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\textbf{COST REDUCTION OF TiAl BY ALTERNATIVE PRODUCTION AND INTEGRATION OF TiAl SCRAP RECYCLING – CONCEPTS AND VACUUM-METALLURGICAL EQUIPMENT}

\textbf{ABSTRACT}

Due to high corrosion resistance and low density titanium aluminides show a great potential as material for structural applications in the aerospace and automotive industry. However the high actual production costs for semi-finished products slow down a break through to mass production of TiAl. Current research projects at IME, Aachen funded by AIF “Otto von Guericke” and BMBF aim on cost reduced production methods of TiAl and on the minimisation of downgrading TiAl scrap.

This article presents firstly the state of the art of TiAl production by vacuum arc (re)melting (VAR) or induction skull melting (ISM). A comparison of new process routes under special consideration of recycling issues will follow. Innovative processing and equipment concepts are shown by intelligent combination of well known vacuum melting and remelting processes such as vacuum induction melting, specialized using ceramic lining and deoxidisation with e.g. electro slag re-melting (ESR).

For each process step and accordingly equipment the metallurgical opportunities are pointed out and the way to make use of them within the process route is described. Requirements on input material and final metal quality addicted to the processing route and refining techniques with their adjustment in respect to TiAl are mentioned. Selected results of laboratory and pilot scale experiments done at IME in Aachen and equipment needs therefore are shown.

\textit{Key words: gamma-TiAl, Recycling, VIM, ISM, ESR, VAR}

\textbf{INTRODUCTION}

Raw materials (e.g. titanium sponge, master alloys and aluminium-metal) for the production of gamma-titanium aluminides have to be very clean due to limited refining possibilities within the well-established production routes (see next chapter). The introduction of cost-saving processes with a refining potential for recycled scraps is a big goal for cheaper TiAl alloys. Particularly the oxygen pick-up of the metal is a big challenge which should be controlled by targeted and well-known economic metallurgical operations. Therefore an induction melting process using ceramic linings and electro-slag re-melting using active slag for deoxidisation are processes investigated at IME, Aachen.
So far no recycling process for converting TiAl-scrap into structural metal is established. This has a strong impact on production cost considering the high metal losses during processing into semi-finished TiAl parts e.g. via the cast route. The overall material yield is very low and the scrap is downgraded e.g. for steel production. The main aim for a recycling process is to keep the expensive TiAl in a closed loop at an economic level, achieved by the use of well established industrialised processes.

### STATE-OF-THE-ART OF TiAl PRODUCTION

Currently two routes for TiAl alloy production are applied. The dominant one is similar to the production of conventional titanium alloys and uses the VAR process to melt and re-melt the alloy. The second is based on induction melting using a water-cooled copper crucibles for melting (ISM Induction Skull Melting). Both processes are shortly described in the following.

#### VAR Process

Similar to standard titanium alloy production like Ti-6Al-4V the precursor materials (titanium sponge, aluminium granules, master alloys) are mechanically mixed and pressed to bars. Such bars are welded together under inert gas atmosphere to obtain an electrode for VAR melting. The first VAR melt serves for consolidation of the alloy. To adjust a homogeneous microstructure and acceptable variation of chemical composition in radial and axial block direction at least one further VAR-melt is necessary. [1] The manufacturing of the prime electrode is difficult and complex. It is almost impossible to mix the precursor materials homogeneously. The compacting and welding technique is cost intensive and the risk for contamination (oxygen and nitrogen pick-up) is given.

#### ISM Process

Induction skull melting is a special kind of induction melting. The crucible material is not a refractory material (e.g. alumina Al₂O₃ or magnesia MgO) but copper. Contaminations due to interactions between melt and ceramics are therefore impossible. The copper crucible is strongly water-cooled and complex slitted into segments allowing the electromagnetic field to reach the input material and whose inductive connection. ISM is either used to produce semi-finished products (e.g. slab or block) or final cast products (e.g. valves). Charging materials to produce TiAl are Ti scrap or sponge, aluminium granules as well Nb and Cr as crude metals. [2] The melt composition can be achieved exactly e.g. for aluminium in an accuracy of about 0.5 at.% [3]

Comparing both processes the advantages of ISM are:
- high purity of the melt
- no electrode manufacturing
- excellent chemical homogeneity of the melt due to the inductive stirring effect
- thermal homogeneity of the melt due to stirring and heating by eddy current
The main disadvantages of ISM are:
- poor superheat of the melt
- small batch sizes
- low energy efficiency due to inductive connection of copper hence heat losses through cooling water

