Experimental research on the recycling potential of precision cast γ-TiAl during electroslag remelting

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Keywords: pressure electroslag remelting, TiAl, recycling, deoxidation

Abstract

Implementation and serial production of γ-TiAl cast parts is imminent for aero- and automotive engines. During the investment casting process a significant amount of the material solidifies in the casting system. This material cannot be directly reused due to the contact with ceramic and the high oxygen content.

In current investigations a recycling process is developed. First, γ-TiAl scrap is melted in a vacuum induction furnace to produce an electrode. In a second step the manufactured electrode is remelted in an inert gas electroslag remelting furnace. The optional final step is a remelting process in a vacuum arc furnace.

To proof the recycling potential of γ-TiAl during IESR with concomitant reduction of oxygen and yttria concentrations, a series of tests was performed. The produced alloy has been used for casting of low-pressure-turbine-blades in investment casting. Chemical analysis was conducted to prove the quality of the recycled material.

Introduction and Thermodynamics

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 (Figure 1). Detailed investigations on each process step were performed by Lochbichler [1] Stoephasius [2], and Reitz [3], [8].

An important aspect of the project 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 during VIM and ESR. Calcium residues and remaining non-metallic inclusions can be removed during a final VAR step.

Especially for the material class of γ -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]

This paper focuses on the recycling route of γ -TiAl from investment casting scrap (figure 1, “scrap route”). Aim of the project route is to provide a cost-effective possibility for the industry to recycle scrap internally. With using VIM as a first consolidation step, the process offers high flexibility regarding scrap shape and composition with the possibility of online sampling and composition corrections.

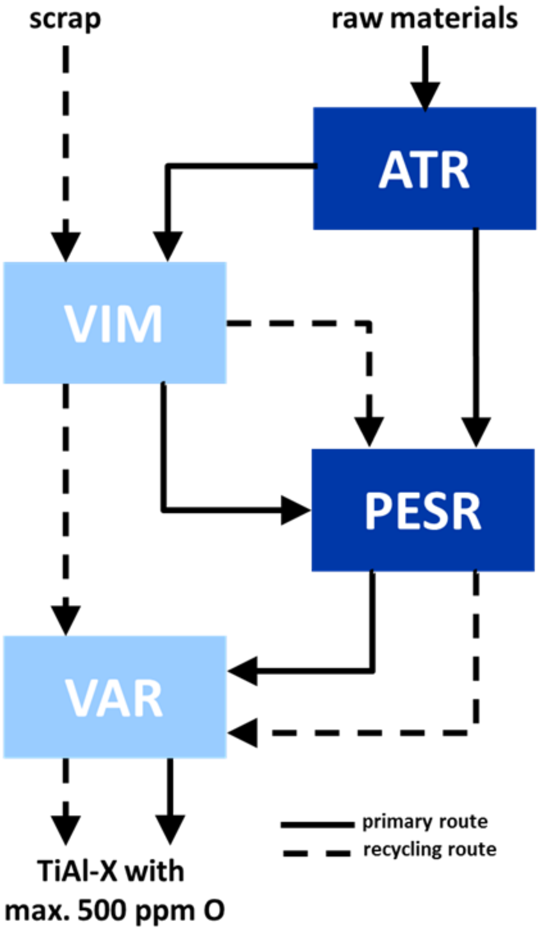

Figure 1: Scheme of the IME alternative processing and recycling route for TiAl-alloys

Major obstacle while handling titanium and its alloys is the strong affinity to oxygen. Besides of this, titanium can dissolve more than 30 at-% O (Figure 2) until an oxide phase segregates. Therefore, all metallurgical processes that involve handling liquid titanium have to be conducted under a controlled inertgas-atmosphere.

Lochbichler [1] calculated, that although the Titanium activitiy in TiAl alloys is remarkably decreased in comparison to commercial pure titanium (Table 1), the use of alumina crucibles for Vacuum Induction Melting of TiAl leads to an oxygen pickup 5000 ppm or more depending on the temperature which is above the specs of approx. 800ppm.

