Generation of low oxygen Ti-Al-V-alloys from oxidic raw materials via aluminothermic reduction (ATR), subsequent refining via electroslag remelting (ESR) and vacuum arc remelting (VAR)

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In order to find a cost effective way avoiding the environmental and economical drawbacks of the Kroll process, the Institute for Process Metallurgy and Metal Recycling (IME) of the Aachen University is investigating an alternative processing route for the production of Ti-Al-V-alloys. These alloys can especially be used for applications in non-aviation sectors like the automotive and chemical industry. Starting from pure rutile, concentrates and pigments, the ATR process avoids chlorine-based booster by using CaO_2 instead while aluminium is used as a reductant and alloying element. The obtained Ti-8Al-12V alloy is then consolidated in a conventional vacuum induction furnace (VIM) by adding scrap to achieve a homogenized ingot of the desired Ti-6Al-4V alloy. In order to reduce the oxygen content and impurities/inclusions, this alloy is remelted afterwards in a pressure ESR by adding pure calcium as deoxidizing agent to the slag under a protective gas atmosphere followed by the final refining step of vacuum arc remelting meeting international production standards. This paper represents the current status of a 15 years research progress in Aachen triggered by the automotive industry to introduce Titanium in high class cars.

Keywords: titanium alloys, aluminothermic reduction, electroslag remelting, vacuum arc remelting

1 Introduction

Titanium metal has several advantages over other materials in terms of properties such as low density combined with good corrosion behavior and high strength that makes it suitable for special applications. Important examples are the aviation and automotive sectors. In addition, the chemical industry, ocean- and energy-engineering have to be stated out. The widely usage of titanium started over 70 years ago with the development of the multi-step and quite energy/resource consuming Kroll- and Hunter-Processes. Table 1 shows some possible applications for Titanium alloys in the automotive sector. [1]

Table 1: Possible vehicle components made of Ti-alloys [1]

Application	Titanium alloy
Off-gas valves	Gamma titanium aluminides
Springs	Ti-3Al-8V-6Cr-4Mo-4Zr, Timetal LCB
Connecting rods	Ti-6Al-4V, Ti-3Al-2V
Off-gas systems	Commercial pure titanium

Despite its outstanding properties, the use of titanium remains relatively low due to the high costs of the raw materials and production compared to other materials, see figure 1. It also illustrates the main matters of expenses from the production of titanium sheet starting from raw material.

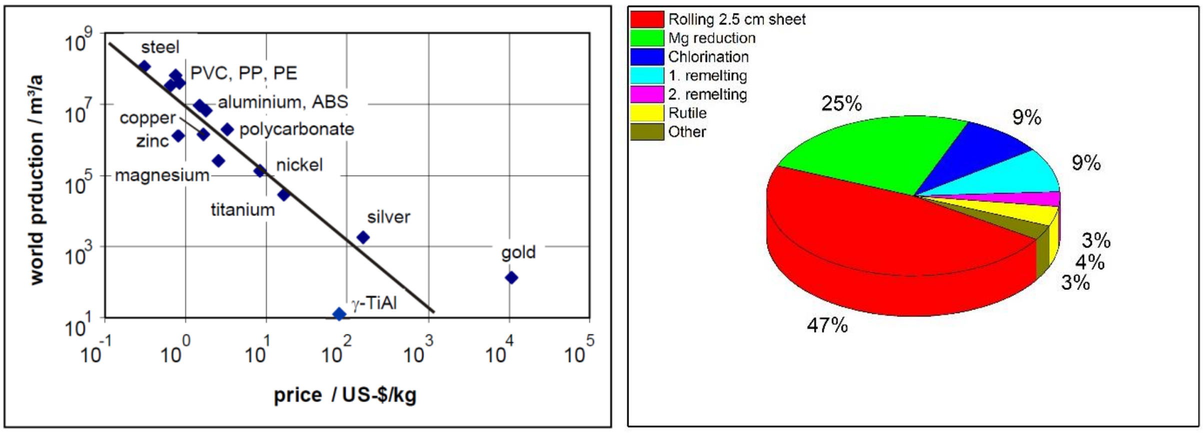

Figure 1: Cost comparison and production cost structure of titanium [2]

Both figures were state of the art at the beginning of this research at the IME in 2001 and shall give an impression of the motivation that lead to this project. Figure 1 shows that the most expensive step in the production is the rolling of titanium into sheet. However, the chlorination and reduction of titanium oxide to titanium sponge is the second most expensive step. There are a few possibilities to reduce the costs of titanium metal and its alloys. Other than increasing the production capacity, it can be achieved by reducing the amount of processing steps and/or consumption of resources. The alternative process route at the IME Institute can be seen in figure 2.

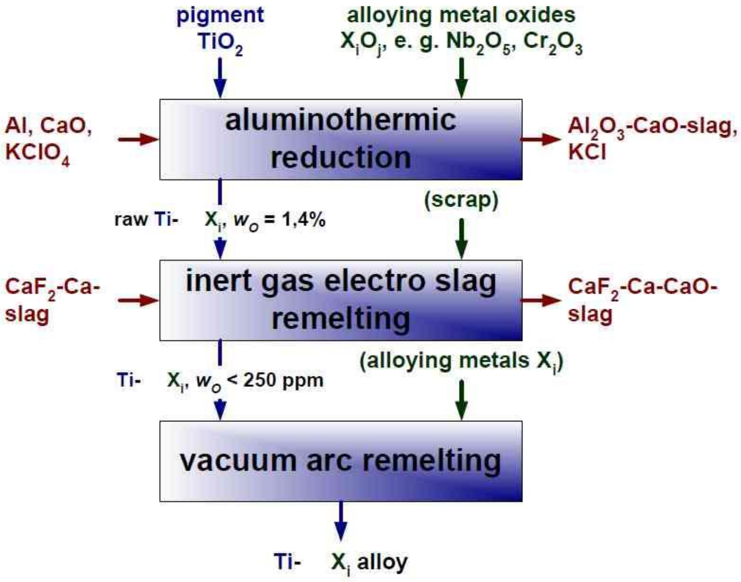

Figure 2: IME-TiAl-process flow of aluminothermic Ti-Al-X production [3]

