A Complete Recycling Circle for Precision Cast Low Pressure TiAl Turbine Blades

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Abstract

Titanium based alloys gain a more and more important role in the manufacturing of aerospace turbine blades. In a modern aircraft turbine, all of the turbine blades and fans except the high temperature high pressure turbines are made out of Ti-based alloys. Due to the expensive primary Titanium production, an efficient recycling route for Ti-based alloys is crucial for decreasing the price of the whole turbine. Over the past decade, the IME has focused on the recycling potential of titanium aluminides (TiAl) used for low pressure turbine blades. To do so a full triple melt TiAl recycling route consisting of VIM, PESR & VAR was established at the IME. Even using ceramic crucibles in VIM it was possible to obtain a material which meets all specifications even the low limit for oxygen. This material can and will be directly reused for casting turbine blades.

Introduction

For more than 10 years investigations on the recycling of TiAl-alloys have been carried out at the IME, RWTH Aachen University. Target was to recycle a scrap which is highly contaminated with oxides using a triple melt route. Investigations on each single recycling step have been carried out by Lochbichler [1], Stoephasius [2] and Reitz [3]. The main task during all of these steps is the minimization of oxygen in the alloy. This work now is the combination and validation of all their results over the whole triple melt recycling route.

To achieve a recycling process that can be implemented in existing industrial structures the three process steps Vacuum Induction Melting (VIM), Pressurized Electroslag Remelting (PESR) and Vacuum Arc Remelting (VAR) are used as shown on Figure 1.
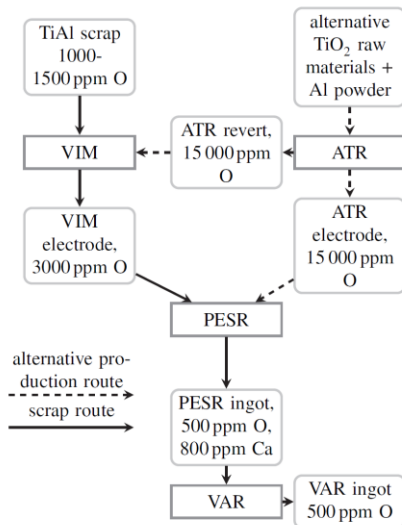

Figure 1 Flow chart of the TiAl recycling route developed at the IME compared to the primary TiAl production

To reduce the amount of oxygen, that is unavoidable when using recycling material, calcium is used as reducing agent. It is either added during the consolidation in VIM or as a slag addition in ESR. The main difficulty working with Ti-based alloys is the high oxygen affinity of Ti combined with a solubility of O in Ti of about 30 at.-%. Therefore all of the metallurgical process steps where TiAl is in a liquid state have to be conducted under vacuum or inert gas atmosphere.

Fundamentals

Crucible selection

Calculations show that, although the titanium activity in TiAl alloys is remarkably lower than it is for pure titanium (Table 1), the most common crucibles used for vacuum induction melting, alumina crucibles, cannot be used because they lead to an oxygen pickup of 5000 ppm or more whereas specifications only allow an oxygen content of less than 600 ppm.

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

Alloy	T_{liq}	a_{Ti}
Cp Ti	1668 °C	~1
$TiAl_6V_4$ (wt.-%)	1698 °C	0.87
$FeTi_{70}$ (wt.-%)	1120 °C	0.56
$TiAl_{48}Nb_2Cr_2$ (at.-%)	1514 °C	0.24
$FeTi_{30}$ (wt.-%)	1417 °C	0.05

As can be seen in Figure 2 the Gibbs free energy of formation reaction of Y_2O_3 is much lower than the ones of TiO and TiO_2 whereas the Gibbs free energy of formation of Al_2O_3 and CaO are very close or above them. Therefore yttria can be assumed as thermodynamically much more stable against a reduction by titanium.
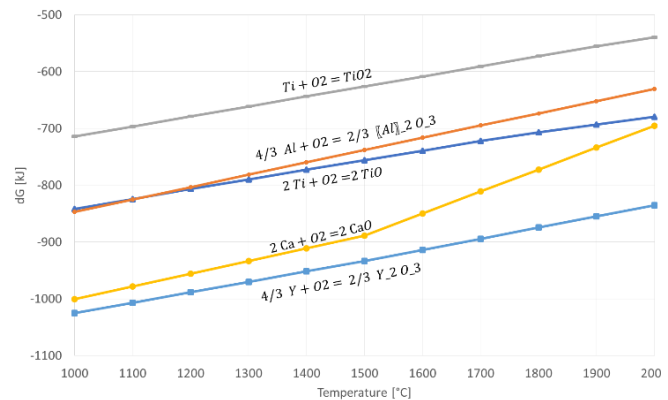