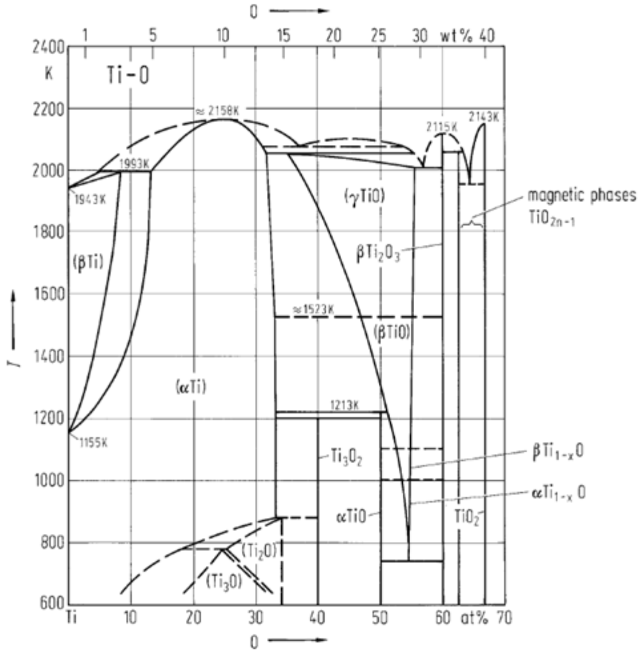

Figure 2: Ti-O Phase Diagram [12]

Table 1: Titanium activities and liquidus temperatures of chosen Ti-bearing alloys (Data: FactSage, ELEM)

alloy	T_{Liq}	a_{Ti}
cp Ti	1668 °C	~1
TiAl6V4 (mass%)	1686 °C	0,87
FeTi70 (mass%)	1109 °C	0,56
TiAl50 (at%)	1517 °C	0,24
FeTi30 (mass%)	1433 °C	0,07

Consolidation by VIM

The first step in terms of processing TiAl scrap materials (Figure 3) is the consolidation melt via VIM. Aim is to achieve a homogeneous melt and therefore a homogeneous product in terms of chemistry for further processing. Since Titanium has a strong affinity to oxygen, the selection of a suitable crucible is essential. As mentioned before, alumina is not suitable because of the lack of thermochemical stability.

Figure 3: massive casting scrap

Generally, oxide and non-oxide ceramics need to possess an appreciably higher solidus temperature than that of Ti and Ti alloys, no addiction for volatilization and a sufficient stability against Ti and Ti alloys thermochemically. The referred attributes can be expressed by the standard Gibbs free energy of oxide and non-oxide ceramics. Thus, the chemical stability of oxide and non-oxide ceramics against Ti can be grossly classified.

The thermochemical stability of oxides and non-oxides (except B4C, SiC, and TiC) is dramatically reduced with temperature. None of the non-oxides is more stable than TiC and TiN respectively, i.e. titanium possesses the highest affinity to C and N at all. According to standard Gibbs free energy calculations of oxides, only CaO, Y2O3 and ZrO2 seem to be sufficiently stable against titanium, whereas CaO should be most stable. Beside of the mentioned thermochemical stability, lime is the best choice in terms of costs. On the other hand, the main problem when using pure lime is its hygroscopic nature, so the crucibles have to be handled carefully. Another disadvantage is the combination of low pressures and high temperatures during VIM. As a result, lime dissolves in the melt as Ca and O. Due to its high vapour pressure, metallic calcium evaporates and condenses at the water cooled furnace walls. Therefore, this reaction cannot reach its thermochemical equilibrium which results in further dissolution of CaO and subsequent oxygen enrichment in the melt. The reaction speed of this dissolution step is strongly influenced by the temperature.

For consolidation, a vacuum induction furnace with a crucible capacity of 14 l is used, which corresponds to approximately 30 kg of material (Figure 4). In this work, lime and yttria were chosen as crucible material. The furnace pressure during melting is 800 mbar (Ar), the casting temperature is ~1550°C. The material is cast into a cylindrical water cooled copper mould to produce a suitable electrode for further remelting (Figure 5).