This processing route is able to achieve titanium without the steps of enrichment, chlorination and distillation (which at the same time represents a reduction of the environmental impact). Conventionally, the reduction of Titanium follows the magnesiothermic reduction of $TiCl_4$ with liquid magnesium [4]:

$$TiCl_4 + 2\,Mg \rightarrow Ti + 2\,MgCl_2 \tag{1}$$

The new concept at the IME exchanges this magnesiothermic reduction with an aluminothermic reduction. Instead of liquid and high reactive $TiCl_4$-solution this reduction uses titanium oxides in a cheap intermediate quality from large scale pigment production because it is widely available and has already a sufficient high purity. Such the first steps in this research project were the investigation of the aluminothermic reduction process and subsequent calculations using computer programs for thermochemical calculations regarding the new reduction process. [2] Later on, the process was experimentally investigated within each processing step.

2 Aluminothermy (ATR) - Theoretical background and own calculations

In aluminothermy, metallic aluminium is used as the reducing agent instead of magnesium in the Kroll-Process. Another difference is that the used reductive metal is not liquid but in a solid-state, ground to an intermediate sized powder. Oxidic raw materials (TiO_2), aluminium powder and additives (slag forming agents and boosters, if necessary) are mixed together and subsequently are forced to react through ignition.

During this reaction, TiO_2 is reduced to metallic titanium while metallic aluminium is oxidized. The driving force behind this oxygen transfer is the higher affinity of aluminium to oxygen compared to the oxygen affinity of titanium. Generally, metallic compounds whose enthalpy of formation is lower than that of the given oxide can reduce any oxide. However, aluminium is used as reducing agent in metallothermy because it is widely available. An idealized reaction equation, which occurs during the reaction, shows equation 2:

$$3\ TiO_2 + 4\ Al \rightarrow 3\ Ti + 2\ Al_2O_3 \qquad (2)$$

The production of titanium via aluminothermic reduction has already been investigated by Fletcher [5] as well as Kubaschewski and Dench [6]. As a product, a titanium-aluminum alloy, or an alloy containing these two components, is produced consisting of a mixture of different intermetallic Ti-Al-compunds. It is possible to control the amount of intermetallic phases by adjusting the Al/TiO_2 (φ, equation 3) proportion, as can be seen in the ternary phase diagram Ti-Al-O (figure 3 left).

$$\varphi = \frac{n_{Al}}{n_{TiO2}} \qquad (3)$$

At 1400 °C and low aluminum contents ($\varphi < 0.746$), various titanium oxides are formed that are in equilibrium with Al_2O_3. At $\varphi = 0.746$, hcp titanium phase is formed for the first time, which is not economically feasible due to its high oxygen content of 33 at.-%. γ-TiAl is stable starting at $\varphi = 2.00$. Increases of aluminum portions above $\varphi > 2.84$ result in the formation of $TiAl_3$. [7]
As can be seen from figure 3 (right), an acceptable oxygen content of below 0.5 % can be reached with a molar proportion of Al/TiO_2 of 2.8. The theoretical content of aluminum in the alloy is 45 % at that point.

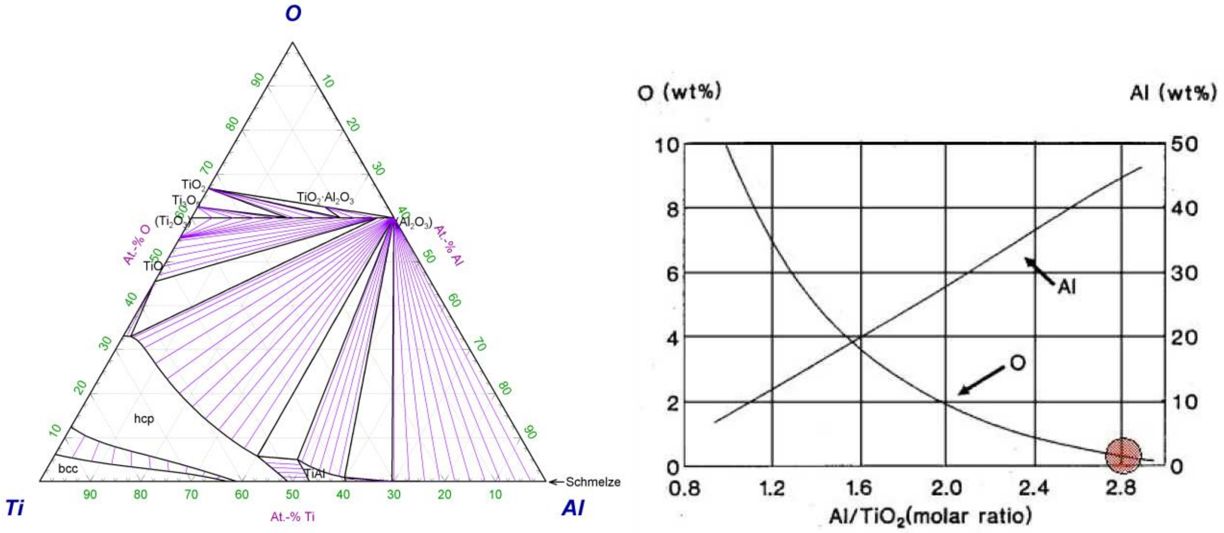

Figure 3: Left: Ternary phase diagram of the system Ti-Al-O at 1400 °C [8]. Right: Oxygen and aluminum contents as a function of Al/TiO_2 molar ratio [2]