Figure 2: Free reaction enthalpy of different oxides (FactSage, data: FToxide

Deoxidation using calcium

The reduction of TiO as well as the removal of dissolved oxygen from the alloy is carried out by a calcium reduction where the following reactions take place:

$$[TiO]_{TiAl} + [Ca]_{TiAl} \quad\leftrightarrow <CaO> + Ti \qquad (1)$$

$$[O]_{TiAl} + [Ca]_{TiAl} \quad\leftrightarrow <CaO> \qquad (2)$$

The main problem that occurs when using calcium as reducing agent is its high vapor pressure which is illustrated in Figure 3.
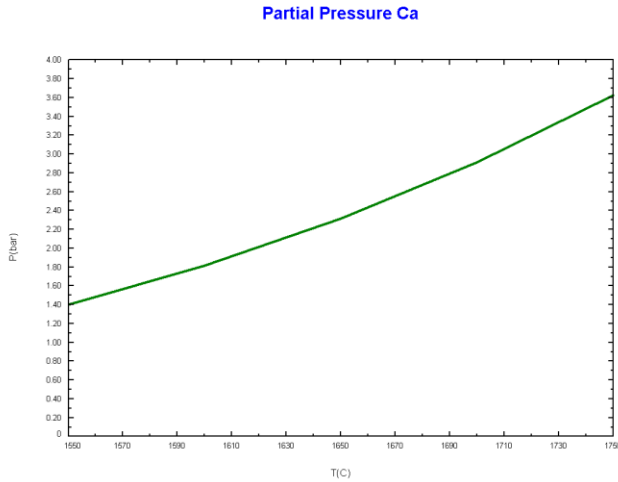

Figure 3: Vapor pressure of pure metallic Ca at different temperatures (FactSage, data: SGPS)

This high vapor pressure leads to a nearly instant evaporation of calcium under standard conditions. In the course of this work a VIM at a pressure of 800 mbar as well as a pressurized ESR with a pressure of 20 bar are used for Ca deoxidation. For the VIM but partially also for the PESR with its high pressure there is still a certain evaporation of calcium as the high atmospheric pressure only obstruct the evaporation of calcium kinetically and not at all in a thermochemical way. Therefore equations (1) and (2) can be partially rewritten as:

$$[TiO]_{TiAl} + \{Ca\} \quad\leftrightarrow <CaO> + Ti \qquad (3)$$

$$[O]_{TiAl} + \{Ca\} \quad\leftrightarrow <CaO> \qquad (4)$$

Despite its high vapor pressure and the associated losses calcium is used as reducing agent for several reasons:

1. Calcium has a very high affinity towards oxygen which is much higher than that of Titanium and Aluminum (Figure 2)
2. Calcium and oxygen form CaO which floats on top of the liquid TiAl melt
3. Calcium is cheap and easy to obtain which is an advantage compared to other suitable reducing agents (e.g. yttrium)

Calcium removal by VAR

After deoxidation certain traces of calcium in the alloy are unavoidable. The method of choice in removing these is the vacuum arc remelting furnace. As can be seen in Figure 4 even at low calcium concentrations the partial pressure of Ca is much higher than the atmospheric pressure inside a VAR (~10^{-2} mbar). Therefore the remaining Ca traces should easily be removable by VAR.
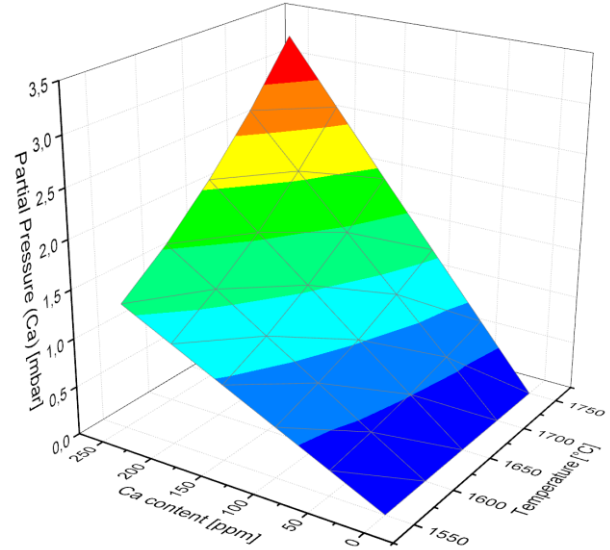