Figure 4: Vacuum induction melting of TiAl scrap

Figure 5: Cast electrode after VIM step

Vacuum induction melting offers the possibility of influencing the melt chemistry via charging of alloying elements or reacting agents. In the case of this presented project, a deoxidation technique was developed. Idea is the introduction of $CaAl_2$ (when using lime crucibles) or metallic Y (when using yttria crucibles) as deoxidation agents to achieve the following reactions:

$$[TiO]_{TiAl} + [Ca]_{TiAl} = \langle CaO\rangle + Ti \quad (1)$$

$$[TiO]_{TiAl} + \{Ca\} = \langle CaO\rangle + Ti \quad (2)$$

$$3[TiO]_{TiAl} + 2[Y]_{TiAl} = \langle Y_2O_3\rangle + Ti \quad (3)$$

< > solid, [ ] dissolved, { } gaseous

The deoxidation step by $CaAl_2$ offers sufficient deoxidation of TiAl to less than 700 ppm O experimentally, but leads to Al2O3·CaO spinel type precipitation. The application of Y metal as deoxidant to TiAl has not succeed. Even alloying of approx. 10000 ppm Y in TiAl do not effect in acceptable oxygen contents. Background is the higher solubility product of Y_2O_3 in comparison to CaO in the melt. Figure 6 shows thermochemical calculations of the Ca-O and Y-O equilibria in TiAl melts as a function of temperature.

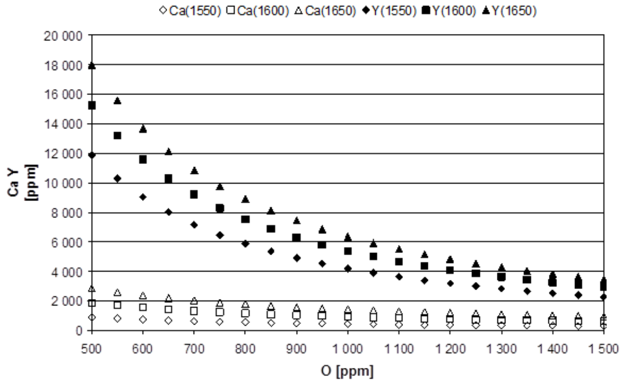

Figure 6: Dissolved Ca and Y in CaO and Y_2O_3 saturated liquid TiAl versus dissolved oxygen at three different temperatures, note: a(CaO), a(Y_2O_3) = 1 [1], [9], [10]

The total impurity degree of TiAl by Ca and O in application of CaO is much less than applying Y_2O_3 (i.e. Y and O) as coil infeed. The oxygen pick up due to dissolution of CaO adds up to 2600 ppm on average versus 3100 ppm applying Y_2O_3 infeed (without deoxidation). Generally the metallic cleanness is better in the application of CaO in opposite to Y_2O_3 as well. Possible Aluminium losses during melting can be estimated and compensated by charging a higher Al concentration from the start.

As mentioned before, final deoxidation of TiAl may be carried out by ESR as an intermediate step of the recycling process. Due to the high vapour pressure of Ca the deoxidation step of Ti and Ti alloys by Ca at 0.8 bar process pressure is not possible experimentally.

Deoxidation by Electroslag Remelting

Fundamentals

Electroslag remelting (ESR) is widely applied in the production of speciality steels and superalloys nowadays in order obtain ingots with superior cleanliness, minimized segregation and a homogeneous microstructure. As a basic principle the tip of a consumable electrode, made from the alloy to be refined, is dipped into a molten slag, contained in a water-cooled copper crucible (Figure 7). Electrical currents (most commonly AC) are applied between the electrode and the flux and result in joule heating up to the melting point of the metal. A liquid metal film forms on the downside of the electrode and as a consequence, droplets detach from the electrode tip and sink through the slag and are collected in a liquid metal pool. Refining reactions, such as dissolution or flotation of nonmetallic inclusions, take place between the liquid slag and metal. Through cooling at the mould surfaces, solidification occurs and the process continuously builds up a refined ingot with a controlled microstructure and smooth outer surface. Depending on the furnace complexity, the gas atmosphere composition, furnace pressure and the slag chemistry can be adjusted [5], [6].

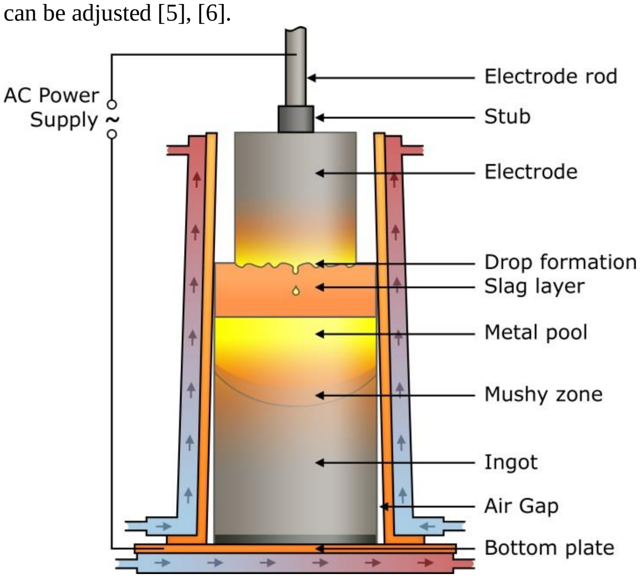

Figure 7: Scematic figure of the ESR process [7]