Enthalpy balancing is an important factor to ensure adequate heat generation within the system. However, reaction enthalpy supplied by reducing steps might not be sufficient to balance the enthalpies needed. Therefore, additional oxidizing agents may be added to boost the reaction enthalpy. $KClO_4$ is often used because it does not influence the main reaction chemically. Equation 4 gives the main reaction occurring with $KClO_4$ as booster, especially in the case of Titanium.

$$3\ KClO_4 + 8\ Al \rightarrow 3\ KCl + 4\ Al_2O_3 \quad (4)$$

KCl is in its gasous state at temperatures above 1475 °C and is therefore removed from the process as dust. The additional formation of Al_2O_3 needs to be taken into account. In order to minimize/avoid the use of chlorine compounds, the addition of CaO_2 as booster has been successfully established as well, having the advantage of lower evaporation and dust formations and also the in-situ formation of the slag component CaO. Also, the activation of rutile by mechanical milling with the effect of enhancing the internal enthalpy of the TiO_2, enabled a 32 % booster reduction, while maintaining the same level of product quality. Futhermore, the co-reduction of Ti and V also exhibits additional enthalpy benefits. [9]

Due to the nature of the processes' oxidic product, Al_2O_3, slag design is important in order to reduce liquidus temperature, viscosity and O_2 uptake of the non-metallic phase. By lowering the activity of Al_2O_3 in the slag, CaO is an additive crucial for process improvement. Ceramic complexes, such as $(Al_2O_3)_6 \cdot CaO$ or $(Al_2O_3)_2 \cdot CaO$ shift the equilibrium in the metal phase towards lower contents of oxygen. With the alternation of the molar ratios listed below (equation 5), drastic oxygen content reductions may be achieved. [7]

$$\Psi = \frac{n_{CaO}}{n_{Al2O3}} \quad (5)$$

Minimum oxygen contents in the metal phase may be realized by high CaO contents ($\Psi = 1$) and Al surplus with respect to TiO_2 ($\varphi = 3$). By increasing Ψ about 1/6, oxygen content decreases by about 14 %. Even more, changing the value of φ from 2 to 3, oxygen contents decrease from 50 % to 70 % at $\Psi = 2$. Oxygen solution is also strongly depending on the temperature, with less dependency when CaO is added (18 % for $\Psi = 0$ and 9 % for $\Psi = 1$). [7]

It may be stated that according to thermochemical considerations, low oxygen contents in Ti-Al-alloys are achieved with optimized energy, slag chemistry and aluminum to titanium dioxide ratios. Due to the use of Al as reducing agent and as a vital component to lower oxygen uptake, it is possible to produce Ti-Al alloys using this approach. However, oxygen contents are forecasted to be too high for specifications as given in material data sheets. The relevant source for this alloy is ISO 5832-3 [10]. Thus, additional steps are necessary. In this context the focus is on electroslag remelting (ESR) of the Ti-Al alloy produced via ATR. The fundamentals of the ESR process are presented in chapter 3.

3 Electroslag remelting (ESR) - Fundamentals

The ESR process is mainly a refining step for Ni- and Fe-based alloys used for example in the aviation or energy sector where very clean alloys are needed. The metal about to be refined has to be in the shape of a cylindrical electrode. This electrode dips into a bath of molten slag, over which it is electrically connected to the metal ingot beneath the slag bath (figure 4). A high current is directed through electrode, slag bath and metal ingot. The slag bath acts as a resistance medium in which the current partly is converted into heat via the Joule heat generation. During the process, the metal melts gradually, eventually molten metal droplets drip through the slag bath. Due to the contact of metal and slag ingredients a mass transfer can happen with which the metal can be refined. To minimize the risk of an oxygen pickup during remelting, a protective argon gas atmosphere is implemented. [2]

The mold in this process is made of copper or copper alloys. Because of the high temperature during the process, the mold is intensively water-cooled. The slag system used for classical remelting is usually containing CaF_2 (as base component), Al_2O_3 and CaO are used frequently as additives but are not mandatory.

As already shown there is the need of a metallic reduction component as a slag additive for the remelting of oxygen containing Ti-Al-alloys in order toenable a sufficient desoxidation. The choice which metal shall be used is important, theoretically yttrium, zirconium, aluminum, magnesium and calcium can be used as reducing agent (see figure 5). Yttrium and zirconium are too expensive, magnesium has a vapor pressure, which is too high and can therefore cause procedural problems. The equilibrium of aluminum and oxygen is nearly reached in the ATR step so that calcium is the only additive which can be reasonable be used. [8]