Figure 4: Vapor pressure of Ca according to VAR pool temperature and Ca content in γ-TiAl (FactSage, data: FTlite (activity Ca) & SGPS (partial pressure Ca))

Experimental procedure

Vacuum induction melting – small scale (crucible tests)

Prior to the series of experiments testing a triple melt route as a recycling route for γ-TiAl several small scale trials in a vacuum induction furnace have been carried out to test the durability of the crucibles made of Y_2O_3 coated Al_2O_3.

Figure 5: Small scale VIM furnace for crucible tests

The crucibles are filled with 1 kg of TiAl scrap (Figure 5) and after evacuation to a pressure of 1.9 x 10^{-2} mbar the furnace is filled with

a process pressure of 780 mbar argon. After a slow preheating up to 200 °C to avoid a cracking of the crucible the furnace is put to its full power of 15 kW to 20 kW depending on the electromagnetic coupling of the material. After meltdown of the material it is held for three minutes at reduced power before it is cast into an Y_2O_3 coated cast iron mould.

There are three series of nine to eleven trials to evaluate crucible stability. For each series one crucible is used which means that every single crucible has to withstand up to eleven melts.

For each series a different binder system of the Y_2O_3 was used.

Vacuum induction melting – large scale (Triple Melt)

The first step of the IME recycling process is a consolidation melt in a VIM to create round ingots that can be used as electrodes for remelting in PESR.

To achieve that approximately 30 kg of the recycling material are put into an Y_2O_3 coated Al_2O_3 crucible and melted under a pressure of 800 mbar (Ar). The final casting temperature is ~1550°C and the liquid metal is cast into a cylindrical water cooled copper mould (Figure 6).
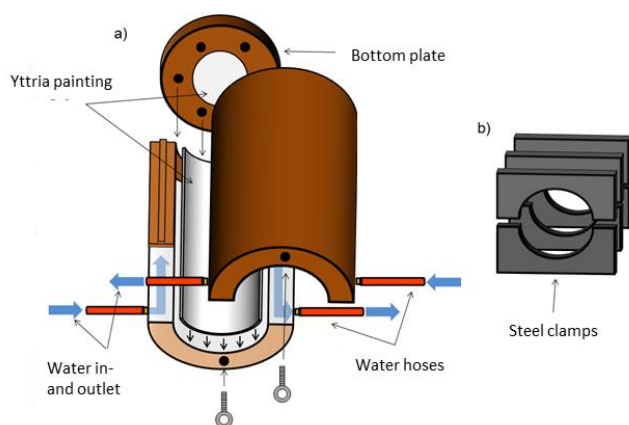

Figure 6: Cylindrical water cooled copper mould for electrode casting in VIM

After complete meltdown of the charged material the liquid TiAl is either directly cast into the mould (Figure 7 c) or deoxidation treatment is done.

As described above the vapor pressure of pure calcium at process temperatures of around 1550 °C is at nearly 1000 mbar. Therefore pure metallic calcium cannot be used as reducing agent in a VIM under a pressure of 800 mbar as most of it would evaporate immediately.

Figure 7: a) Input material in VIM prior to melting; b) AlCa master alloy prepared for dipping; c) Mould with cast electrode inside

As an alternative an aluminum coated calcium wire as well as a calcium - aluminum master alloy (Figure 7 b) are used for deoxidation in VIM. The aluminum coated calcium is used to prevent a direct reaction surface between calcium and the melt when the reducing agent enters the melt so that the calcium does not evaporate directly on the surface of the melt. Unfortunately the wire turns out not to prevent the Ca evaporation sufficiently. The approach of the CaAl master alloy is a different one: Here the already lowered activity of the Ca in the master alloy is successfully used to prevent an immediate evaporation of the Ca before a reaction between calcium and oxygen can take place.