Thermodynamics of Deoxidation

For deoxidation by Pressure Electro Slag Remelting (PESR), slags based on CaF_2 offer the best combination of thermochemical stability, stable processing conditions, availability and final ingot quality [4]. Thermochemical calculations in the system Ca-CaO-CaF_2 have shown that even the deoxidation of pure titanium should be possible by ESR using “reactive slags” where metallic calcium is added to the flux as a deoxidation agent [11]. Ca is chosen as a reactant, because of its high oxygen affinity, good solubility in the slag and available experimental data for the equilibrium of Ca and O in titanium melts.

The main principle of deoxidation by Ca (Figure 8) is based on the reaction between oxygen dissolved in the metal phase as TiO with calcium dissolved in the slag which results in precipitation of CaO according to (1):

$$[TiO]_{Ti/TiAl} + [Ca]_{CaF_2} \rightarrow [Ti]_{Ti/TiAl} + [CaO]_{CaF_2} \quad (4)$$

$[A]_B$ – Element or compound A dissolved in molten phase B

As a main characteristic of the ESR process only a partial volume of the total metal is in the molten state at any time of the process and backmixing is limited to this volume. Thus to ensure a uniform oxygen content with respect to the full length of an ingot, the oxygen potential in the slag has to be carefully controlled during the whole melting process. Unfortunately, the slag enriches in CaO during the melt and is being depleted in calcium, hence thermochemical equilibrium will naturally shift to the left side of equation (4), decreasing the effect of deoxidation over time. The result would be a non-homogeneous ingot in terms of oxygen content. It becomes obvious from the law of mass-action in (5) that when constant temperatures are assumed (i.e. constant equilibrium temperature K) and concentrations and respective activities of TiO and Ti are fixed by the specifications of the alloy, a constant ratio f according to (5) throughout the whole melting time is key to a successful deoxidation procedure.

$$f = \frac{a(CaO_{slag})}{a(Ca_{slag})} \equiv const \qquad (5)$$

Thus with increasing CaO concentration the Ca activity has to be continuously increased during the process for compensation. Additionally the CaO-activity can be decreased by dilution via addition of virgin CaF2. In order to synch both measures of interaction with the metal-slag system, modelling of the activity coefficients of Ca and CaO in the chosen slag system as a function of Ca and CaO concentration and temperature was conducted [2]. Due to the current lack of reliable methods for online-surveillance of the activities of Ca and CaO in the slag, a process model was introduced based on mass-balance calculations that include dissolution of Ca in the metal, pressure dependent evaporation of Ca from the flux and the assumed deoxidation equilibrium. This was put into practice as a spreadsheet which can be adjusted to melting parameters, e.g. metal melt rate, initial oxygen level of the metal, operating pressure etc. which calculates feed-rates for both calcium compensation and feeding of virgin slag. The melts presented here are both conducted based on that spreadsheet calculation and the assumption that the system operates close to chemical equilibrium.

