A Closed Loop Recycling Technology for γ-TiAl from Precision Cast Low Pressure Turbine Blades

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Titanium based alloys gain a more and more important role in the manufacturing of aerospace turbine blades. As can be seen on figure 1, 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.

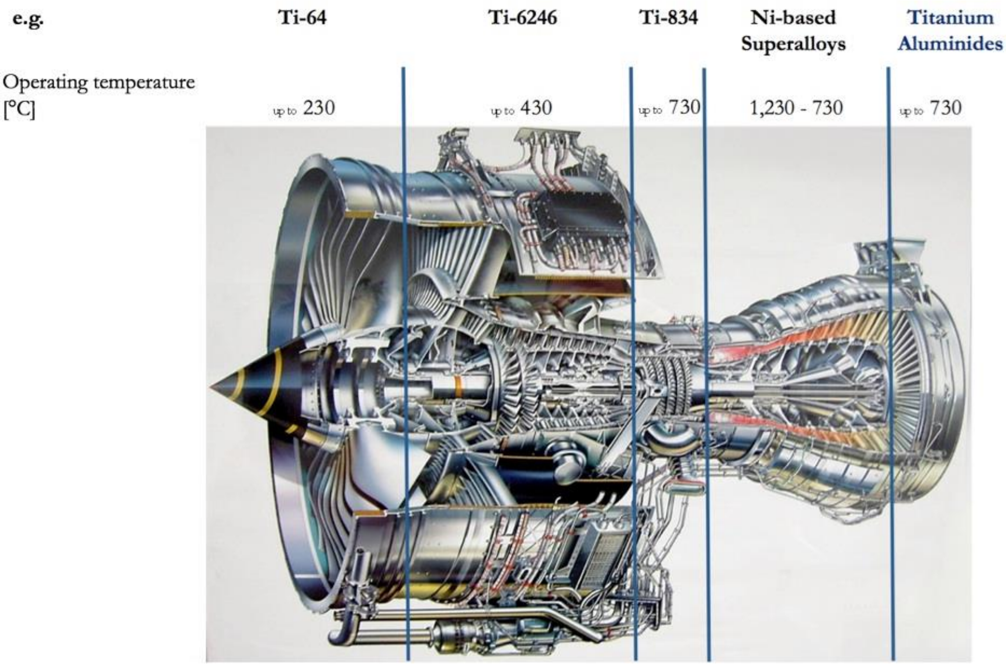

Figure 1: Material used for the different stages in a modern aircraft turbine [IATA 2009]

Due to the high cost of primary Titanium production an efficient recycling loop for Ti-based alloys is crucial for decreasing the price of the whole turbine.

This paper focuses on the recycling potential of the titanium aluminides used for the low pressure turbine blades right in the end of the turbine.

Introduction and thermodynamics

For more than 10 years investigations on the recycling of TiAl-alloys have been carried out at the IME, RWTH Aachen University. Investigations on each single recycling step have been carried out by Lochbichler [Lochbichler 2011], Stoephasius [Stoephasius 2006] and Reitz [Reitz 2013]. The main task during all of the steps is the minimization of Oxygen in the alloy.

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 2.

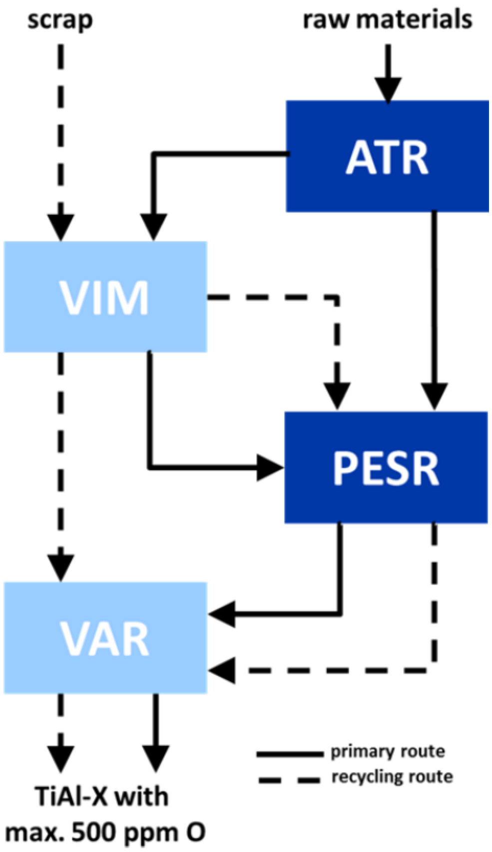

Figure 2: Flow chart of the TiAl recycling route developed at the IME compared to the primary TiAl production

To reduce the amount of oxygen, that is unavoidable when using recycling material, Calcium is used as a reducing agent. This is either added during the consolidation in VIM or as a slag component 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.