Electroslag remelting

As can be seen on Figure 8 two of the VIM cast ingots are welded together to produce an electrode that can be used in the PESR furnace.
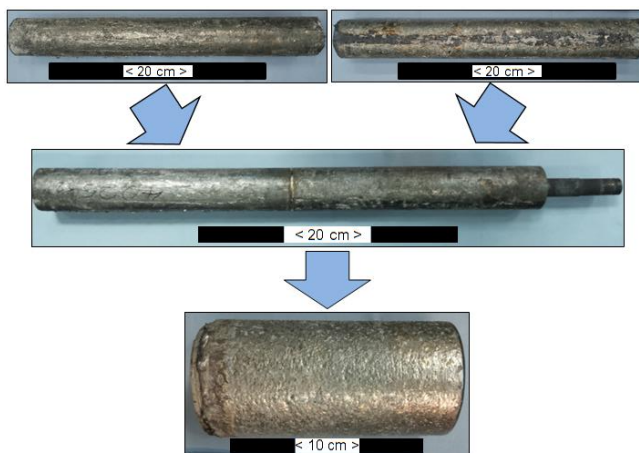

Figure 8: Two VIM ingots (top); VIM ingots welded together to one ESR electrode (middle); ESR ingot (bottom)

The electrode is attached to the electrode rod of the PESR furnace via a stub as can be seen on Figure 9 b. The slag which is specified later on is charged in a solid form (Figure 9 c) around a starting tower made out of sputter targets (Figure 9 a). This starting tower is needed to melt the slag as it cannot be started with a molten slag in the closed chamber of the PESR furnace. The meltdown of the slag hereby works by resistance heating of the starting tower. When the slag is molten the electrode is pulled back a little so that the

starting tower can be melted by electric arcing between the tower and the electrode. After that the electrode is lowered into the liquid slag and a "normal" swing controlled melt phase starts.
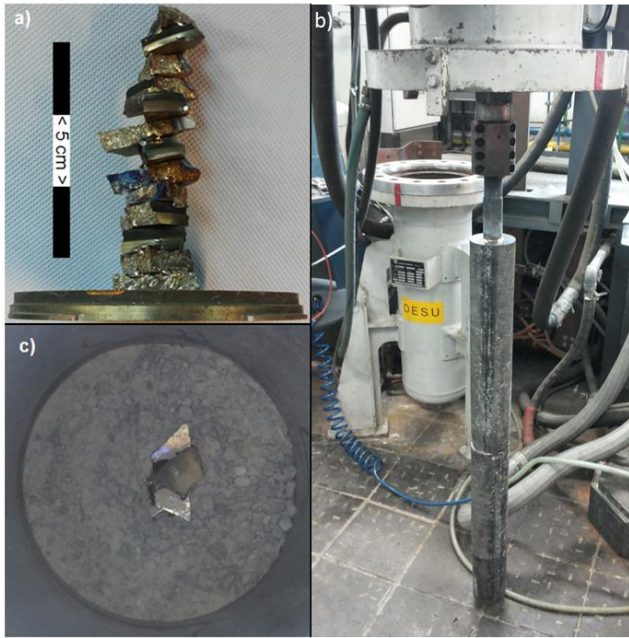

Figure 9: a) Starting tower made out of Ti - sputter targets; b) Starting tower inside the reactive slag; c) TiAl electrode prior to installation in the PESR furnace

Electroslag remelting uses the principle of a small metal droplet sinking through a slag. In case of the IME triple melt recycling route for TiAl a reactive slag with a certain amount of Ca as reducing agent is used.

Besides the large reaction surface another advantage of PESR remelting for TiAl recycling is the high process pressure of 20 bar. As is explained above by applying 20 bar of argon pressure above the liquid slag the evaporation of Ca can be kinetically suppressed and therefore pure metallic Ca can be used as reducing agent. [4] However this does not affect the vapor pressure of Ca and a small amount of Ca can still be found at the water-cooled walls of the furnace after the melt.

Regular ESR slags that usually contain a lot of oxides would lead to a further oxidation of TiAl. Therefore the slag that is used consists of CaF2 with an addition of metallic Ca as reducing agent. The main principle of deoxidation by Ca (Figure 10) is the reaction of oxygen with calcium to CaO which then remains in the slag.
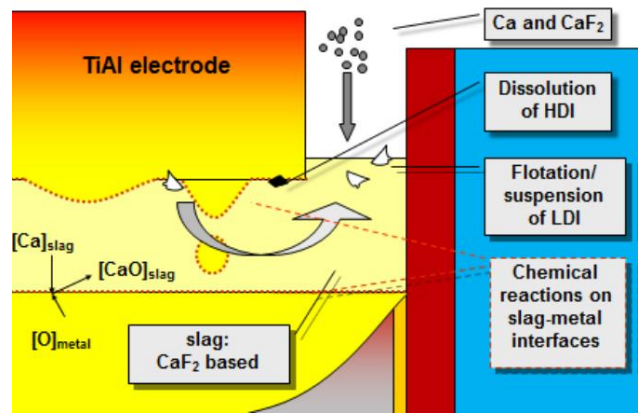

