



Fundamentals of desoxidation behaviour of Ti-alloys by chamber ESR with Ca-reactive slags

Dipl.-Ing. Jan Reitz, Prof. Dr.-Ing. B. Friedrich, Dr.-Ing. Jan-Christoph Stoephasius

IME Process Metallurgy and Metal Recycling, RWTH Aachen University

Intzestrasse 3, 52056 Aachen, Germany

Abstract

The special thermochemical and kinetic characteristics of electroslag remelting (ESR) require an advanced process control in order to apply this process for the desoxidation of titanium alloys. Based on the example of high oxygen containing γ -Titanium Aluminides, that have been prepared from oxidized scrap or via metallothermic reduction, the application of Ca-reactive slags is modelled using a quasi-equilibrium approach, taking into account the effects of varying slag composition and evaporation. This leads to a detailed design of experiment and parameters for process control in order to receive a chemically homogeneous product with low oxygen content.

1 Introduction

Due to high scrap generation in the processing of semi-finished and final products made of titanium and titanium alloys, recycling shows a great potential to substitute titanium sponge, economise the titanium market and to apply secondary low cost titanium in new applications. Unfortunately, due to its high affinity to oxygen and nitrogen and the tremendous negative effects those interstitials have on the mechanical properties, the recycling of titanium scraps needs unconventional remelting techniques to deliver quality secondary titanium ingots. These operations should on one hand be able to remove inclusions and impurities arising from mechanical processing steps, on the other hand they should prevent further pick-up of oxygen and nitrogen from the melting atmosphere.

Such a process is electroslag remelting (ESR) where a partial volume of a metal billet is melt by contact with a defined liquid slag and is later resolidified. Solid inclusions with melting points above that of the base-metal will float and eventually dissolve in the slag. Furthermore chemical reactions as desulphurisation, desoxidation, alloying or removal of alloying elements can occur at fast rates on the liquid-liquid phase-boundary between the metal and the slag. Those reactions are thermochemically controlled by the oxygen potential of the slag-phase. If melting under inert-gas conditions, i.e. I-ESR or chamber-ESR, oxygen and nitrogen pickup from the melting atmosphere can be avoided.



A proven method to influence the oxidation potential in return is the addition of reactive metals, like Ca, Mg, Si, Al or rare earth metals. Thermochemical calculations in this paper will show, that even the desoxidation of titanium, a metal with remarkably high oxygen affinity, is possible by electroslog remelting using reactive Ca-CaF₂-slags and an inert atmosphere. To ensure a uniform oxygen content with respect to the full length of an ingot, oxygen potential in the slag has to be carefully controlled during the whole melting process. Due to the current lack of industrialized methods for online-measurement, suitable to deliver reliable data under the harsh remelting conditions, Ca-content of the slag has to be levelled using mass-balance calculations and continuous feeding of desoxidation agents accordingly. Because Ca vapour-pressure in the slag is near one atmosphere, also calcium evaporation has to be included in this process control model.

2 Fundamentals

2.1 Properties of the starting materials

Efficiency improvements in turbo-systems applied in the power-, aerospace or automotive sector, nowadays demand an increase in operating temperatures and pressures while decreasing the total mass of turning parts. Titanium-Aluminium intermetallics, delivering high temperature stability at comparably low density, belong to a new generation of high-tech materials aimed for application on this sector.

At present, these materials are produced like classic titanium alloys by remelting metallic raw materials in a vacuum arc furnace (VAR) process. It has been proposed by Hammerschmidt [2], that the production cost can be significantly reduced, when TiAl is gained from aluminothermic reduction (ATR). Unfortunately these ATR-type TiAl-alloys show extreme high oxygen contents of about 1,5 w% while the technical specification for castable TiAl-alloys allows at max. 800 ppm and thus this material has to be deoxidized e.g. by subsequent electroslog remelting. Because the oxygen level in the named material is even higher than that in Ti-scrap from turning and milling operations, a successful treatment of ATR-TiAl can serve as a worst case scenario for the application of ESR for deoxidizing Ti-scrap. Table 1 shows the analysis of a typical as cast ATR-TiAl electrode.

Table 1: Analysis of a aluminothermic reduced γ -TiAl electrode [1]

mass.-%	Ti	Al	Nb	Fe	Si	Zr	Cu	P	O	N	C	Σ
analysis	48,6	35,7	7,00	2,13					1,59	0,052	0,10	95,2

It should be noted that the analysed oxygen-content shows good agreement with thermodynamical calculations [1] and that it is highly above specifications. The given specification for nitrogen-content in TiAl is around 300 ppm and must therefore also be slightly reduced by ESR.



2.2 Electroslag remelting

In the second half of the 20th century, electroslag remelting (ESR) was increasingly applied for the refining of special steels and super alloys. Nowadays the process is in the transfer to more reactive alloy systems like titanium based materials, chromium and certain intermetallics, using remelting furnaces that apply inter-gas atmospheres in pressure vessels.

The principle of ESR is based on the fact that the electrical resistance of slags as ionic conductors is much higher than that of metals. When such a slag, commonly based on fluorides and oxides is molten in a water-cooled copper crucible and conducts an electric current, the main potential and therefore the largest part of the electrical power contributes to the slag.. The tip of a consumable electrode, that dips into the slag, is melted continuously and the metal droplets travel through the slag due to their higher density. After melting off enough material from the electrode, the slag itself floats on a liquid metal bath. Throughout the process, the metal pool solidifies, continuously building up an ingot with a controlled, directional solidification microstructure. Figure 1 (left) is illustrating the melting principle.

