



Challenges in Titanium Recycling - Do We Need a New Specification for Secondary Alloys?

B. Rotmann¹, C. Lochbichler², B. Friedrich¹

¹IME Process Metallurgy and Metal Recycling, RWTH Aachen University
Intzestraße 3
D-52056 Aachen, Germany

²Formerly IME, now Voestalpine Giesserei Traisen GmbH
Mariazellerstraße 75
A-3160 Traisen, Austria

Abstract

Despite their outstanding properties, applications for titanium alloys are still mainly limited to fields where either no adequate substitution is available (e.g. process engineering in corrosive media) or their high material costs are subordinated to performance (e.g. military, aerospace, medical care, sporting goods). Although huge efforts have been made to replace the inefficient Kroll Process in order to cut the high production costs for titanium, alternative production routes are not likely to be established within the next decade. On the other hand, the recirculation of Titanium alloys focuses generally on selected and classified scrap, whereas the contaminated and inhomogeneous scrap is mostly downgraded to the ferrotitanium production line.

Consequently, the utilization of the currently downgraded scrap fraction as feed material in a recycling process results in a new cost-competitive secondary titanium alloy. The processing route developed at the IME consists of scrap pre-treatment, vacuum induction melting in a high-purity calcium crucible, deoxidising by CaAl₂-treatment and further refining by vacuum arc remelting.

Due to the wide range of probable contained elements in complex scrap mixtures such as V, Al, Fe, Zr and Cr, strong diluting with titanium sponge or “new” scrap as well as subsequent alloying would be necessary to meet the established alloy specifications. Since this procedure contradicts cost reducing efforts, a new and broader alloy specification is essential in order to open mass-application markets for the resulting secondary titanium alloys.

This paper presents the impacts of scrap compositions, scrap pre-treatment and various refining operations on final alloy compositions in the introduced process route. Based on these results, a potential element band width is anticipated, representing the inevitable first step for the elaboration of a new secondary titanium alloy specification.



1 Motivation

Titanium and titanium alloys exhibit a wide range of interesting properties, representing a first class choice for applications where high strength levels at low density, high corrosion resistance and biocompatibility are required. However, with current titanium sponge prices of 11.38 \$/kg [1], it still only plays a minor role in mass applications due to cost considerations. In contrast to other high-priced metals, these price levels are not justified by a raw material shortage: While the TiO_2 capacity reached 5,660,000 t in 2010 - the main share being designated as pigment for paint, paper and plastics industries - the titanium sponge capacity accounted for only 238,000 t. Similar figures can be found in recent years [1]. Instead, the reason for the elevated price can be found in the production procedure of titanium. Titanium production is subdivided into three main steps: titanium sponge production, remelting and further processing to semi-finished products and final components.

The first step in sponge production is the chlorination of titanium dioxide concentrates. As the minimum TiO_2 concentration is 85 %, the following raw materials are suitable: rutile, synthetic rutile and TiO_2 -rich slag from the Sorel process. The concentrates are heated with chlorine gas and carbon, resulting in the chlorination of all impurities and of titanium to titanium tetrachloride. These remaining impurities can be removed via fractional distillation and precipitation. Chlorination and refining are followed by the next production step, where titanium tetrachloride is reduced by liquid magnesium to a porous sponge [2]

The given thermochemical bonding energies demand high quantities of energy to produce titanium metal from titanium dioxide. Even under these circumstances, the well-established Kroll Process is a comparatively ineffective and expensive solution, requiring 30-40 kWh per kg titanium sponge [3]. Its time-intensive batch operations and the utilization of magnesium as reaction agent make the Kroll Process a true cost driver. As a result, alternative approaches have been investigated [4]. However, none of these approaches has surpassed the laboratory scale yet, lowering expectations for a drastic price drop within the next decade.

Before manufacturing, the titanium sponge has to be remelted. Due to titanium's high affinity towards oxygen, carbon and nitrogen, all processes are carried out under vacuum or inert gas atmosphere. Furthermore, it makes utilization of conventional ceramic crucibles unfeasible, limiting remelting to processes with water-cooled copper crucibles: Vacuum arc remelting (VAR), cold hearth melting (CHM) and induction skull melting (ISM). Remelting allows the removal of volatile impurities from the Kroll Process as well as alloying to the desired composition. In order to minimize segregation and guarantee a homogeneous ingot, multiple remelting steps are often required, hence increasing the total production costs.