Figure 10: Principle of Ca – deoxidation in ESR

Throughout the remelting process more and more Ca is reacting to CaO. The oxygen dissolved in the metal can be assumed as constant over the process as only a very limited amount of TiAl is in reaction zone. Therefore the law of mass-action can be expressed as:

$$K = \frac{a(CaO)}{a(Ca)} \tag{5}$$

It is obvious that K has to be constant to achieve a constant reduction rate throughout the reduction process. To achieve this Ca as well as CaF2 have to be added to the process continuously. Ca has to be added to restore the reacted Ca and keep the Ca level in the slag constant and CaF2 to lower the activity of the CaO as the formed CaO cannot be removed.

Besides CaF2 and Ca a small amount of MgF2 is added to the slag as studies carried out by Reitz [3] have shown that by adding a small amount of MgF2 the size and amount of NMIs in the PESR ingot can significantly be lowered.

Vacuum arc remelting

After PESR remelting there are traces of calcium in the ingot. This has two reasons: The first reason is that it is not possible to control the Ca activity in the PESR slag perfectly so that it has to be worked with excess Ca. Secondly as there is an equilibrium between Ca solubility in the molten TiAl and the reactivity of the Ca with oxygen there is no way of preventing a small amount of Ca to be dissolved in the TiAl.

Due to its high vapor pressure Ca can be removed by a vacuum distillation as is stated above. The perfect furnace for such a distillation is the vacuum arc remelting furnace (VAR) as in this furnace very low process pressures (~10^{-2} mbar) are combined with a large metal gas interface.

The PESR ingot is therefore mounted to the electrode rod of the VAR (Figure 11 c) after its surface is mechanically turned to prevent an unnecessary contamination with adhering process slag from the PESR.

After the furnace chamber is evacuated to a pressure of nearly 10^{-5} mbar and flooded with argon twice to remove the remaining oxygen content, the process is started. During the process the pressure in the chamber rises to an average of 1.5 x10^{-1} mbar with peak values of 6 x 10^{-1} mbar.
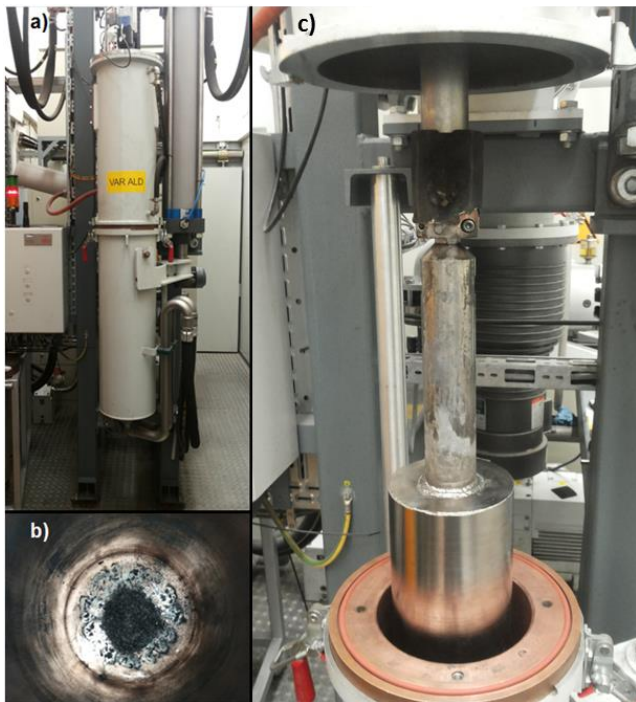
Figure 11: a) VAR furnace; b) TiAl shavings on the bottom of the crucible; c) VAR electrode mounted to the electrode rod prior to melting

After the melt calcium and lime can be found on the crucible walls. This can originate from CaO that has been formed during PESR but did not remain in the process slag and can now be found as nonmetallic inclusions in the metal. At the same time CaO and Ca on the VAR crucible walls can come from Ca that was distilled out of the metal during VAR. After flooding the VAR with air some of this Ca reacts to lime whereas some of it remains as metallic calcium.