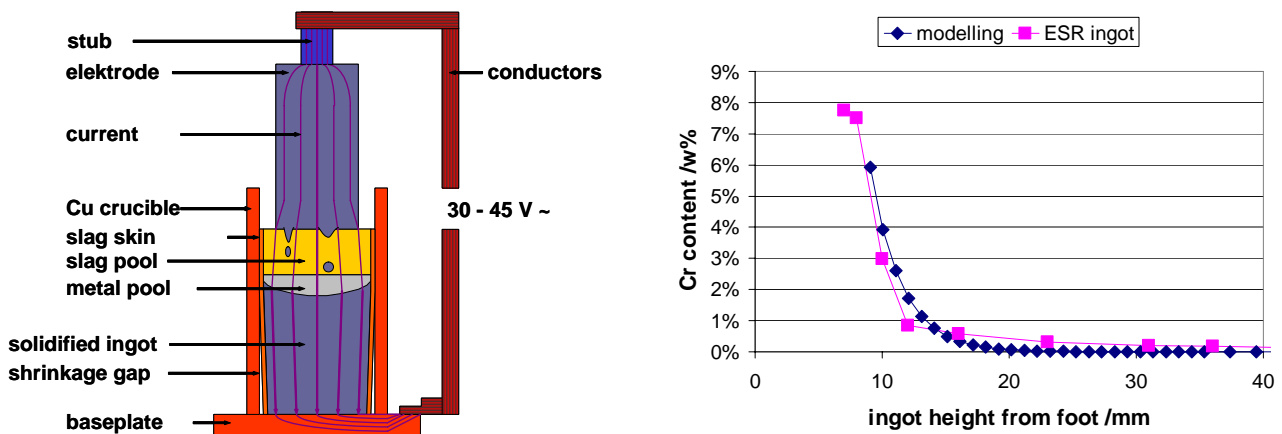


Figure 1: (left) ESR melting principle, (right) pick up of Cr from the starting box containing slag plus Cr-alloy turnings.

Alternating current (AC) is applied to avoid polarisation of the slag, but generates turbulent flow in the slag and metal bath, especially when frequencies are high. If the liquid flow is too fast, slag inclusions and failures in the ingot structure, so called “freckles”, that derive from dendrite arms breaking off, are likely to occur.

It should be noted as a main characteristic of the process, that only a very small partial volume of the bulk electrode is being melt at a time. This is unlike to other metallurgical melting operations where usually the full load of a crucible is molten, allowing for mixing and homogenisation before casting.

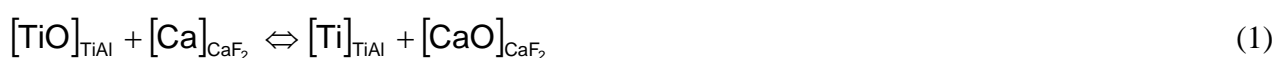


Because mixing in the solid state does not take place, it is crucial in ESR to reach stationary process conditions in terms of melting rate, temperature and especially in terms of slag-metal equilibria, in order to receive a homogeneous ingot. Depending on the volume of the metal pool and thus on the melting rate, effects from the start phase of the process can therefore have a noticeable influence on metal composition.

An example of this particular effect in ESR is shown in Figure 1 on the right. As slags do not conduct electric current when they are solid, the process is usually started on a mixed bed of metal turnings and slag granules, a so called starting-box or -bin. Figure 1 shows the Chromium content in a molten steel ingot of a total 210 cm in height and 15 cm in diameter, molten from a 30kg electrode of a construction steel, containing traces of Cr of about 0,11 w%. The process has been started on a mix of slag and 420g of turnings from the CRONIDUR30 alloy containing 14-16% Cr. The ingot has then been split into half and Cr concentration was determined by spark emission spectrometry about every cm in height. The modelled Cr content is based on the assumption of a 6 cm deep, parabolic melt pool of a diameter of 15,5 cm and a molten metal content of about 0,74 kg which fits reasonably well with the measured results.

2.3 Thermochemistry of desoxidation

It is common understanding, that in titanium-alloys, higher oxygen contents are dissolved in the form of TiO. With a free enthalpy of formation (ΔG^f) of -513,3 kJ/mol, this oxide is regarded as comparatively stable. Its solubility amounts up to 33% in pure Titanium. Hence the removal of oxygen from titanium alloys can be regarded a quite challenging task. Simple degassing in vacuum arc remelting (VAR) or electron beam melting (EBM) is not possible as it would require oxygen partial pressures below 10^{-19} bar. Calculations with FactSageTM, a Gibbs-energy minimization tool, indicate, that for a binary γ -TiAl-system, partial pressures need to be well below 10^{-13} bar for degassing which is impossible to reach in state-of-the-art vacuum melting equipment. Thus a chemical method for desoxidation, based on the principle of precipitation has to be applied. In this present work Ca was chosen as a reactant, because of its high oxygen affinity, reflected by a ΔG^f of -603 kJ/mol for the formation of CaO which is lower than that for TiO. The temperature dependency of the solubility product L_c of Calcium and Oxygen can be approximated by a linear expression in the temperature range of 1550°C to 1750°C as has been examined by Tsukihashi et al. [3]. It shows that desoxidation of TiAl by solution of Calcium is feasible in the desired range [4]. This can be achieved in ESR, using a Ca-CaF₂ melt according to equation (1). The equilibrium between the slag, containing metallic calcium and oxygen in the metal was previously examined by Okabe et al. [5], who gave also first experimental data on activities in the system.





As mentioned above, only a partial amount of the total metal is in the molten state at a time and gets into contact with the slag in ESR, so that the above reaction can occur. Thus over the process, the slag would be enriched in CaO and depleted of Ca, hence the thermochemical equilibrium will shift to the left side of equation (1), decreasing the effect of desoxidation over time. The result would be a non-homogeneous ingot in terms of oxygen content. Thus, from a thermochemical point of view, Ca-activity has to be increased continuously and well controlled during the process, e.g. by adding over-proportionally more metallic calcium. Additionally the CaO-activity has to be decreased, e.g. by diluting the solution trough the addition of CaF₂.