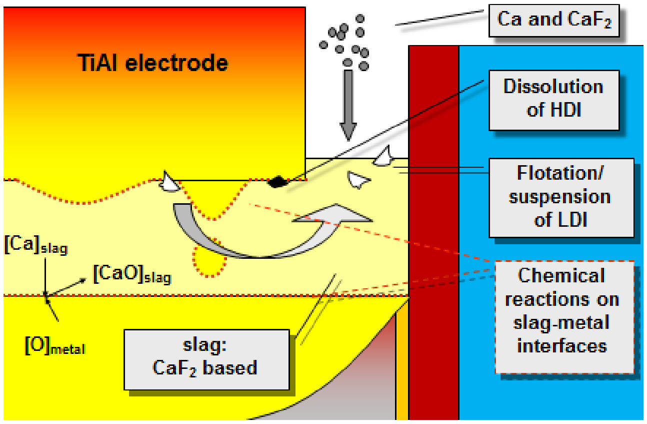

Figure 8: PESR deoxidation of TiAl

Process pressure

As mentioned before, the processing of liquid titanium has to be performed under inertgas-atmosphere. In addition to this, during PESR of TiAl, a system pressure of 20 bar is set up. Reason for this is the high vapor pressure of calcium (Figure 9) at process temperatures (indicated with the highlighted area). During dissolution in the slag, the calcium activity is decreased, but an evaporation at 1 bar is still noticeable after remelting due to calcium residues at the crucible wall. Overpressure does not affect the partial pressure of calcium in the slag, but it slows down evaporation kinetics, serving as a barrier for the formation of gaseous calcium at the slag/gas interface.

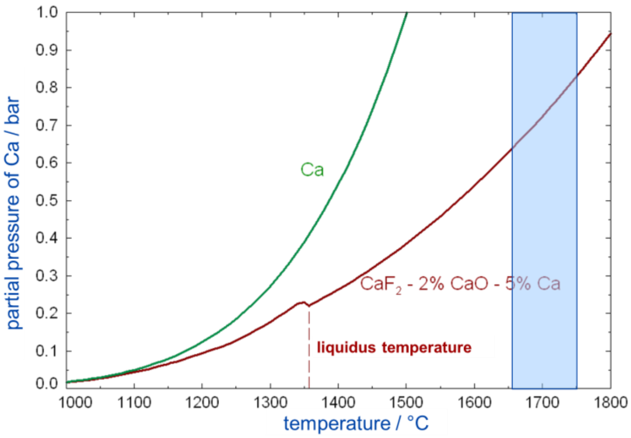

Figure 9: Partial pressure of pure Ca and process slag containing typical Ca-contents of 5 wt-%

Experimental

The PESR furnace located at IME, RWTH Aachen University used for the trials (Figure 10) is capable of operating under inert-gas at a maximum pressure of 50 bar. It is equipped with a 5 kA power supply and a new control and monitoring system. The nominal electrode diameter is 110 mm, and the ingot diameter is 160 mm, slightly conical. The furnace is equipped with two bunkers and screw feeders for introducing additives during remelting. The feeders are driven by pneumatic cylinders which turn the feeder screw by a wrench-like set-up in 90° steps. With every turn, a controlled amount of the additive is extracted from the respective bunker and charged to the melt. The number of wrenching impulses per minute can be set independently for every feeder in the furnace control system. The furnace interior, the bunkers, and the cooling water are all maintained at the operating pressure. This furnace is not equipped with load cells, and the melt rate is calculated from ram travel.

Figure 10: PESR/ESR furnaces at IME Aachen

For start-up, a plate made of TiAl sputter targets (Figure 11) is placed on the crucible bottom to ensure electrical contact during the starting phase. The process slag (Wacker 2052, > 97 % CaF_2) is filled in the gap between the starting plate and the crucible walls. After putting the crucible into the furnace, the whole assembly is sealed and filled with process gas. The IME PESR furnace is equipped with a modern closed loop process control system which allows to tracing and adjustment of necessary process parameters on-line.

Figure 11: starting plate (left), top view of crucible with slag and starting plate (right)

Figure 12 shows a remelted TiAl ingot directly after remelting (left) and after removing the cap- and skin-slag right). For chemical analysis, discs at different heights are cut out of the ingot. Small (30 x 30 mm) samples are taken at half radius and the concentration of metallic components was determined by XFA with a PANAnalytical, Model: Axios. Oxygen was determined by inert gas fusion on a Ströhlein ON-Mat 8500. Results are presented in Figure 13.

Figure 12: Obtained TiAl Ingot after PESR

Main advantage of deoxidation during PESR is the use of a water cooled copper crucible instead of ceramics. Since the activity of CaO is lower than unity, it is possible to achieve material which is low both in calcium and oxygen. Typical oxygen values after PESR of TiAl are between 500 – 1000 ppm. With increasing the calcium addition during remelting, these values can be shifted down to below 100 ppm, however the process becomes hard to control since the evaporation of Ca is increasing. Ca residues remaining in the alloy, can be removed during a subsequent distillation step via VAR.

Ongoing investigations at IME show, that the Y- content in the metal (when previously melted in yttria crucibles) can be decreased to below 50 ppm.