An example for a final ingot can be seen on Figure 12 and has a final weight of between 25 kg and 35 kg, a height of ~250 mm and a diameter of 200 mm.

Figure 12: Example of a final ingot after triple melt

Results and Discussion

Vacuum induction melting – small scale (crucible tests)

The evaluation of the crucible durability during the small scale trials is based on three principles:

1. A visual inspection of the crucibles after each melt
2. A deeper inspection of the crucibles after each series of experiments
3. A chemical analysis of the TiAl ingot

The visual inspection of the crucibles has shown that directly after the first trial a blackish layer has formed on the crucible wall wherever it was in contact with the molten TiAl.
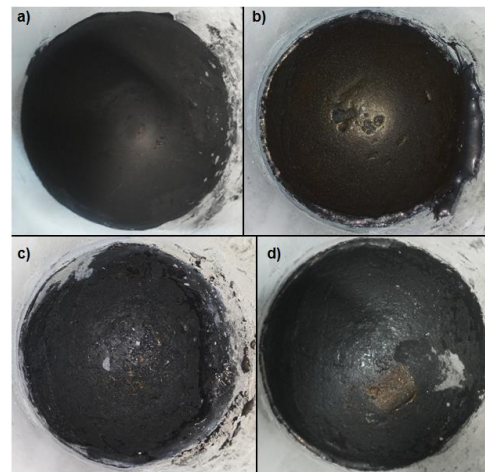

Figure 13: Crucible III a) after one melt; b) after seven melts; c) after eight melts; d) after nine melts

As can be seen on Figure 13 over the set of trials there are small damages to the crucible but the blackish layer stays intact and no major damage to the crucible can be detected.

Also the comparison of the three used crucibles that can be seen on Figure 14 shows no significant difference between the different crucibles.
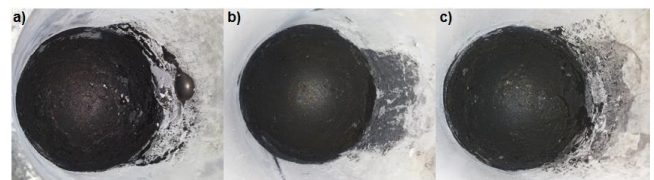

Figure 14: a) crucible I; b) crucible II; c) crucible III after usage

After their usage the crucibles have been analyzed with a CT to get an optical impression of the thickness of the surface layer as well as with a SEM/EDX to see what the layer consists of.

The CT images that can be seen on Figure 15 show that there is still a small layer (white) on top of the Al_2O_3 base material of the crucible.

Figure 15: CT images of crucible I (left) and crucible II (right) after their usage

To see what this layer that was originally Y_2O_3 consists of now a set of SEM/EDX analysis have been performed. One of them is shown on
Figure 16. It can clearly be seen that the darker areas of the image consist of oxidized alloy as there are mainly Al, Ti and O present. The presence of Nb and Cr can be explained with small metallic droplets within the new formed oxide layer. The lighter parts of the image seem to consist of mainly Y_2O_3 with a little bit of Al or more probably Al_2O_3 in it.
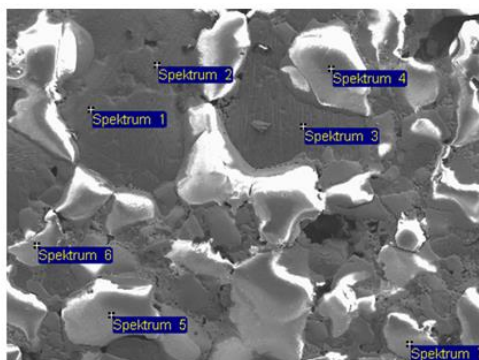
	O	Al	Ti	Cr	Y	Nb
Spektrum 1	33,8	20,9	41,9	0,7	0,8	1,9
Spektrum 2	26,1	21,4	47,7	1,2		3,6
Spektrum 3	24,8	22,1	48,1	1,1		4,0
Spektrum 4	44,9	1,9			53,2	
Spektrum 5	44,8	2,7			52,6	
Spektrum 6	32,0	1,8			66,2	
Spektrum 7	27,6	2,4			70,0	