**ALTERNATIVE PRODUCTION AND RECYCLING CONCEPTS**

Due to high production costs in the mentioned state-of-the-art processes and high material losses in ingot processing, a recycling process or/and an alternative production process are developed and in test at IME, Aachen. Figure 1 shows the simplified overview of the new integrated concept. The main steps of primary synthesis of TiAl alloys are aluminothermic reduction (ATR) for producing crude TiAl metal followed by electro-slag re-melting (ESR) and vacuum arc re-melting (VAR) as refining steps. The recycling process applies a conventional vacuum induction melting (VIM) step including direct deoxidisation followed by a refining step by VAR.

In order to remove segregation and for residual slag removal from ATR, pre-deoxidisation and homogenisation can be performed by VIM as an intermediate step in the primary production route. Final deoxidisation of ATR-TiAl takes place by ESR, final vacuum refining by VAR.

TiAl scrap is molten and deoxidised by VIM and cast into electrodes for further remelting by ESR (as a final step for the control of specified oxygen contents) and for VAR.

Synergies are found in following important points:
- no dependence on the volatile titanium sponge market

*Figure 1: Integrated IME concept for alternative production and recycling of TiAl*
direct integration and supplementation of recycling and primary TiAl production

Metallic residues of the ATR process, unconsumed electrode parts of the ESR and VAR process and cut ends of VAR blocks can be directly recycled by VIM. Production of gamma-TiAl alloys by conventional VIM using Ti sponge or scrap, aluminium and master alloys as input material is an alternative to ISM. As ceramic linings, suitable for TiAl-contact and pre-deoxidisation are used, the energy efficiency is much higher compared to ISM.

Primary Production

Since 2000 a new alternative process for TiAl production has been developed at IME, Aachen. Crude gamma-TiAl metal is directly produced by aluminothermic reduction (ATR) from pigment (TiO$_2$) and co-reduction of alloying metal oxides (Me$_x$O$_y$) as raw materials. The metallothermic reaction takes place inside a simple reactor. A thin aluminium sheet at the bottom of this reactor is molten immediately after the reaction has finished and the liquid metal enters without air-contact a refractory mould to obtain a prime electrode. [4]

![Figure 2: ATR-cast TiAlX electrode (Ø 110 mm, L 1350 mm, approx. 60 kg) for ESR refining](image)

Advantages of the aluminothermic reduction process (ATR) are:

- no mechanical electrode manufacturing
- increased homogeneity in the prime electrode
- reduced process steps
- reduced investment costs
- less scrap
- no production and crushing of master alloys necessary
- reduced energy consumption

It can be easily seen that there is no compaction and welding process necessary for electrode manufacturing. Also a more homogeneous, because pre-molten electrode compared to mechanical mixing technique is produced. [5] But due to thermochemical facts the metal phase is highly oxygen containing. Therefore a deoxidisation step using Ca metal is necessary, using an active slag in chamber ESR-furnaces. Deoxidisation takes place by the following simplified reaction:

\[
[\text{O}]_{\text{TiAlX}} + [\text{Ca}]_{\text{CaF}_2} = (\text{TiAlX}) + [\text{CaO}]_{\text{CaF}_2} \quad (1)
\]
The deoxidisation product is CaO, which becomes dissolved in the ESR slag. Therefore the Ca content has to be increased during the re-melting process in order to obtain a constant oxygen level of about 500 ppm across the re-melted block length. Re-melting is done under over-pressure to minimise Ca vaporisation. [4] The requirements on the ESR furnace equipment due to process parameters and safety arrangements concerning high titanium containing alloys are: [6]

- vessel works under over-pressure conditions in order to minimise Ca vapour losses during re-melting
- charging equipment for feeding Ca metal and CaF$_2$ during re-melting
- fully automated control unit for process monitoring and reproducibility
- installation of protection walls and remote control in case of industrial scale equipment (also valid for VAR equipment)

A third step is final re-melting by VAR to remove dissolved metallic Ca and smallest non metallic inclusions from metal as well as to adjust directional solidification inside the re-melted block.