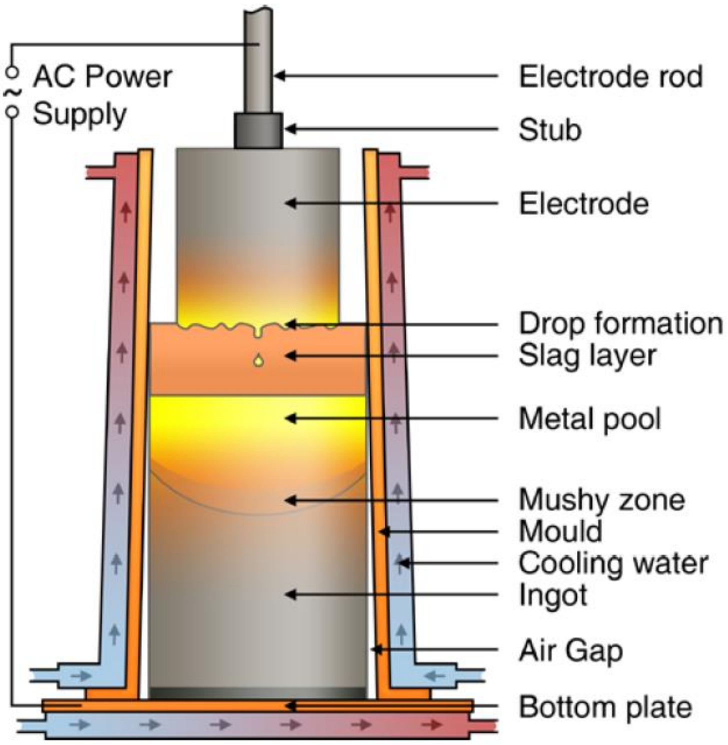

Figure 4: Basic technical scheme of the ESR process [15]

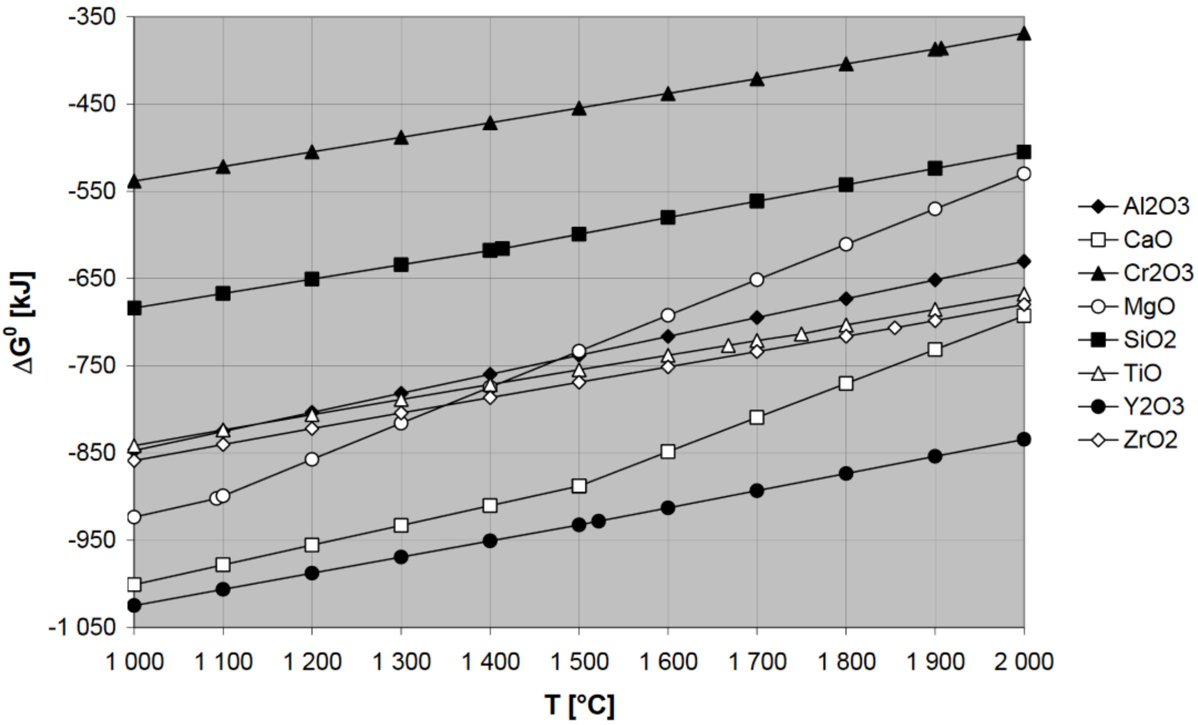

Figure 5: Ellingham diagram of possible desoxidation agents for Ti [16]

There were already investigations from Benz and Carter [17] as well as Tsukihashi [18] showing that a significant decrease of the oxygen content can be achieved by adding metallic calcium during remelting. The oxygen concentration depends in this case on the calcium content of the slag and the temperature. At a medium temperature of 1650 °C it is possible to decrease the oxygen content to 0.05 wt.-% with 0.3 wt.-% calcium in the slag phase.

Calculations by Lochbichler [19] show that the dependence of the oxygen content in a TiAl50 melt from the calcium content is a hyperbolic function at constant temperatures. However, especially at low oxygen contents < 1000 ppm, temperature influences the equilibrium dramatically (figure 6).