Calculations done by Lochbichler [Lochbichler 2011] 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 (Data: FactSage, ELEM)

Alloy	T_{liq}	a_{Ti}
cp Ti	1668 °C	~1
TiAl6V4 (wt.-%)	1686 °C	0.87
FeTi70 (wt.-%)	1109 °C	0.56
TiAl50 (at.-%)	1517 °C	0.24
FeTi30 (wt.-%)	1433 °C	0.07

Consolidation and deoxidation by VIM

The first step for all recycling processes is a consolidation melt in a VIM to create round ingots that can be used in a remelting step which can be PESR or VAR (Figure 3).

Figure 3: Electrode for ESR/VAR obtained by VIM

To achieve that approximately 30 kg of the recycling material are put into an Y_2O_3 coated Al_2O_3 crucible (Figure 4) and molten down 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 3).

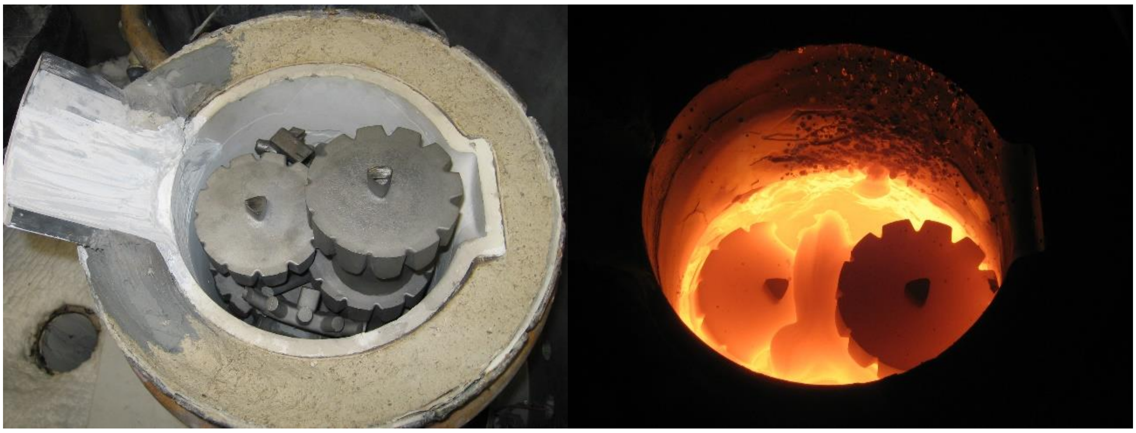

Figure 4: Vacuum Induction Melting of TiAl scrap

After everything is molten down the liquid TiAl is either directly cast into the mould or deoxidation treatment is done. For several reasons calcium is used as deoxidizer

1. Calcium has a very high affinity towards oxygen which is much higher than that of Titanium and Aluminum

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)

Unfortunately the vapor pressure of pure calcium at process temperatures of around 1550 °C is at nearly 1000 mbar (Figure 5). Therefore metallic calcium cannot be used as reducing agent in a VIM under a pressure of 800 mbar. As alternative Ca alloys as well as Al wire with a Ca core are used. Once the Ca is successfully brought into the TiAl melt the following reduction reactions are achieved:

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

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

<> solid, [] dissolved, {} gaseous

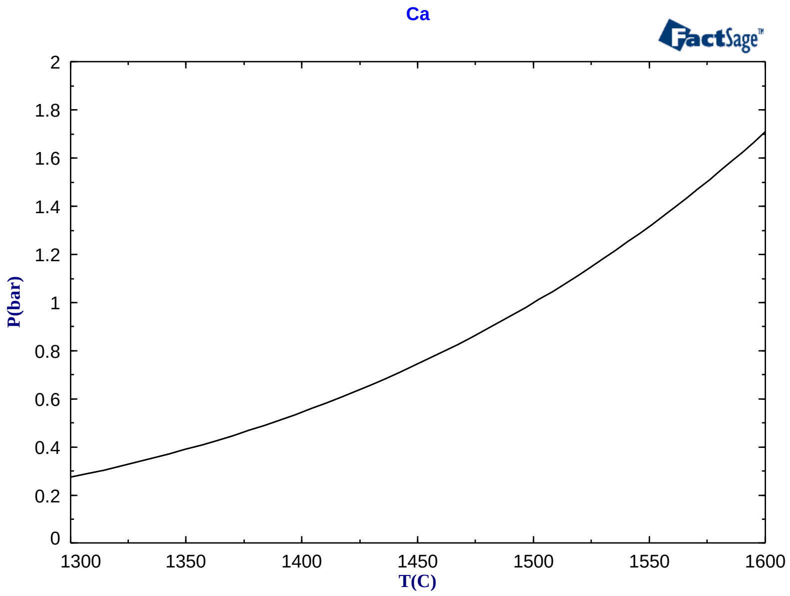

Figure 5: Vapor pressure of Ca over processing temperature

The reduction with the Al-Ca wire is not successful due to the fact that inside of the Al wire there is still metallic Ca which starts evaporating as soon as there is contact with the melt. In contrast the reduction with CaAl alloys, especially with $CaAl_2$, leads to a deoxidation down to a remaining oxygen content of less than 700 ppm. The final deoxidation of the TiAl is done using a pressurized Electroslag Remelting (PESR) furnace.

Deoxidation by Electroslag Remelting

Electroslag remelting uses the principle of a small metal droplet sinking through a reactive slag. By that a very large surface of the metal comes into contact with the slag.

Besides the large reaction surface for the TiAl recycling another advantage of PESR remelting is the high process pressure of 20 bar. 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. [Stoephasius 2007] 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.

Slags made out of oxides would lead to a further oxidation of TiAl. Therefore the slag that is used consists of CaF_2 with an addition of metallic Ca.

The main principle of deoxidation by Ca (Figure 6) is the reaction of oxygen with calcium to CaO which then remains in the slag.

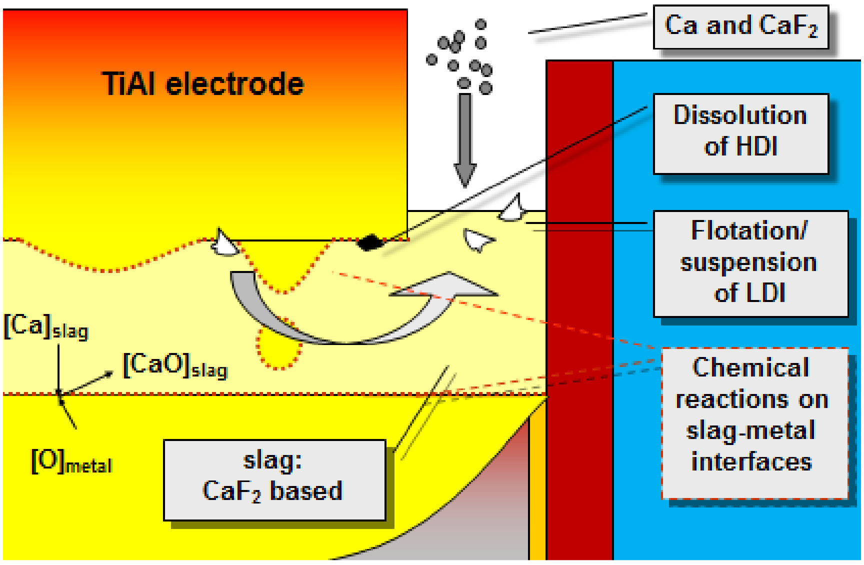

Figure 6: The principle of PESR deoxidation of TiAl with Ca

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:

$$f = \frac{a(CaO_{slag})}{a(Ca_{slag})} \stackrel{\text{def}}{=} const \tag{3}$$

With a starting mixture of 93 wt.-% CaF_2, 2 wt.-% CaO and 5 wt.-% Ca and a final CaO amount of approximately 4 wt.-% the calculated CaO activity rises during the process from $1.3x10^{-2}$ to $2.5x10^{-2}$. While this activity is far away from a significant impact on the reaction kinetics, for a practical approach it is sufficient to keep the Ca amount in the slag at a constant level. This is done by continuously adding metallic Ca by a charging device inside of the pressurized chamber. To compensate slag losses to the skin-slag of the ingot (Figure 7 left) also a small amount of CaF_2 is added continuously throughout the process.

Figure 7: Obtained TiAl ingot after PESR

After the remelting via PESR the ingot is stripped from the skin- and cap-slag and is either prepared as electrode for a final VAR remelting step or sent to an investment caster to obtain new turbine blades.

Removal of Ca and other impurities by Vacuum Arc Remelting

A certain absorption of Ca is unavoidable when using Ca as reducing agent. Especially the PESR process leads to an increased Ca absorption as the Ca evaporation is inhibited by the high process pressure.