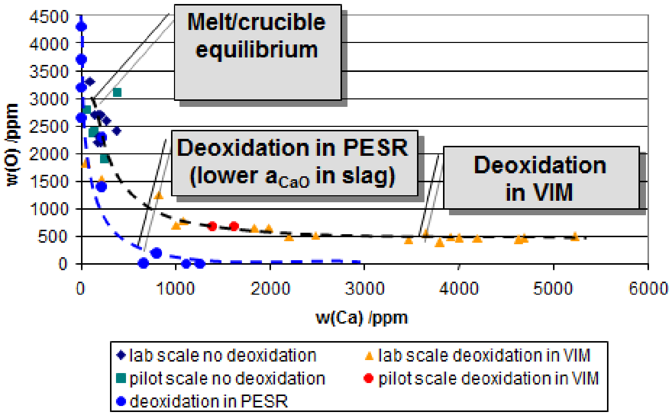

Figure 13: Deoxidation effect after VIM (CaO crucible) and PESR

Vacuum Arc Remelting

Well known metallurgical opportunities of the Ti-VAR process are vacuum refining (e.g. Mg distillation from Ti sponge and hydrogen degassing) and production of structurally homogenous and substantially macrosegregation free metal. VAR offers excellent metallic cleanness due to the removal of small non-metallic inclusions (NMI), mainly by flotation effects.

Due to the sufficiently high Ca vapour pressure, it is assumed that Ca distillation according to equation (6) from TiAl seems to be possible by VAR. Even at low metal pool temperatures, Ca contents less than 40 ppm are thermochemically possible at 5 Pa pressure (Figure 14).

$$[Ca]_{TiAl} = \{Ca\} \qquad (6)$$

[ ] dissolved, { } vapour

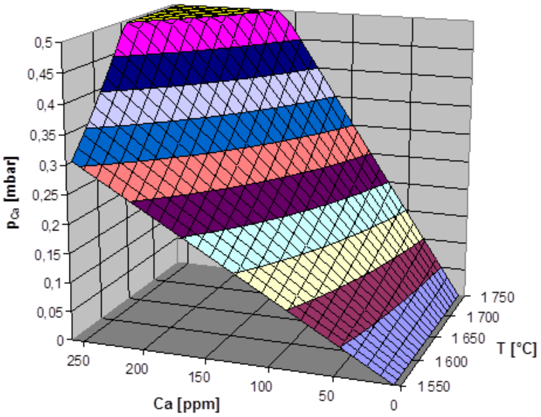

Figure 14: Vapour pressure of Ca according to VAR pool temperature and Ca content in γ-TiAl (FactSage, data: ELEM, with γCa = 1)

If the total pressure of the process is less than the partial pressure of e.g. Ca and H, classical boiling can occur. If that is not applicable, distillation (degassing) will be diffusion controlled and thus may effect in less refining efficiency. In VAR, only a small amount of the total electrode mass is in molten state concurrently for a short time. Thus, distillation may be controlled kinetically and sufficient distillation may not be illustrated just thermochemically.

Conducted VAR trials at IME with Ca contaminated TiAl material proof the distillation effect. VAR at low pressures (i.e. less than 0.5 Pa) offers a virtually complete removal of dissolved Ca as it is no longer detectable in TiAl by AAS. CaO-residues at the crucible walls, as well as the remelted ingot are shown in Figure 15.

Even at process pressures less than 0.5 Pa no appreciable aluminium losses in TiAl occurred in VAR. The metallic cleanness of TiAl is equally to or even better than that of the virgin alloy. Generally, the applied calcium-metallurgical recycling concept offers a superior metallic cleanness.

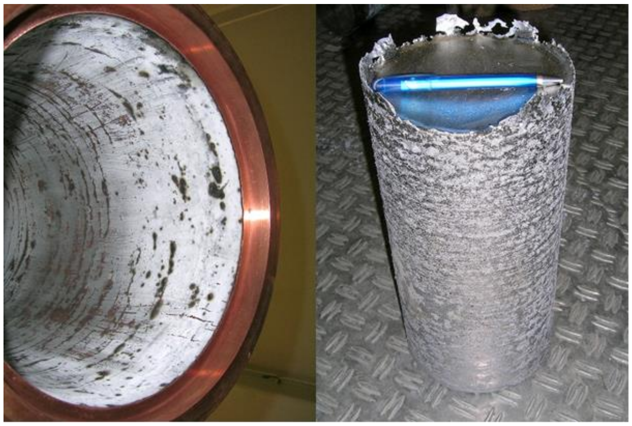

Figure 15: Crucible with residues (left) and VAR Ingot (right)

Investment Casting

In order to validate the application potential of the recycled material, centrifugal investment casting of was performed at Access e.V., Germany. For casting, an exemplary TiAl (50:50) alloy was chosen, which was melted in a yttria crucible and subsequently deoxidised in the ESR process. As a last step, a final VAR refining step was performed.