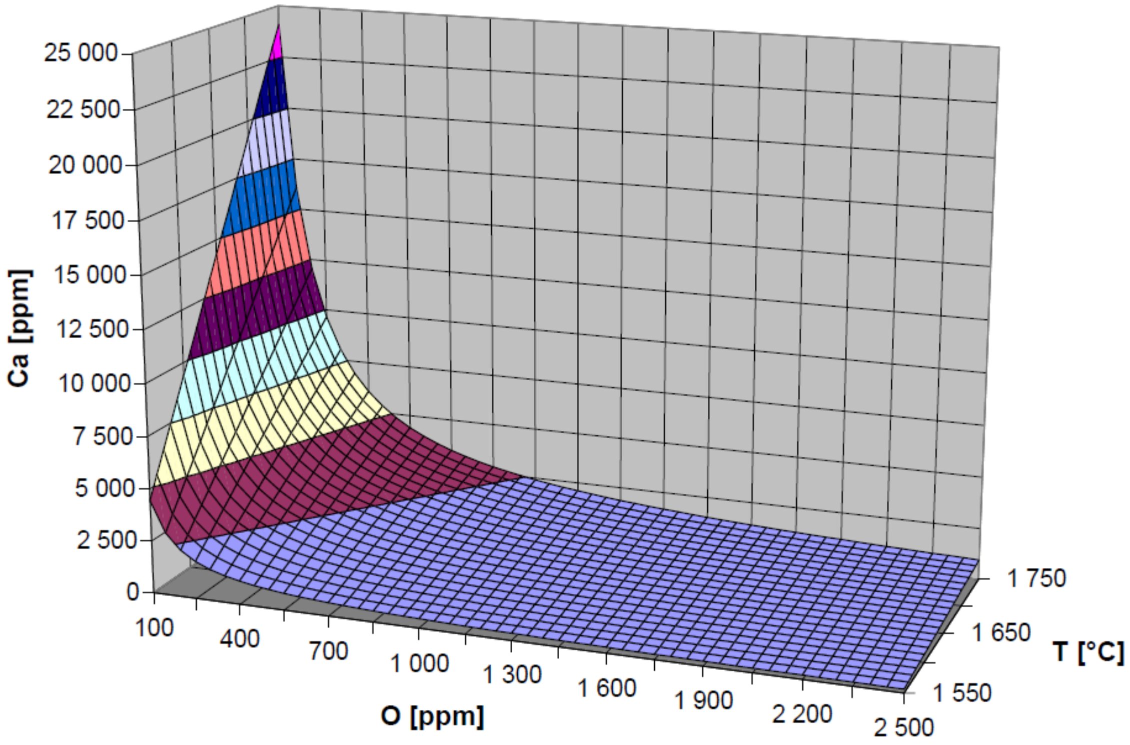

Figure 6: Thermochemical equilibria of O and Ca in TiAl50 [19]

4 Experimental - Part 1: Aluminothermy

To verify the theoretical data, first experiments were carried out in which three mixtures of TiO_2 and aluminum granules with different mole fractions were investigated. The obtained alloy composition is between 45.15 and 60.70 wt.-% Ti and 33.77 to 52.80 % Al. Oxygen is reduced to amounts between 0.8 and 3.45 %. It is notable that the oxygen content decreases with a contemporaneous increase of the aluminum content of the initial ATR mixture. Thus the statement made in chapter 2 is confirmed. Table 2 shows the exact values of these trials. [2]

Table 2: Metal composition with different Al to TiO_2 ratios [2]

n_{Al} / n_{TiO2}	1.5	2.3	3
Element	Content in wt.-%		
Ti	60.70	62.73	45.15
Al	33.83	33.77	52.80
O	3.45	1.32	0.80

Although the obtained results shown in table 2 are a good start for an alternative production route for the TiAl6V4 alloy, they do not serve the required limits of the oxygen content in this alloy. According to the ISO standard 5832-3, this content has be lowered beneath 0.2 wt.-% [10]. One way to face this problem is to rise the mole fraction Al/TiO_2, further more it can be considered to raise the mass of the production batches or the implementation of a protective gas atmosphere.

In the first steps of this project, it was shown that the aluminothermic reaction process is suitable to produce Ti-Al alloys with a sufficient low oxygen content, as predicted by theoretical calculations. In the following the ESR process step could be implemented. A task was to find a way to produce suitable electrodes for the remelting process. Because of the high brittleness of gamma-titanium alloys, which did not allow a conventional production of the desired alloy via crushing and pressing, the first considerations to produce a usable electrode thought to be successful were to cast an electrode directly after the ATR process. Therefore a water-cooled copper mold, flushed with an argon protective gas atmosphere, was implemented directly beneath the ATR reaction vessel. Furthermore, there was a hole in the bottom of this vessel sealed with a sheet of aluminium. 20 kg of input reaction mixture were ignited in the ATR vessel and as soon as the reaction front reaches the Al-sheet melted and allowed the liquid raw alloy to float into the water-cooled mold. One task was to calculate suitable dimensions of this Al-sheet because it had to melt prior of a potential freezing of the meld on the one hand. On the other hand it should have last long enough to let the molten alloy settle and separate from the formed slag system. [3] A schematic drawing and the actual set-up can be seen in figure 7.

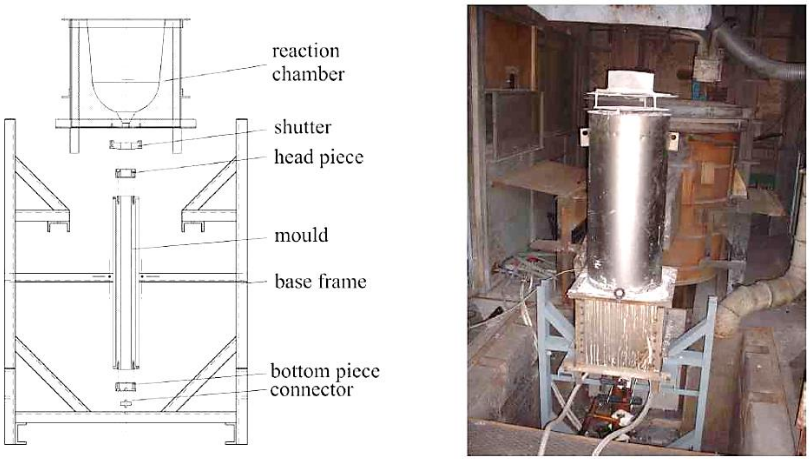

Figure 7: Set-up for in-situ casting of ESR electrode with ATR [3]