In order to allow for these measures, the activities of the slag components in the system CaF₂-CaO-Ca have to be known on a broader range than given by Okabe. A calculation of the ternary system CaF₂-Ca-CaO was therefore conducted using the OptiSage-Module within FactSageTM and applying a sublattice type according to the Kohler-Toop approach, assuming that there was neither a tendency for near range ordering (like in silica melts where a quasi-chemical model is applied) nor a tendency for alloying (like in metal melts, where the compound energy formalism holds) [1]. The modeling according to Kohler-Toop was chosen instead of the Muggianu method because of better accuracy on the outer rims of the system. The model was further based on the eutectics and liquidus lines of the accepted binary systems Ca-CaF₂, Ca-CaO [6] and CaF₂-CaO [7]. Figure 2 (left) shows the liquidus isothermals of the calculated system for illustration [1].

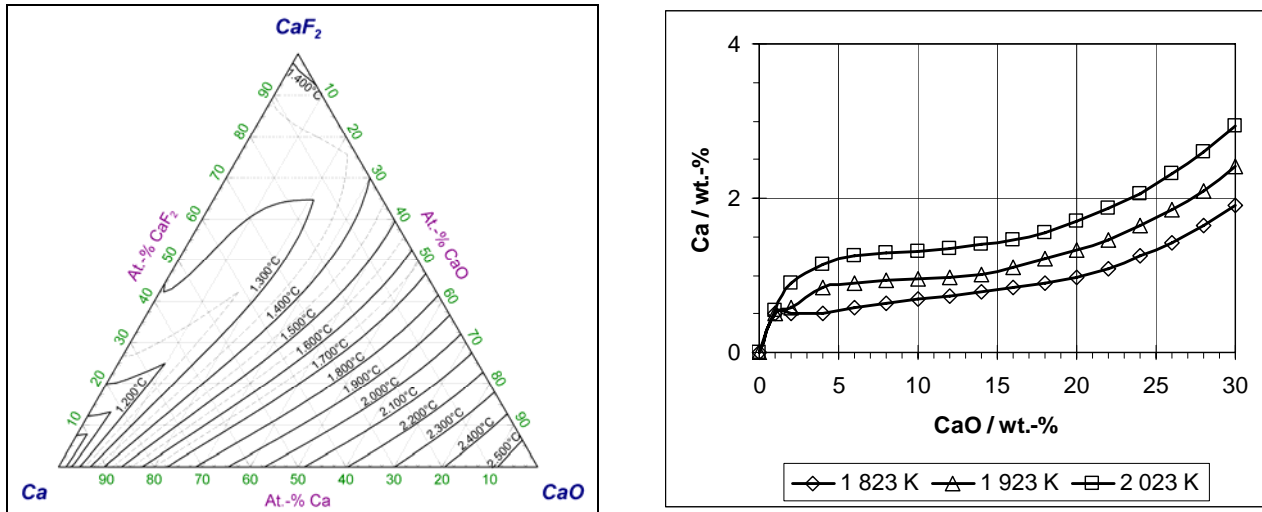
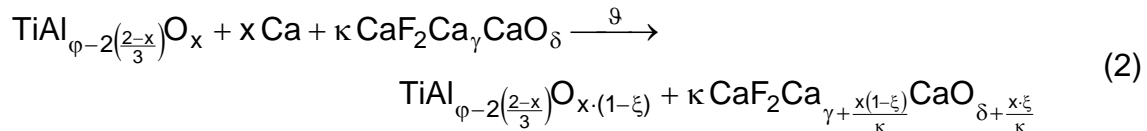


Figure 2: (left) liquidus isothermals of the calculated Ca-CaF₂-CaO system [1], (right) necessary Ca content in the slag for maintaining constant reduction potential depending on CaO-content (ensuring a oxygen content of 800 ppm)



Based on the calculated activities, the chemical equilibrium between oxygen in the metal and oxygen in the slag can be modeled by expanding equation (1) to the following equation (2) in order to forecast the desoxidation efficiency of the metal phase.



(κ : molar ratio of slag-phase to metal-phase; γ : molar Ca/CaF₂-ratio in the slag; δ : molar CaO/CaF₂-ratio in the slag; ξ : extent of reaction)

The degree of reaction, i.e. the measure for the completeness of desoxidation, given by ξ , was varied in discrete steps as a function of slag composition (γ , δ) and temperature (ϑ) to determine a simple function by least-squares method. It can be clearly expected that a 100% desoxidation can only be reached with extremely low CaO contents, while already a 99% desoxidation should be possible throughout the full scale of CaO solubility of the slag by adjusting Ca content. Figure 2 (right) shows the necessary Ca-content for increasing CaO contents in the slag in the form of oxygen-equiconcentration-lines at different temperatures. sufficient to treat the TiAl materials mentioned earlier down to 800 ppm oxygen.

2.4 Kinetic considerations

It has to be taken into account that the above thermochemical calculations reflect an ideal state in which full equilibrium is reached. It is most likely that this will not be the case in ESR remelting as a chain of different chemical reactions, physical effects and transport-phenomena is in place. Thus theoretical desoxidation of the metal will not be achieved if only one single step in the chain is slower than the melting rate of the metal. Figure 3 illustrates the major kinetic interactions in this matter.

While some of the kinetic effects inherent to the system have been understood or/and modelled (e.g. the evaporation of Ca from the slag phase) others are difficult to isolate because of the complexity of the ESR chemistry. Therefore the process is considered to be “close to equilibrium” for the following calculations. Once a comparison is possible between the oxygen content actually achieved and the desoxidation suggested by equilibrium models, efforts can be undertaken to determine and pursuit the rate limiting step.

