Extended Abstract

Due to the high and still increasing price of titanium sponge as a raw material for titanium and titanium alloys, recycling of scrap becomes more important than ever before. Furthermore there are high metal losses within the processing of semi-finished titanium and titanium alloy products. State-of-the-art processes (e.g. vacuum arc (re-)melting and cold hearth electron beam melting) have limited refining possibilities (e.g. deoxidisation). For this reason high quality raw materials (e.g. Ti sponge and master alloys) are required and hence only ultra clean scrap with known origin can be recycled to structural metal again. As high sophisticated vacuum metallurgy utilising water-cooled copper moulds and crucibles are used those processes are quite expensive, too.

The development of cost-saving processes with improved refining potential for converting all kinds of scrap to low cost secondary titanium should be the main challenge to stop the currently conducted downgrading of valuable scrap. Many restrictions are also presently existing as no standards for e.g. structural application in automotive industry exist in case of secondary titanium and titanium alloys. But this could substitute titanium sponge and economise the critical titanium market.

The attempt of the new more economic recycling process developed at IME in Aachen is the intelligent combination of well-known industrialised processes simplified shown in figure 1.

![Figure 1: simplified process steps of the recycling concept at IME](image-url)
The recycling process is based on two main process steps. The first process step comprehends two process phases. Vacuum induction melting (VIM) of scrap (phase 1) is follow by direct deoxidation (Deox) of the melt (phase 2). In spite of the well-known chemical aggressiveness of titanium and titanium alloys in molten state, scrap melting is done in conventional vacuum induction furnaces using refractories. To evaluate the chemical and thermal stability of refractories, thermochemical modelling is done. Target is the calculation of the thermochemical equilibria (i.e. oxygen content of liquid metal phase) as a function of process temperature T and system configuration (i.e. crucible material and melt composition). The procedure consists in searching for the minimum of total Gibbs energy $G_{\text{tot}}$ of the considered system and accordingly to the change in free Gibbs energy of reaction $\Delta G_R = f(\delta, T) = 0$ for the equation R:

$$\alpha <\text{Me}_m\text{O}_n> + (X) = \alpha - \delta <\text{Me}_m\text{O}_n> + (\text{XMe}_m\text{O}_n\delta)$$

$<\text{Me}_m\text{O}_n>$...solid crucible material (e.g. $\text{Al}_2\text{O}_3$)

$(X)$...liquid Ti or Ti/TiAl alloy

$\delta$...extent of reaction, $\delta [0, \alpha], \alpha = 1$

Starting with induction melting tests under protective gas atmosphere in laboratory scale, results of the modelling are verified and the stability of commercial refractories is investigated to identify possible fields of application. This leads to a fundamental understanding of the occurring interactions between melt and ceramics in a qualitative and quantitative way. Because of the unavoidable oxygen pick-up during melting, so called direct deoxidisation by dipping a Ca-Al master alloy directly into the melt is employed. The master alloy is quickly dissolved and Ca vapour reacts with dissolved oxygen according to following reaction:

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

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

Solid CaO is floated up and accrues at the crucible wall, excess calcium is partly dissolved in the melt to keep the equilibrium constitution. The melt is finally cast into a water-cooled copper mould to obtain a electrode. The second main process step is vacuum arc re-melting of the VIM-cast electrode to remove dissolved calcium and hydrogen and to adjust directional solidification inside the re-melted VAR block.

For each process step and accordingly equipment the metallurgical possibilities are pointed out and the way to make use of them within the process route is described. Positive results are validated in pilot scale firstly in case of TiAl. About 30 kg of TiAl scrap are successfully melted down in a crucible made of calcia with an acceptable oxygen pick up less than 3.000 ppm and direct deoxidised during induction melting.

The complete paper belonging to this abstract and speech at EMC 2007 in Düsseldorf, Germany will be published in Erzmetall – World of Metallurgy soon.