After a test series to evaluate the optimum parameters for the described aluminum sealing, the aim of the second test series with this furnace set-up was to cast electrodes suitable for the ESR process. The first electrodes had some cracks due to the high cooling-rate of the copper mold. This disadvantage could be significantly decreased by controlling the flow rate of the cooling-water (or the heat transfer coefficient, respectively) and a suitable refractory lining in combination with a 0.17 mm titanium foil as a heat isolator. However, this technique still needed optimization.

Nevertheless, the chemical composition of the casted electrodes were in good accordance with the thermodynamic calculations, see chapter 2. For the electrodes produced with a high cooling rate and without heat isolation the average content of oxygen within these electrodes were 1.46 wt.-% and a standard deviation of 0.49 wt.-%. In contrast to these findings, a reduced flow rate of the cooling water and a heat isolation at the same time resulted in a lower average oxygen content of 1,17 wt.-% with a standard deviation of 0,21 wt.-%. [3] A suitable electrode made with this alternative processing route can be seen in figure 8. [11]

Figure 8: In-line cast ESR electrode from ATR [11]

The electrode shown in figure 8 has a dimension of a 113 mm diameter and a height of 1 320 mm and is therefore suitable to be used in the Pressure-ESR furnace of the IME Institute. During the project the ATR direct cast set-up changed slightly. Because of the higher oxygen content in the electrode after casting (see above) the mold was no longer a water-cooled copper mold but instead a square box with ceramic lining. But more important, to avoid too much turbulence during casting this box was laid down on the ground with a 10 ° slope for the melt to pass. However, the basic principle was the same as in the first trials in 2002. [12]

Based on small scale trials for determination of thermochemical equilibria four pilot scale trials were conducted with this new set-up. The first trial was made to verify the possibility of producing the desired y-Ti-Al alloy (in this case containing niobium). The second trial should show the mass- and energy balances, the third and fourth one were carried out with a lower energy density, but they showed an undesired metal yield of about 50 % (with a higher energy density it was about 87 %) at a reaction temperature of about 1 900 °C. The proposed energy density found in these investigations was 2 910 J/g with a theoretical reaction temperature of about 1 937 °C. The oxygen content in the pilot scale electrode no. 2 was comparable to these ones found a few years ago and showed a value of about 1.26 wt.-%. [12]

5 Experimental – Part 2: Refining the obtained titanium alloys

The main drawback of direct electrode casting was the uptake of oxygen from the crucible material /slag inclusions as well as dissolved gases/volatile elements.. This led to the decision to use a vacuum induction furnace (VIM) to consolidate Ti-bearing material from ATR or various scrap. One of the main issues is to find a suitable refractory crucible for the melting process, due to the high reactivity of Ti alloys with conventionally used refractory material (mainly oxidic). Ti-Al alloys are less problematic due to reduced Ti activities that inhibit oxygen pickup compared to commercial pure Ti. For example, the activity value for Ti is at 0.87 in TiAl6V4 and may be as low as 0.24 in conventional TiAl alloys. [13] Still, the oxygen pickup is at 5000 ppm when melting in an alumina crucible, so measures must be taken. An approach investigated was the application of a yttria coating on an alumina crucible, due to the fact that the Gibbs free energy of formation of Y_2O_3 is much lower than for TiO or TiO_2. Another way tested is the use of CaO crucibles. [14]

To counteract the decomposition of CaO refractory material during melting of titanium, metallic calcium is added to the melt. However, the high vapor pressure inhibits an efficient use as desoxidation agent, thus $CaAl_2$ was identified among other strategies as the superior compound to be added. The desoxidation material is immersed into the melt (figure 9) after the temperature has reached 1560 °C and the pressure is adjusted to 700 mbar. Massive smoke emissions are visible for 30 seconds with a turbulent melt. Chemical analysis show a moderate pickup of oxygen and calcium (table 3), even though calcium levels are much lower than expected, mainly due to strong evaporation. [14]

Figure 9: Desoxidation can; left: filled with $CaAl_2$ granules, right: with lid [14]

Table 3: Composition of TiAl alloy before and after immersion desoxidation [14]

composition	Ti / wt.-%	Al / wt.-%	Ca / ppm	O / ppm
initial	62.9	36.71	-	512
final	59.7	34.50	1200	960

For Y_2O_3 coated alumina crucbiles, small scale experiments were conducted first, in which the prepared crucibles were filled with 1 kg TiAl scrap. No major damage to the crucibles was observed after heating with 15 to 20 kW and holding for three minutes prior to casting. However, Y_2O_3 pickup is a problem, because it cannot be removed later on due to its higher density compared to TiAl. With an average oxygen concentration of 1168 ppm in the scraps, a slight oxygen uptake is probable, since the values after VIM vary between 980 and 1700 ppm. The phenomena was verified by large scale experiments (30 kg) after which an average of around 3000 ppm was the outcome. [13] These results strongly suggest additional refining steps to deoxidize the material, as will be shown.

