the second test series was to produce electrodes, which can be refined in an inert electro slag remelting furnace (IESR). Because of the limited capacity of reaction chamber and mould, it was not possible to produce larger electrodes than 800 mm in length and 50 mm in diameter. The electrode, which was won in first experiment, showed several deep cracks resulting from the high cooling rate (fig 4). Therefore, in next experiments the flow rate of cooling water and thus the heat-transfer coefficient was reduced. This was assisted by using different types of refractory dressings and a 0.17 mm titanium foil isolation respectively. Due to this modifications cracks could be significantly reduced, but further optimisation is necessary.

The chemical composition of the produced electrodes is close to the thermodynamic calculations. The mean oxygen content is 1.46 wt.-%, the standard deviation is 0.49 wt.-%. Using a high cooling rate the oxygen content is higher than using slow cooled conditions in ceramic crucibles, where mean oxygen content is 1.17 wt.-% and deviation is 0.21 wt.-%. All electrodes have very little slag inclusions. This proofs that the adjusted melting time of the aluminium sheet is long enough.
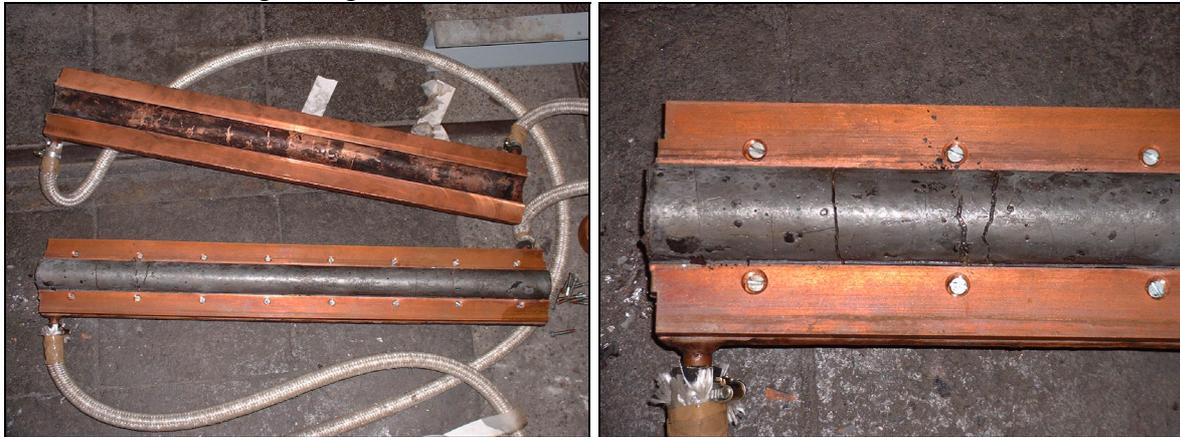
Figure 4: Aluminothermic electrode with overcooled conditions (right)

3.3 Theoretical Oxygen Content in TiAl after Electro Slag Remelting

The calculation of the theoretical oxygen content in TiAl after electro slag remelting is based on the ternary Al-Ti-O system (metal phase) as mentioned in chapter 3.1 and the ternary Ca-CaF_2-CaO system (slag) which has been optimised using data from Zaitsev and Mogutnov [11] and FACT database [9]. For simplification reason the following coefficients are introduced to describe chemical reactions during the remelting process.

$$\gamma \equiv \frac{n_{Ca}}{n_{CaF_2}} \tag{6}$$

(γ = Ca coefficient [-], n_{Ca} = amount of Ca in the slag [mol], n_{CaF2} = amount of CaF$_2$ in the slag [mol])

$$\delta \equiv \frac{n_{CaO}}{n_{CaF_2}} \tag{7}$$

(δ = CaO coefficient [-], n_{CaO} = amount of CaO in the slag [mol], n_{CaF2} = amount of CaF$_2$ in the slag [mol])

$$\kappa \equiv \frac{n_{slag}}{n_{metal}} = \frac{\rho_S \cdot M_M}{\rho_M \cdot M_S}\left(\frac{A_{electrode}}{\frac{\dot{m}_M}{\rho_m v_{Tr}}} - 1\right) \tag{8}$$