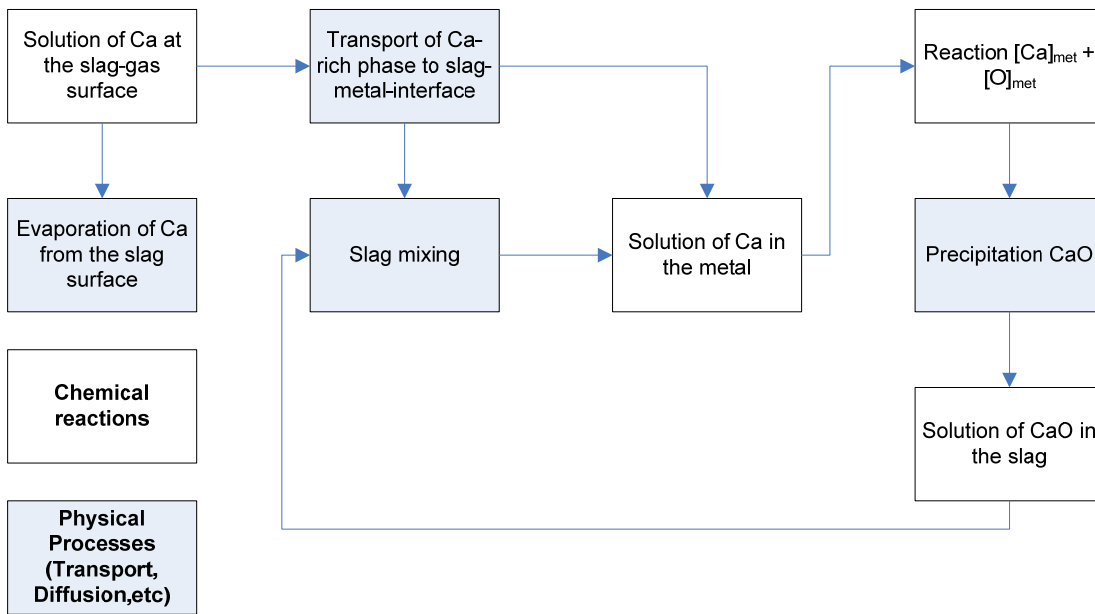


Figure 3: chain of the main kinetic effects affecting ESR desoxidation

2.5 Evaporation of calcium from the slag

ESR of TiAl-alloys typically takes place at 1650°C-1750°C, far above the boiling point of Ca. Additionally the solution of Ca in a fluoride slag decreases calcium activity, Ca vapour pressures can still amount up to ~0,8 bar when concentrations are in the range of 5%, as shown in Figure 4. Thus significant evaporation of the reducing agent under the process must be taken into account for.

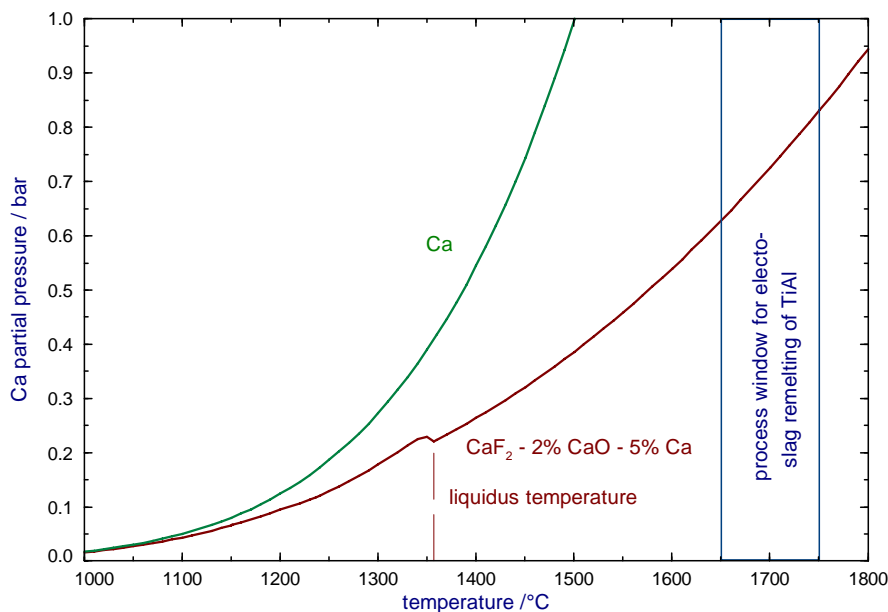


Figure 4: Ca partial pressure in CaF₂-CaO melt



Because natural convection in the gas phase, driven by the temperature gradient between the slag bath and the colder furnace atmosphere, is transporting Ca vapour away from the bath, towards cooler regions of the furnace, where it will condense, significant amounts of Ca are lost for the process. As presented in a previous paper [4], the rate controlling step for this evaporation procedure has been identified as being the transport in the gas phase and not, like in many vacuum metallurgical processes, the evaporation from the melt as described by the Hertz-Knudsen equation. It has been shown experimentally that Ca-depletion of the slag is of magnitudes slower than this equation would suggest for the given conditions. The speed of transport in the gas-phase has then been modelled as a combination of interdiffusion, given by the Stefan-Maxwell equation from kinetic gas-theory and a convective effect. This effect is described by Grasshoffs number (Gr), which can be transformed into the Sherwood number (Sh), the mass-flow-equivalent of the better known Nußelt number (Nu) from heat-flow calculations. For easier understanding, the combination of these effects is translated into the thickness of a virtual diffusion boundary layer above the slag following equation (3), which can then provide the evaporation speed by application of Fick's first law. Function $f_2(\text{Sc})$ is a corrective function for Schmidt's number, available in mass-transfer literature.