The main challenge for the desoxidation of titanium alloys via electroslag remelting (ESR) is to establish a process control that takes the thermochemical and kinetic characteristics of the process into account. Given the ATR electrodes described before, the effects of varying slag composition and the evaporation of Ca are important factors to design a continuous and best possible desoxidation.

By keeping the equilibrium expression in equation 6 constant, continuous removal of oxygen is ensured. In order to achieve this, Ca has to be added continuously due to its consumption and evaporation during the process. The evolving CaO is dissolved in the CaF_2 slag phase and is therefore continuously increasing in concentration and therefore also in thermochemical activity. To lower this term, CaF_2 is also added to suppress CaO activity increase.

$$\mathrm{K} = \frac{a(CaO)}{a(Ca)} \tag{6}$$

In order to kinetically retard Ca evaporation, an Ar pressure of 20 bar is applied within the ESR unit. γ-TiAl electrodes used were aimed to have a diameter of 110 mm and 1325 mm in length. Oxygen concentration was analyzed beforehand and determined to be 1.59 % (gas extraction method). The slightly conical ESR mold has a diameter of 178 mm at the bottom and 159 mm at the top (880 mm in height). As slag, WACKER 2052 (> 97.5 % CaF_2) with a CaO content of 1.17 % was used. [20]

Figure 10 shows the Ca content versus the O content obtained by different desoxidation strategies. Overall, lowest oxygen values are obtained by ESR desoxidation of electrodes formerly molten via VIM. Desoxidation of scraps only by VIM melting reaches quite low oxygen contents that consequently correspond to high calcium values. Due to the high initial oxygen contents of the ATR electrodes, low levels are not attainable, but are also related to low Ca values. Overall, the dependency of O and Ca is of the same slope for all processes, even though the effectiveness varies. [20]

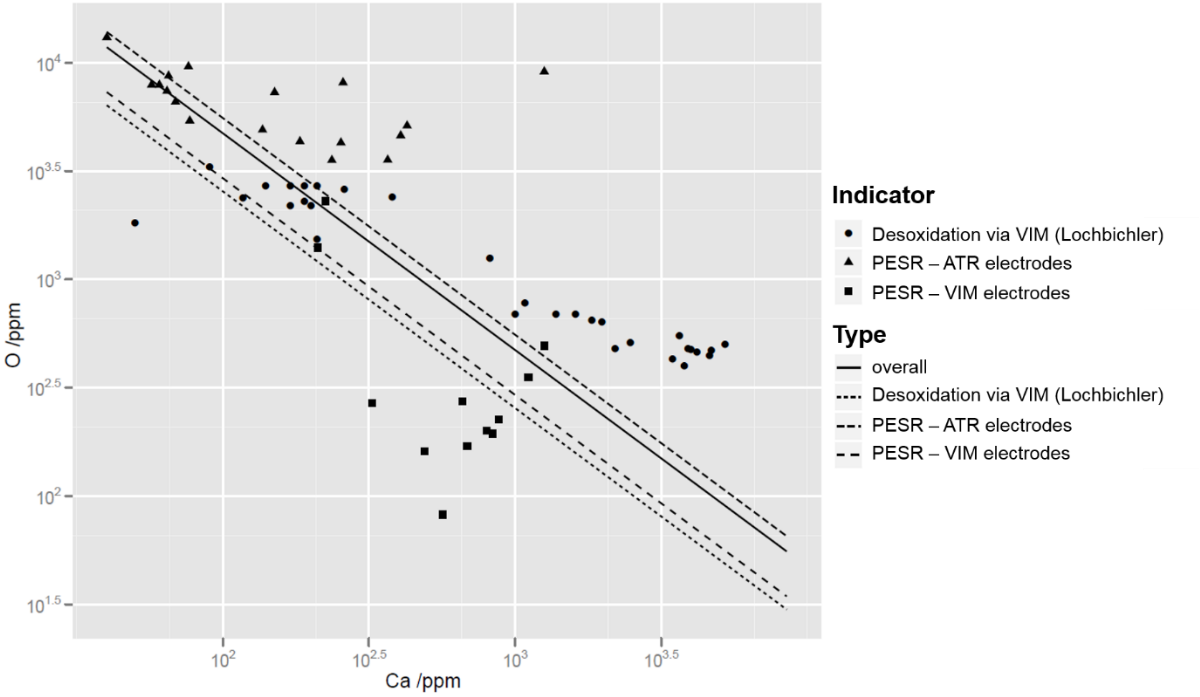

Figure 10: Ca versus O content for different desoxidation processes [20]

Decomposition of the fluoridic CaF_2 slag at processing temperatures around 1800 °C to TiF, which is incorporated in the metal phase, is unavoidable but to a certain extent also desired to increase oxidation resistance. However, the slag influences the degree of fluorine pickup strongly. Investigations by Spiess and Friedrich [21] show that a partial substitution of CaF_2 by MgF_2 accounts for minor fluorine pickups in the melt. In conclusion, variation of the slag composition and the temperature does not account for an adequate fluor content that would have a substantial effect on oxidation resistance. [22]

In total, TiAl originating from scrap with subsequent VIM and ESR treatment was proven to be desoxidizable to oxygen contents below 500 ppm. The material extracted by ATR has higher oxygen contents from the beginning, thus oxygen could not be reduced to values less than 4000 ppm. The results indicate high potential for further improvement in understanding the reaction mechanisms that are occurring during desoxidation via ESR. [20]

Within a conventional triple melt route, vacuum arc remelting (VAR) is the last remelting step to adjust the ingot’s microstructure. Due to volatile elements still present after ESR (especially Ca), an additional refining step making use of distillation phenomena is employed. VAR is exceptionally well suited for this case, due to the large surface area of molten metal in droplet form, as well as low achievable pressures during the processes (here: ~ 10^{-2} mbar). Thus, Ca is found on the crucible walls after the process.