(κ = molar slag to metal ratio [-], n_{slag} = amount of slag [mol], n_{metal} = amount of metal drops in the slag [mol], ρ_S = slag density [$^{kg}/_{m^3}$], ρ_M = metal density [$^{kg}/_{m^3}$], M_S = molar mass of slag [$^{g}/_{mol}$], M_M = molar mass of Metal [$^{g}/_{mol}$], $A_{electrode}$ = electrode section [m²], $\dot{m}_M$ = melting rate [$^{kg}/_{s}$], v_{Tr} = drop off rate [$^{m}/_{s}$])

The refining reaction can be described by equation 9 where ξ is the part of transformed reaction (range 0 to 1). It's necessary to add continuously pure calcium or a Ca-CaF$_2$-mixture to the slag to keep the calcium content in the slag constant.

$$\mathbf{TiAl}_{\varphi-2\left(\frac{2-x}{3}\right)}\mathbf{O}_x + x\,\mathbf{Ca} + \kappa\,\mathbf{CaF_2Ca}_\gamma\mathbf{CaO}_\delta \rightarrow$$
$$\mathbf{TiAl}_{\varphi-2\left(\frac{2-x}{3}\right)}\mathbf{O}_{x\cdot(1-\xi)} + \kappa\,\mathbf{CaF_2Ca}_{\gamma+\frac{x(1-\xi)}{\kappa}}\mathbf{CaO}_{\delta+\frac{x\cdot\xi}{\kappa}} \tag{9}$$
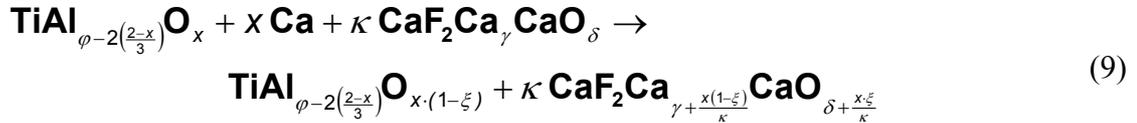
Taking geometry of the IME-ESR-furnace into account the coefficient κ is approximately 100. The composition of the metal phase is TiAl$_{1,05}$O$_{0,07}$ after aluminothermic reduction. The equilibrium calculations in the system metal/slag lead to a approximated correlation between γ, δ and ξ as shown in eq. 10 for $\gamma \in [0.02; 0.10]$ and $\delta \in [0.01; 0.48]$.

$$\xi = 1 - \frac{0,00024837}{\gamma^{0,91395}} - \frac{0,0025203}{\gamma^{0,86201}}\delta \tag{10}$$