$$\Delta x = \frac{L}{\text{Sh}} = \frac{L}{0,15 \cdot \sqrt[3]{\text{Gr} \cdot \text{Sc} \cdot f_2(\text{Sc})}} = \frac{1}{0,15 \cdot \sqrt[3]{\frac{T_s - T_m}{T_m} \cdot \frac{g}{v \cdot D_m} \cdot f_2(\text{Sc})}} \quad (3)$$

(L: characteristic length [m]; Sh: Sherwood number; Gr: Graßhoff number; Sc: Schmidt number; $f_2(\text{Sc})$: corrective function between viscosity and diffusion; T_m : mean gas temperature in the furnace [K]; v : cinematic viscosity [m^2/s]; D_m : diffusion constant in the gas phase [m^2/s])

It could be shown from the above equation, that evaporation losses exhibit a cubic root dependency of the total pressure in the system, because the thickness of the diffusion layer decreases with increasing pressures. This can be contributed to the fact that the cinematic viscosity of the gas as well as the diffusion coefficient are anti-proportional to the system pressure, even though the partial pressure of calcium itself is independent of the total pressure.

The model has been proven in a pressure range from 1 to 40 bars by melting St37 II steel electrodes of 100 mm diameter in a technical CaF_2 -slag (WACKER Type 2052) with a Ca content under melt start of 5 w%. As the experimental results show good agreement, with calculated evaporation rates, the presented model is applied below to predict Ca losses from the slag during melting and to allow for compensation by feeding Ca granules. Figure 5 shows the dependency of the Ca evaporation rate on the system pressure for a CaF_2 slag, containing 2 w% CaO and 5 w% Ca at 1700°C and the dependency on slag temperature for a pressure of 1 bar respectively. The values presented are based on geometrical dimensions and machine constants of the ESR furnace applied in this study.

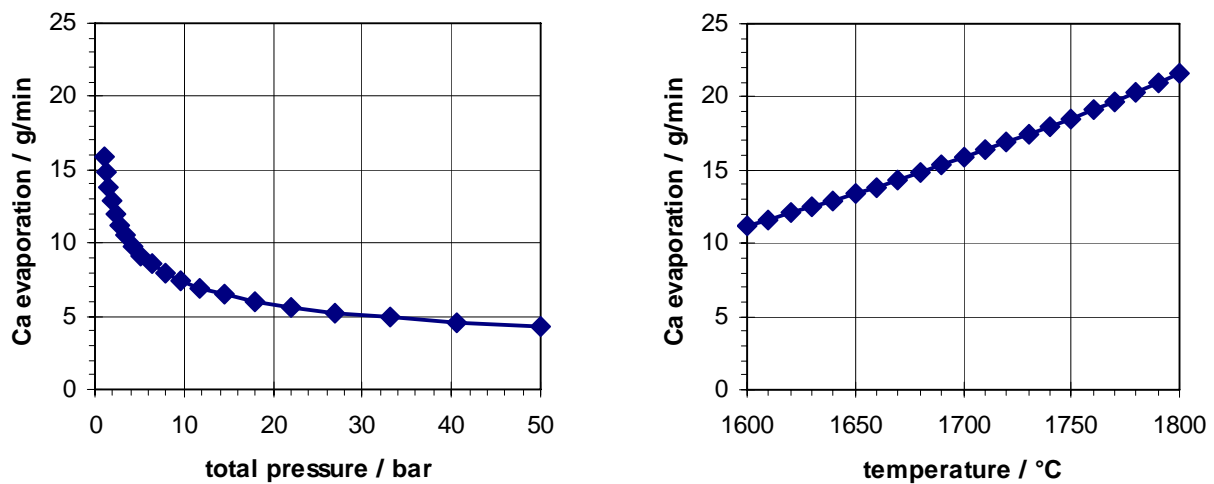


Figure 5: evaporation of Ca from a CaF_2 slag, containing 2 w% CaO and 5 w% Ca depending on the system pressure at 1700 °C (left) and depending on temperature at 1 bar (right), for the applied ESR furnace.

2.6 Process considerations

As stated above, the ESR slag applied in the process undergoes a change in composition during melting, being continuously enriched with CaO, and the content of reactive Ca must be increased accordingly to keep thermochemical equilibria into place. This also effects physical properties of the slag and thus influences the ESR process in return. Of interest in ESR are changes in electrical resistance, in melting point (which relates to viscosity), in surface tension and in density.

As ESR is based on the principle of resistance heating, a change in resistance also means a change in heat-supply for the system. While modern ESR furnaces possess automatic power control, this change may be compensated for during the process, by on-line measuring of the potential and subsequent readjustments. But if specific resistance of the slag is falling under a certain level, the transformer of the furnace may reach it's limiting current. At this point the potential drop over the slag distance is reduced to a minimum and the electrical power supplied to the slag becomes too low to guarantee for sufficient melting rates. Thus, the influence of increasing CaO-concentrations, as well as the effect of metallic Ca additions has to be taken into account as a boundary for experimental design in order to secure constant melting rates. For the present slag system, there is no clear consensus in literature about the effect of CaO addition to the slag. While some authors report an increase in resistance with increasing CaO-content others report a decrease. It has been found by Morinaga et. al. [9] that in pure CaF_2 -melts the electrical resistance is independent of the atmosphere above the melt. On the other hand the resistance shows a clear dependence on oxygen partial pressure, when CaO is added. In an evaluation of different sources in literature, the results of Mitchell et. al. [8] have been found suitable for the present slag-system, as they have been conducted under reducing conditions as being expected when using Ca-reactive slags (see Figure 6).



These results indicate that the resistance will be increasing with the CaO level during melting (i.e. there should be no loss in melting efficiency due to a drop in resistance). The effect of metallic calcium on the slag resistance is yet unknown.