Figure 16: SEM image with EDX values of the surface layer of crucible II

The analysis of the metal ingot is not only useful for the evaluation of the Y, Al and O pickup from the crucible but shows also the quality of the alloy after the first step of the triple melt route.
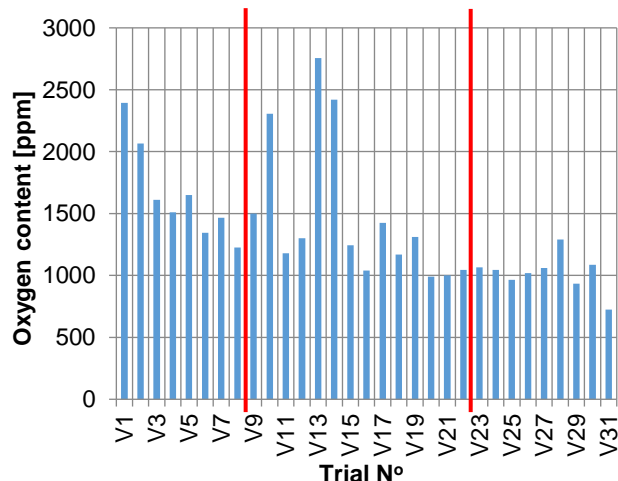

Figure 17: Final average oxygen content of each small scale trial

The final average oxygen contents of the ingots of each trial can be seen on Figure 17. With an average oxygen contamination of the scrap of 1168 ppm it shows that for most trials there has been an oxygen pickup during the melt.
As the values of the input scrap analysis vary between 980 ppm and 1700 ppm the resulting oxygen pickup is not very reliable as it is not possible to tell the oxygen contamination prior and after each melt. It can only be assumed that there has been a slight oxygen

pickup during the melt which has been confirmed by the results of the later trials in a larger scale.

Vacuum induction melting – large scale (Triple Melt)

For the large scale trials as the first step of the triple melt route only the metal quality was of interest as the durability of the crucibles has been confirmed to be good enough for several melts in the small scale trials.
As the VIM ingots are being used as PESR electrodes a sampling can only be done at the head and bottom of the ingot as any other sampling would destroy the ingot/electrode for any further use.
The exact positions where the samples have been taken from are shown in
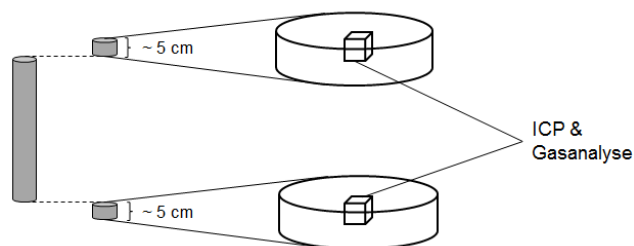Figure 18.

Figure 18: Sampling of the VIM and PESR ingot

The analytical focus is set on the oxygen content to see if there is any oxygen pickup during VIM melting. Nonetheless an ICP analysis of the alloying elements and the most probable impurities (e.g. yttrium) is done.
The oxygen content pictured in Figure 19 shows that most probably there was an oxygen pickup during the VIM melts. The horizontal black line shows the average initial oxygen content of the scrap even though it is not too reliable as stated above.
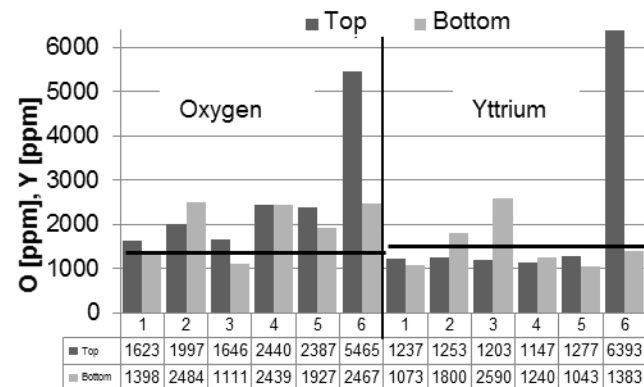

		Oxygen					Yttrium					
	1	2	3	4	5	6	1	2	3	4	5	6
Top	1623	1997	1646	2440	2387	5465	1237	1253	1203	1147	1277	6393
Bottom	1398	2484	1111	2439	1927	2467	1073	1800	2590	1240	1043	1383

Figure 19: Oxygen and yttrium content of the VIM ingots

The striking oxygen content of trial six at the top of the ingot can be explained by the corresponding yttrium content. The yttrium content also is extraordinary high. Most probably the analysis was affected by an yttria particle.
In this set of experiments deoxidation has been performed during trial five. As can be seen on Figure 19 the oxygen content of that trial is in the usual range. Therefore for all the other trials deoxidation treatment has only been done during PESR.