This correlation can be used to calculate the necessary calcium content in the ESR slag at the beginning of the refining process as well as the needed feed of a calcium rich slag during the process, which compensates the calcium loss in consequence of the refining reaction. In opposite to former calculations the calcium content in the slag has to increase during the process in order to reach a homogeneous oxygen distribution in the ingot. Fig 5 shows the calculation of the refining process for a 28 kg electrode (ø 110 x 900 mm) resulting from aluminothermic reduction. The initial oxygen content is 1.4 wt.-%. The starting amount of slag needed for the process is 3.75 kg. To reach a oxygen content of 150 ppm in the ingot, the starting composition of the slag must be 0.9 wt.-% calcium and 99.1 wt.-% calcium fluoride. During the process a refining slag with 75 wt.-% calcium is added. As a result the calcium content in the slag increases from 0.9 to 3.7 wt.-%. This eliminates the negative effect of a rising calcium oxide content in the slag and should also keep the slag viscosity constant.
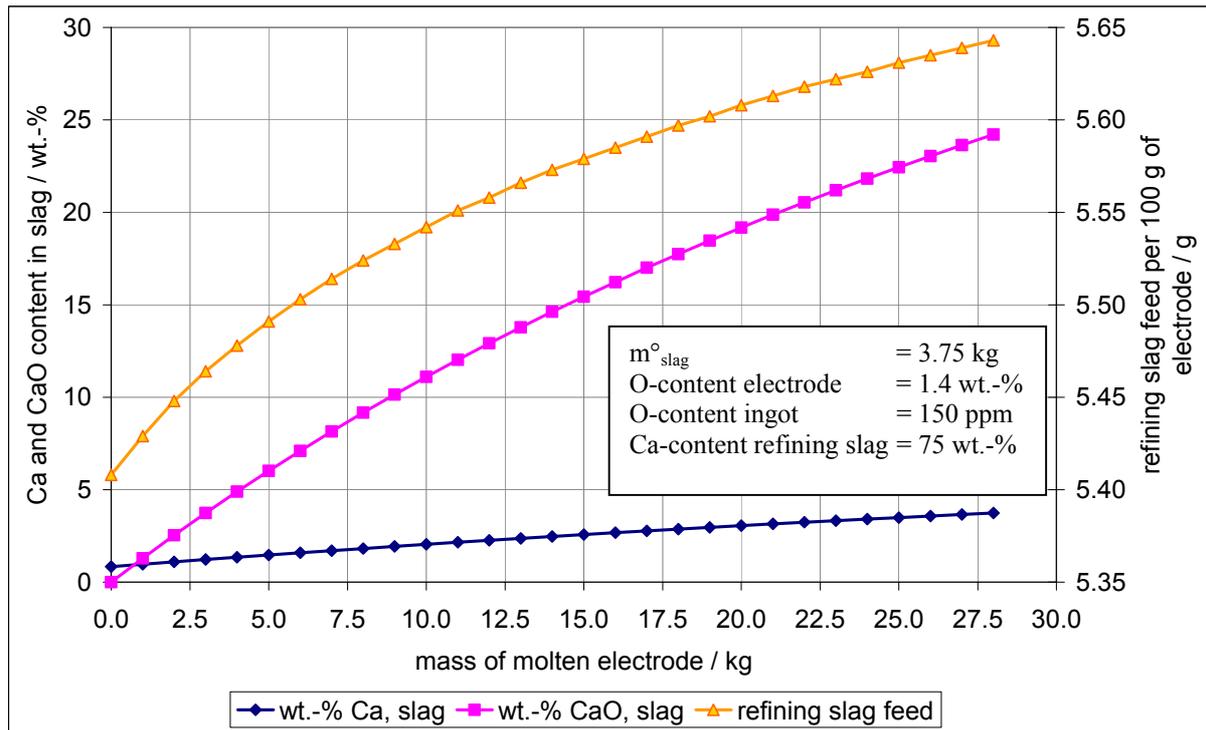
Figure 5: Calculated slag composition and necessary feed of refining slag for remelting of a 28 kg electrode in the IME-ESR-furnace reaching a final oxygen content of 150 ppm in the ingot

4 Conclusions and Further Outlook

Thermodynamic data of several actual available systems were combined to allow the calculation of the theoretical oxygen content of an aluminothermic reduced titanium aluminide ingot. It could be proofed that tapping the alloy less than one second after end of the reaction serves casting electrodes without any contact to air, so forming of nitrates is inhibited. The electrodes have only few slag inclusions but are very brittle due to the high cooling rate. Theoretic calculations and experimental test series resulted in similar oxygen contents in metal. Thermodynamic modelling of the ESR process showed that the oxygen concentration of the aluminothermic titanium aluminide ingot can be reduced from 1.4 wt.-% to 150 ppm by using a calcium containing calcium fluoride slag and adding calcium continuously.

Further investigations will deal with increased electrode diameters, which lead to a better mechanical stability and reduced oxygen content because of a lower cooling rate. Calculations of the ESR-process will be proofed by experiments in the IME pilot plant (ø 160 x 800 mm). Adding of alloying elements like niobium and chromium as Nb_2O_5 and Cr_2O_3 to the aluminothermic mixture as well as substitution of titanium oxide pigment by high grade rutile can further reduce production costs and are subjects to actual investigations.

5 Acknowledgements

6 References

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