The selected casting geometry was a low pressure turbine blade (LPTB) with a length of 28cm. The casting device was a Leicomelt 5TP made by ALD Vacuum technologies GmbH, Germany. In this device, the melting of the material was carried out inductively in a water cooled copper crucible. The crucible has a capacity of 2l which accords to 8kg TiAl alloy. Under the crucible the ceramic shell mould is fixed on a rotation table. The shell mould, used for casting consists of front layers, is made from Y_2O_3 and several back-up layers are based on Al_2O_3. As soon as the material is molten and the desired super heat is reached, the content is being tilt over in a funnel which leads the melt in the rotating shell mould. An illustration of the melting process as well as the cast blade is shown in Figure 16.

After casting and de-moulding all cast parts were heat treated (HT) in Argon atmosphere at 1095°C for 5 h and hot isostatic pressed (HIP) at 1185°C and 172MPa for 4 h. After the HIP a second HT was applied in at 1205°C for 2 h and rapid cooling.

The characterization of the casing parts includes chemical analysis, x-ray inspection and microstructure analysis. The inert gas fusion and combustion method were used for the measurement of interstitial elements. Before analysis the cast surface of the analyzed part was removed by water-jet in order not to distort the results in particular the oxygen content. The results of the chemical analysis are listed in Table 2. During the x-ray analysis no considerable defects were detected. The ceramic shell mould is stable and no spalling was detected.

Results show, that the concentration of interstitial elements is on a satisfactory low level. The oxygen content with 600 ppm is fully meeting the specs.

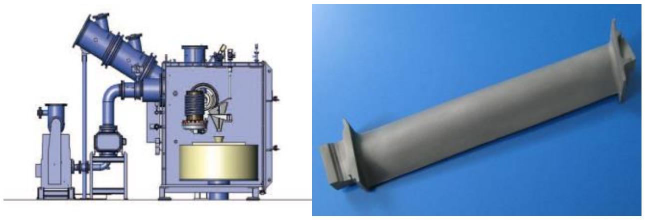

Figure 16: Vacuum Induction Scull Melting and centrifugal casting (VISM, left), TiAl turbine blade after casting (right)

Table 2: Concentration of chosen elements of the cast material

Element	C	N	H	O
Wt-%	0,02	0,02	<0,005	0,06

For analysis of the microstructure cut ups in different areas of the blade e.g. airfoil, root or shroud will be performed. The area ratio of gamma grains in the microstructure will be evaluated in the next stage of the project

Summary

(1) IME developed and proved a recycling concept for high oxygen containing TiAl scrap starting with VIM homogenisation.

(2) The presented process offers a possibility for TiAl cost reduction

(3) CaO crucibles for the consolidation step in VIM showed best performance

(4) Nonmetallic inclusions (NMI), calcium and oxygen uptake is over-compensated by subsequent PESR and VAR double melt

(5) Final thermochemically calculated oxygen values of 500-750 ppm reached experimentally values of 100-600 ppm

(6) The ESR process offers a potential for bulk fluoridisation of the metal (halogene effect), the impact of calcium on the material properties is still unclear.

(7) The presented process still needs full validation by large scale series and full material characterisation

Outlook

(1) Nitrogen and carbon values above 200 ppm cause embrittlement of TiAl, the disposition of these elements has to be investigated

(2) Further research on fluorine-solubility during PESR, there are further research needs on the accurate adjustment of the target value

(3) Applied research of calcium-impact on mechanical properties will be performed with the focus on minimisation of deoxidation-agent additions

(4) The process effect on Y-content demands closer inspection

(5) A thermochemical model is being developed in order to describe the deoxidation kinetics during PESR

(6) The portability of the recycling process on complex, high alloyed TiAl will be investigated

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