A test-melt conducted at IME, Aachen using a CaF_2 -20%CaO slag without addition of metallic Ca has shown that the electric resistance of the slag had levelled to the same value after a 10 minutes start-up-phase, as when melting the same material (construction steel) with a slag based on $\frac{1}{3} \text{CaF}_2$, $\frac{1}{3} \text{CaO}$, $\frac{1}{3} \text{Al}_2\text{O}_3$. This value was determined to be $\sim 2,21 \text{ S/cm}$ at 1873 K, which fits acceptably with the values given in Figure 6. For slags containing metallic calcium, a value of 22 S/cm, given by Ryabtsev [10] was taken as a first measure for conducting the desoxidation trials.

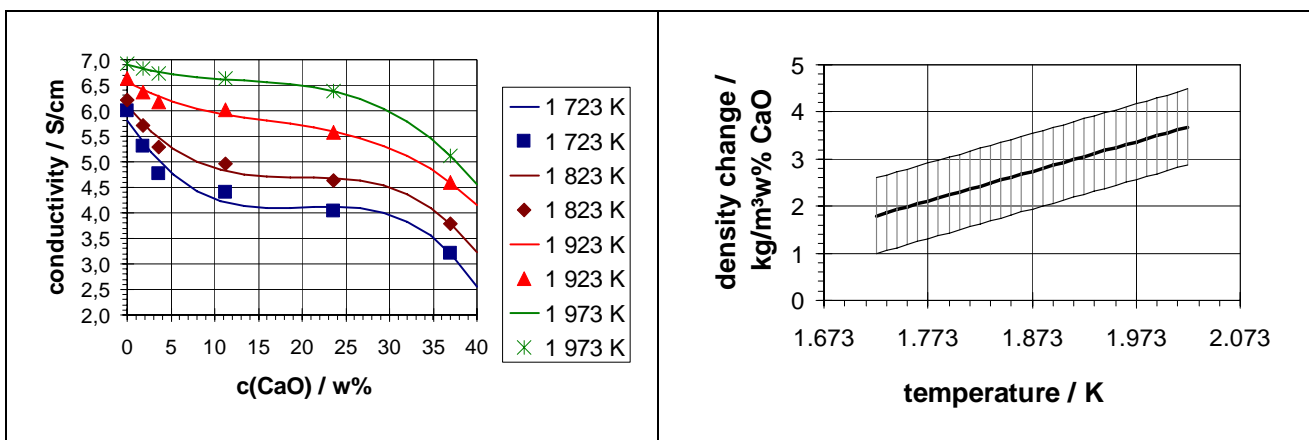


Figure 6: (left) Electrical resistance of ESR-slag as a function of CaO content [8], (right) density change of slag as a function of CaO-content and temperature [1]

With the above kinetic considerations in mind, it is obvious, that in ESR, as a liquid-liquid system, chemical reactions evolve around the phase boundary between slag and metal. While the largest surface area is contributed by the liquid metal pool and the liquid zone below the electrode tip, there is also phase contact between slag and the droplets that travel through it. The size of these droplets and their travelling speed (i.e. retention time) is largely effected by viscosity and surface tension of the slag and by the difference in density between slag and metal. The influence on process kinetics, when these properties change, is subject to speculation and beyond the scope of this paper. Nevertheless the density of the slag and its change with temperature and CaO-content has been modelled based on literature data as it is necessary for proper calculation of the slag height in the process-model presented below. Figure 6 (right) shows the increase in density per additional w% CaO for up to 30% rated to the density of pure CaF_2 over the relevant temperature range. As the density of CaF_2 was measured to 2436 kg/m^3 at 1973 K, a slag with a maximum of 30% CaO would reach a density of 2536 kg/m^3 at the same temperature, which makes an increase of about 4%. Similar effects can be seen for viscosity and surface tension.



3 Design of experiment and process control

3.1 Process control scheme

Based on the above discussed models and assumptions concerning thermochemistry, kinetics and process control-matters of ESR, a calculation scheme was build up, that assists in controlling stationary desoxidation thermodynamics for ATR-TiAl electrodes. This is necessary because to date, there is no method available for on-line measurement of the slag's oxygen potential and adjustment by adding desoxidation agents accordingly.