Electroslag remelting

Pressurized electroslag remelting (PESR) is used to lower the oxygen content of the TiAl. Hereby a differentiation between dissolved oxygen, γ-TiAl has an oxygen solubility of ~2 at.-% [5], and oxygen in form of oxides, mainly Y_2O_3, has to be done. The dissolved oxygen is taken out of the system with the calcium that is within the reactive slag. The problem with oxygen in the form of Y_2O_3 is that Y_2O_3 has a higher density (5.01 g/cm^3) [6] than TiAl (3.9 g/cm^3) [7][8].Therefore Y_2O_3 does not float in the process slag with a density of 2.457 g/cm^3 [9] but sink through the metal pool to its bottom, where it is enclosed as a nonmetallic inclusion (NMI).

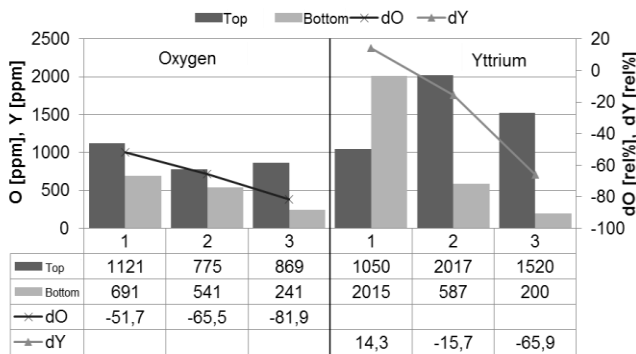|	Oxygen			Yttrium		
	1	2	3	1	2	3
Top	1121	775	869	1050	2017	1520
Bottom	691	541	241	2015	587	200
dO	-51,7	-65,5	-81,9			
dY				14,3	-15,7	-65,9

Figure 20: Oxygen and yttrium content of the PESR ingots

Nonetheless a reduction of the vast amount of oxygen dissolved in the TiAl is possible. The effectiveness of the reduction can be seen on Figure 20 where the final amount of oxygen after each PESR melt as well as the reduction of the oxygen amount in percent compared to the oxygen amount after the VIM melt is shown. It can be seen that an oxygen reduction of up to 82 %, an average of 3062 ppm after VIM vs. an average of 555 ppm after PESR, can be achieved.

Vacuum arc remelting

After VAR the form of the ingot is no longer relevant as this ingot has no further use as an electrode but will only be used as input material for a cold crucible induction furnace to cast turbine blades. This means that after VAR the sampling does not have to be at the very end of the ingot. The sampling positions can be seen on Figure 21.
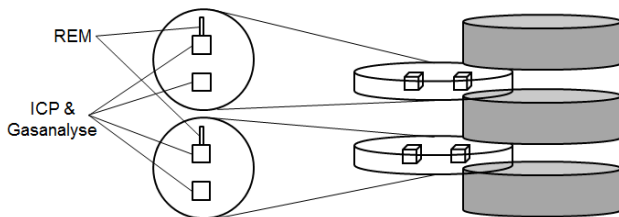

Figure 21: Sampling of the VAR ingot

After VAR additional to ICP- and gas analysis a SEM/EDX is performed. This way it can clearly be differentiated between dissolved oxygen and oxygen in form of oxides.

Here the focus is set on the amount of calcium in the ingot after VAR to see how effective the calcium removal in VAR was. With less than 1 ppm for all samples it is below detection limit for all analysis which shows that the above stated removal of calcium via VAR is very successful.

Conclusions

The research done within this article but also within the last decade shows the following results:

1. It is possible to melt γ-TiAl in a ceramic crucible made out of yttria or yttria coated alumina.
2. Problematic is the pickup of Y_2O_3 as it cannot be removed due to its higher density compared to TiAl.
3. Further research with scraps which are not contaminated with Y_2O_3 is needed to expose the influence of the yttria crucible on the final Y_2O_3 content in TiAl.
4. A significant oxygen reduction of 82 % by reducing the material with calcium is possible.
5. Calcium is the reducing agent of choice as excess traces of Ca can be removed by VAR.
6. With the absence of Y_2O_3 it is possible to reach final oxygen levels of far below 600 ppm which makes it possible to recycle γ-TiAl without decreasing its properties.

Acknowledgement

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