**Recycling Process**

The main part of the IME recycling process is the VIM step. General characteristics of VIM processes are:

- excellent chemical homogenisation of melt due to inductive stirring. Hence production of complex alloys is possible
- excellent heat control and heat distribution due to direct heating by induced eddy current
- possibilities of slag removal
- no emissions
- high flexibility regarding input material (shape, dimension, number of input materials)

In spite of the well known aggressiveness of titanium and titanium alloys in molten state ceramics are used for the furnace lining. In case of TiAl alloys the activity of titanium in molten state is much lower than in high titanium containing alloys. As it can be seen from Figure 3 the Ti activity in liquid TiAl(-X) alloys is just about a quarter of that of titanium ($a_{\text{Ti}} = 1$). The activity is calculated at liquidus temperature of considered alloy. The corresponding liquidus temperature is put in parentheses.
Following figure 4 at first scrap is charged into a VIM-furnace and molten under inert gas (argon) atmosphere. The charge make-up consists of sorted scrap parts and as required of master alloys (e.g. NbAl, CrAl).

The main challenges concerning the melting step are:
- oxygen pick-up to maximal 5000 ppm
- melt contamination by dissolved metals originating from reduced ceramic metal oxides or precipitations
- melt contamination by non metallic inclusions caused by undissolved ceramic oxides
- crucible lifetime (economic point of view)

Suitable crucible materials are pure alumina (Al₂O₃) and pure calcia (CaO). Crude ATR-TiAl from primary alternative production (see above) is already oxygen saturated. Herewith the use of alumina crucible is more economic. For scrap melting and direct deoxidisation the more stable CaO crucibles should be used. The problem of susceptibility to hydration of calcia by moisture is eliminated by using vacuum equipment. By using lock systems CaO is always under vacuum conditions or inert gas atmosphere.

After melting and consolidation direct deoxidisation of the melt is applied by dipping a Ca-Al master alloy into the melt. This master alloy quickly dissolves and Ca vapour is generated inside the melt. The Ca vapour with an activity of 1 reacts with dissolved oxygen according to following reaction:

$$\{\text{Ca}\} + [\text{O}]_{\text{TiAl}} = <\text{CaO}>$$

$$\text{gaseous} \ [\text{dissolved}] \ <\text{solid}>$$

(2)

Solid CaO is floated up due to lower density and predominant melt flow and accrues at the crucible wall. The excess aluminium accordingly to the Ca-Al alloy and charged master alloys is adjusted by charging simultaneous pure titanium scrap.

As it is clearly seen in Figure 4, melting, deoxidising and electrode manufacturing is done in one aggregate within the VIM-step. The melt is cast into a cylindrical water-cooled copper mould (figure 5) to minimise segregation effects. Disclaiming direct deoxidisation by VIM one can use the cast electrode for further processing by ESR for deoxidisation.

Special safety arrangements to the VIM furnace are the installation of a security valve in combination to brackets for grouting vessel and furnace lid. Furthermore the temperature control of the ceramic lining is essential due to increased wear through the aggressiveness of high titanium containing melts. [6]
The final re-melting step is done by VAR to remove dissolved calcium (formula 3) and if applicable hydrogen (formula 4) as well as to adjust directional solidification.

\[
[\text{Ca}]_{\text{TiAl}} = \{\text{Ca}\} \quad \text{(3)}
\]
\[
2 [\text{H}]_{\text{TiAl}} = \{\text{H}_2\} \quad \text{(4)}
\]

During this step a removal of smallest non-metallic-inclusions (NMI) can be expected too.

**CONCLUSION AND OUTLOOK**

The development of all processes involved within the new integrated concept presented in this paper started by thermochemical modelling and experimental work in laboratory scale. Positive experimental results have been scale-up to pilot-scale as shown in Figure 2 and Figure 5. Advantages of the new recycling process are:

- all metallic residues of the entire process can be recycled internally
- easy fabrication of a homogeneous prime-electrode
- high flexibility concerning kind and shape of input material
- possibilities for pre-deoxidisation and slag removal

The set milestone of an oxygen pick-up less than 5000 ppm during VIM melting phase is achieved successfully. The possibility for oxygen removal by direct deoxidisation has
been validated in laboratory scale. First successful deoxidisation experiments in pilot scale by ESR and VIM have been conducted. Vacuum arc re-melting of primary ATR-ESR-TiAl and recycled VIM-TiAl is done currently. The final characterisation of produced TiAl and an overall mass and energy balance will follow.

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