The success of calcium removal is extremely satisfying since no Ca may be found above the detection limit of 1 ppm with the method used (ICP). Sampling of the VAR material is more reliable because the next processing step, for example casting turbine blades, does not require ingots as input geometry, so more samples may be taken from different parts of the product. Figure 11 exhibits typical the experimental setup; for starting the process, TiAl shavings were used. The electrode is remelted in a 200 mm diameter copper mold in a VAR furnace with a maximum melting current of 6 kA.

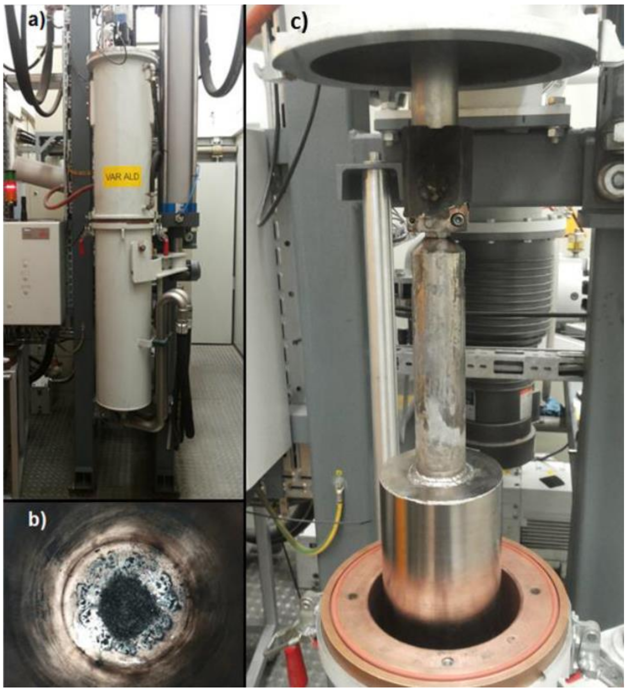

Figure 11: a) VAR furnace; b) TiAl shavings on the bottom of the mold; c) VAR electrode mounted to the electrode rod prior to melting [13]

6 Conclusions and Recommendations

The proposed scheme for Ti-Al or Ti-Al-X alloys is highly interesting in terms of equipment and resources utilization when compared to conventional processes. Due to the fact that the alloying metal aluminum is simultaneously applied as reducing agent, it is not necessary to add it as costly Al-Ti master alloy during remelting. Overall, up to 40 % less production costs are estimated when compared to conventional processes. [8]

Activated TiO_2, in combination with CaO_2 as booster, has the potential to enable an ATR process free of chlorine-based boosters and surpassing the Kroll process. Ideally, the process is extended by in-line casting of ESR electrodes, without the costly consolidation step via VIM that is however still necessary for recycling activities of Ti scrap. [23] The high oxygen contents can be significantly lowered by ESR remelting with reactive slags containing Ca and no fluorine pick-up is taking place, Surplus Ca is later fully removed by VAR. Overall, the process provides the opportunity to not only use primary material, it is also able to incorporate scraps and provides material that is not inferior to Kroll process made titanium alloys.

Nevertheless we reached now a status of TRL-level 5 and an upscaling and reproducibility program must be started in order to proof the reliability of this innovative approach, which could open the window for a large volume use in automotive industry as well as an alternative for the production of gamma-TiAl-alloys. The proposed flow chart is depicted in Figure 12. Recommendations for further research on optimizing the overall process include

1) Chlorine-free booster or the use of substitute approaches, such as activated rutile, need to be investigated further.
2) ATR with the aim of even lower oxygen contents after in-line casting
3) Slag chemistry and understanding of the mechanisms during ESR to promote product quality and final oxygen contents

The process has been carried out in all aspects within the facilities of IME at RWTH Aachen. However, scale up is still to be investigated, which is the next big step towards an establishment of the process. Also, the versatility of the process with the incorporation of closed-loops is remaining an interesting topic, when not only looking at improving the primary process, but also a secondary scrap treatment approach.

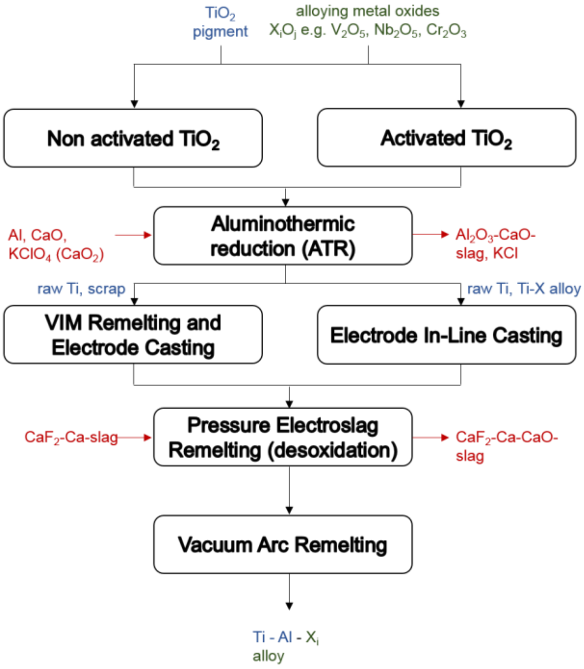

Figure 12: Proposed flow chart for cost efficient Ti-Al-X production process

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