To get rid of the dissolved Ca but also dissolved H or non-metallic inclusions (NMIs) Vacuum Arc Remelting (VAR) is the favorable unit. It combines a low process pressure of down to 10^{-4} mbar with a good NMI separation due to only a very limited amount of the material being liquid at the same time.

With the very low process pressure of the VAR and the relatively high vapor pressure of Ca it is possible to achieve final Ca contents in the melt of below 40 ppm at 0,05 mbar (Figure 8). Also it is possible to use comparably low pool temperatures during VAR and still get a very good Ca removal.

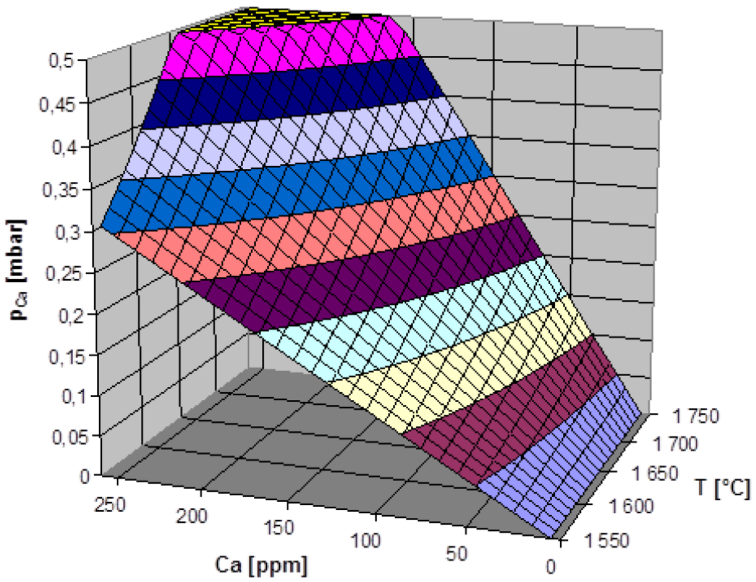

Figure 8: Vapor pressure of Ca according to VAR pool temperature and Ca content in γ-TiAl (FactSage, data ELEM with γCa = 1)

Trials at IME have shown that it is possible to achieve a final Ca content below the detection level by Atom Absorption Spectrometry (AAS). CaO-residues at the crucible walls can be seen in Figure 9.

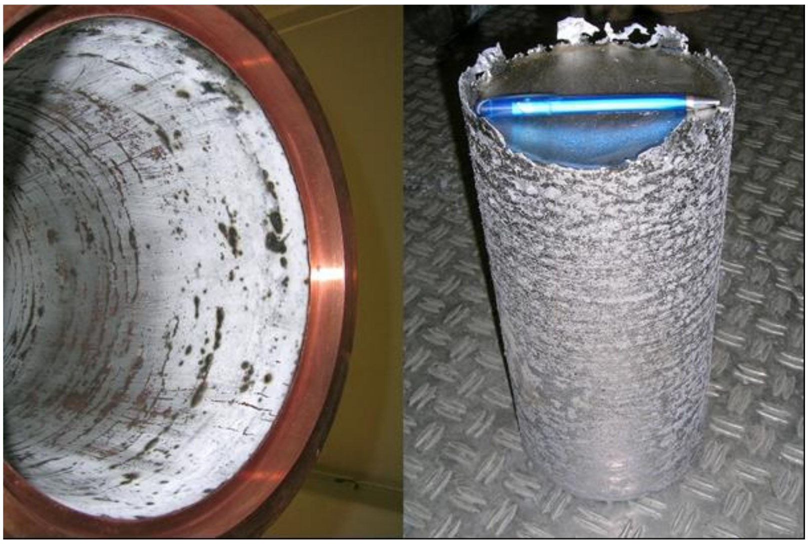

Figure 9: Crucible with residues (left) and VAR ingot (right)

So altogether recycling of TiAl with a Ca deoxidation is technically feasible and leads to an outstanding metal cleanliness.

Summary

1. The recycling of TiAl is possible even when using ceramic crucibles during VIM
2. The thermochemically calculated final oxygen contents of 500-750 ppm are even undercut with experimentally reached values of 100-600 ppm
3. NMI and calcium uptake during VIM is more than compensated by subsequent PESR and VAR double melt

Outlook

1. An upscaling step at an industrial partner needs to be performed to validate the industrial applicability
2. A process step minimized recycling loop without PESR or VAR is part of ongoing studies at IME
3. The portability of the recycling process towards complex, high alloyed TiAl alloys needs to be investigated

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