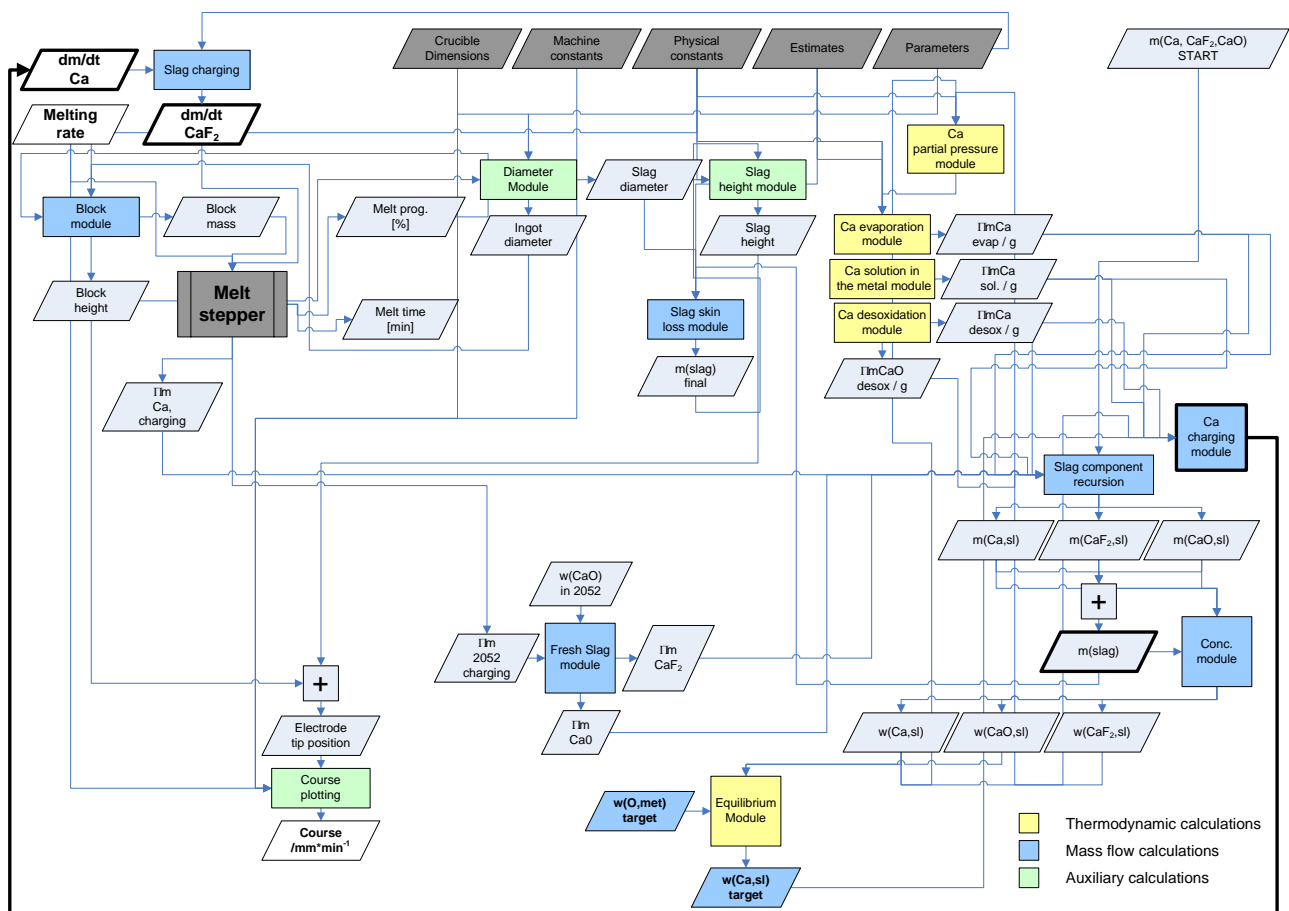


Figure 7: Process control model for desoxidation of γ -TiAl

Using given conditions for the start-up phase (e.g. slag composition, metal-content in starting mixture, system pressure, etc.), the control system calculates the melting progress in discrete steps and assumes chemical equilibrium in each step.



This accounts for the solution of Calcium in the metal, for the amount of Ca consumed for desoxidation, for the amount of Ca evaporated, for the increase of CaO in the slag and successively for the necessary increase of metallic Ca concentration in the slag to compensate for the higher oxygen potential of CaO. This results in the calculation of an amount of Ca to be charged for the next discrete melting step. Based on a fixed charging ratio between CaF_2 and Ca, the system also calculates diluting of the slag with CaF_2 . The resulting composition and mass of the slag are recursively fed back into the next melting step from where thermochemical calculations start again. Figure 7 illustrates the complex interaction between mass flow calculations on one hand and thermodynamics on the other. The feedback-loop of the charging parameters for Ca is indicated by the bold thread.

The scheme was put into action using MS ExcelTM for the recursive calculation. The input of process and machine parameters, physical constants and process estimates is realized by simple worksheets. Activity-data was calculated using FactSageTM and transferred into worksheets for the slag-system and the metal respectively. This data is accessed via database functions implemented in ExcelTM. Visualisation, as shown in Figure 8 is realized by VBATM routines for easier demonstration.

3.2 Design of experiment

The model sketched above was finally applied to plot process control parameters for the melting of a γ -TiAl-electrode with a diameter of 110 mm and 1325 mm in length. In beforehand the oxygen concentration was determined to be 1,59% by the gas-extraction method¹. The ESR crucible applied has a diameter of 178 mm at the base-plate and 159 mm at its rim and measures 880 mm in height. The initial CaO-content of the applied batch of WACKER 2052 slag (>97,5% CaF_2) was determined to be 1,17%. Based on previous experiments, it was decided to use a bin for starting the process, made from Ti-sheet metal of 130 mm height. Sheets of Aluminium and Niobium foil were added to the same amount as Al and Nb in the electrode material, so that the starting bin would not dilute the concentration of these elements in the base of the ingot (inverse effect as presented above). It was further decided to start-off with 5 kg of initial slag mass and to mix the slag with 800 g of TiAl-scrap from the same ATR experiment and thus of the same composition. A melting-rate of 51,5 kg/h was determined, based on a simplified method applied for melting steels, that takes into account just the diameter of the crucible.

¹ Equipment applied was a Ströhlein ON-mat 8500, JUWE Laborgeräte GmbH, Germany. Analysis took place at a temperature of 2000°C in carbon crucibles, adding 1 g of Ni for 50 mg of sample material and was compared against a pure Ti-standard with 1500 ppm oxygen content.

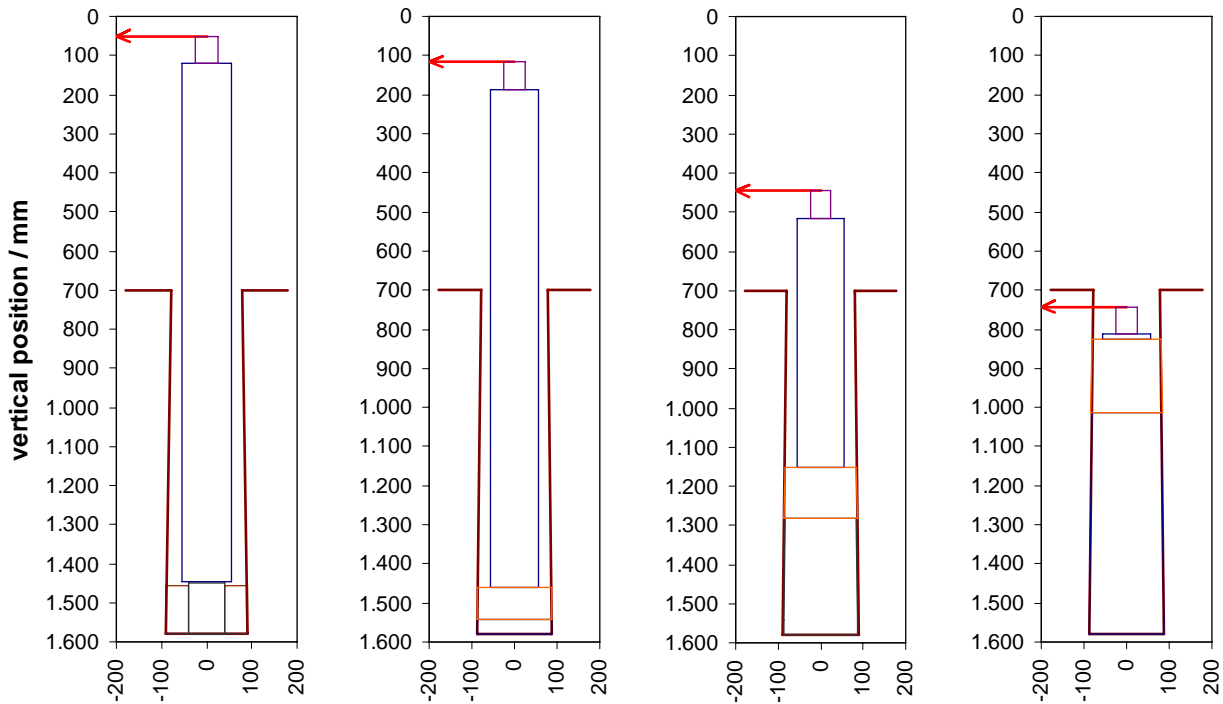


Figure 8: Modelling of ESR melting progress, from left to right: before ignition on starting bin, electrode starts to melt, stationary melting, final melt phase.

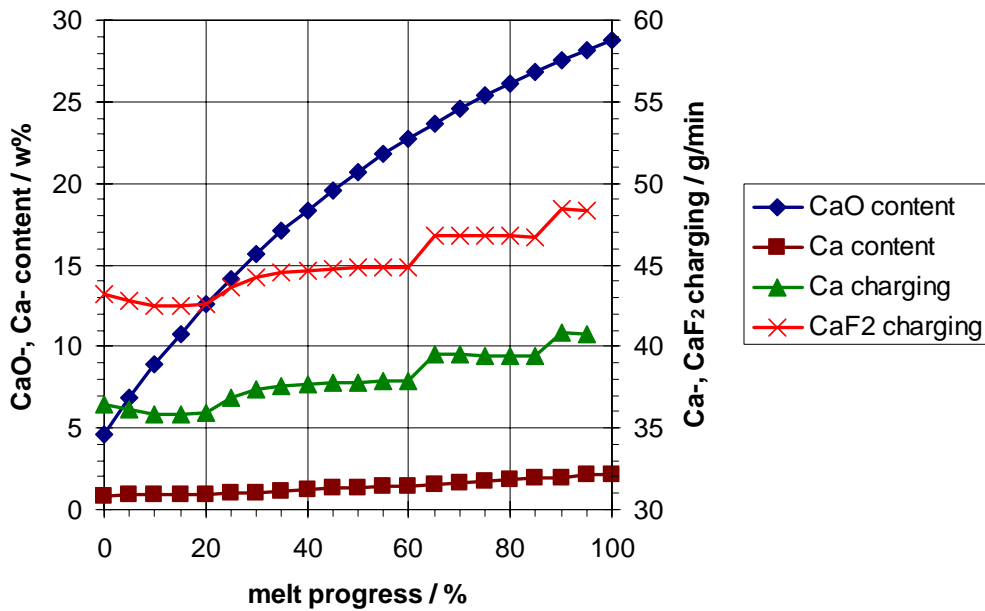


Figure 9: Evolution of the CaO content during melting and necessary Ca content for the desired desoxidation. On the right axis: necessary charging rates for slag and Ca.



Figure 8 shows a graphical representation of the volume calculations for different stages of melting. Note how the height of the slag bath increases, due to enrichment in CaO and charging of additional slag, while the ingot builds up from the melting electrode. Consequently the increasing slag height should not exceed the crucible dimensions and thus limits the process geometrically.

In order to control the slag composition, according with the indications given above, the charging of additional slag and the desoxidation agent is plotted over the processing time, assuming, that the melt-rate given for the calculation is actually reached. Figure 9 shows the projected development of CaO-content in the slag and the necessary Ca-content to keep the chemical equilibrium into place, required to reach the low oxygen contents as desired.

4 Conclusions and Outlook

Desoxidation of Ti-alloys received from scrap recycling or even γ -TiAl material gained via an alternative processing route by aluminothermic reduction is possible applying the chamber electroslag remelting process using reactive Ca-CaF₂-slags. Because only partial volumes of the metal are melt at a time in this process, an advanced process control is necessary to guarantee for homogeneous ingot chemistry. At present there are no technically proven methods available, to measure the desoxidation potential of the slag. Thus the control of constant slag chemistry can only be realized via process modelling and subsequent charging of reactive agents.

The fundamentals of desoxidation via reactive slags have been presented and combined into a calculation scheme. Based on this modelling tool, a desoxidation experiment for the named material has been designed. Melting according to the above calculations and experimental design will be carried out in spring 2007 and thus results were not readily available for this manuscript. A complete analysis of composition and mechanical properties will be given in the oral presentation at EMC2007 in June and will further on be published in an issue of ERZMETALL subsequent to the conference during fall 2007.



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