In a final step, the titanium ingots are processed to final components. The poor formability of titanium complicates processing via rolling or forging. Instead, near-net-shape procedures like casting are favoured where feasible. Nevertheless, the geometrical complexity of many final components, especially in aerospace applications, demands a high extent of machining, leading to a buy-to-fly



ratio as high as 20. Figure 1 shows the cost distribution for an one-inch titanium plate. It illustrates the impact of the Kroll Process (chlorination and magnesium reduction) and the final manufacturing to semi-finished products on total production costs.

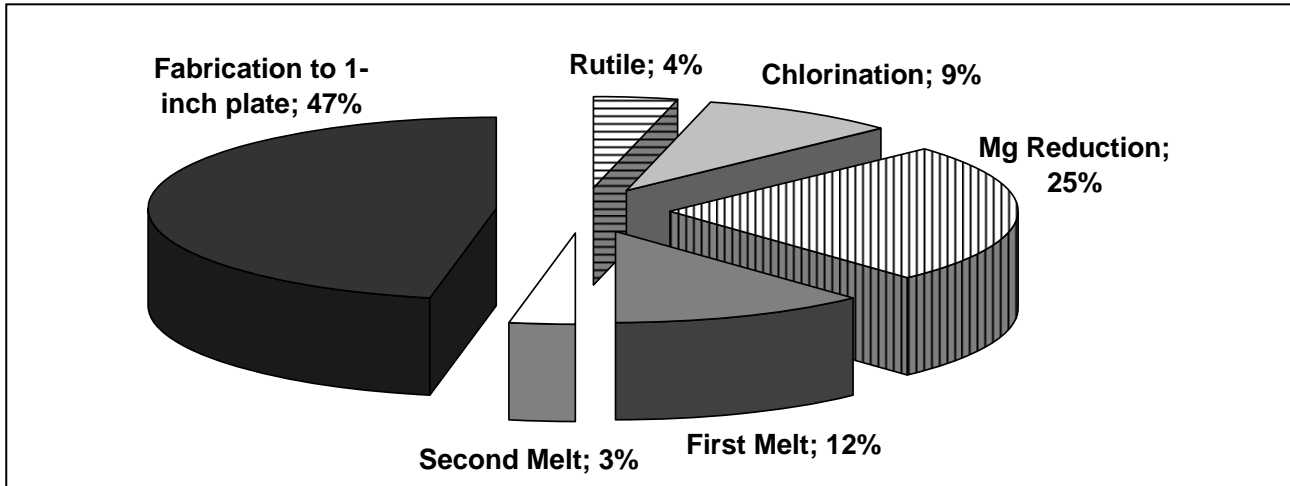


Figure 1: Cost distribution for an one-inch titanium plate [5]

However, substantial cost reduction can be achieved by recycling. Comparable to aluminium recycling, the incentive for titanium recycling lies in the avoidance of a relatively high amount of energy that is needed to transfer the raw material into the metallic state. Therefore, expenses related to the Kroll Process can be avoided. Additionally, intensive machining leads to a substantial production of in-house revert, also referred to as *new scrap*, providing the market with sufficient scrap capacities. In 2006, titanium ingot production accounted for a total of 145,000 t, from which 35,000 t of scrap were recycled as feedstock material [6]. Clean and sorted scrap is usually introduced into the remelting step of the primary route. While loose scrap can be used for CHM without further preparation, VAR demands to mix the scrap with titanium sponge and to compress it to electrodes.

The advantage of cheaper feedstock material is at the expense of additional refining efforts: Scrap can show high levels of various contaminations. This includes carbon pickup from lubricants and oxygen from thick oxide layers, augmented by the high surface-to-volume ratios of turnings and chips. Furthermore, scrap can be polluted by hard metals from cutting tools and various elements from differing alloys. Whereas carbon contamination can be limited by intense cleaning of the scrap, hard metals can only be dissolved or retained by a barrier in CHM. Elements of alien alloys can only be removed if they possess a considerably higher vapour pressure than all other alloying elements. Apart from that, conventional recycling routes exhibit a very limited refining potential with regard to oxygen contamination, narrowing the potential feedstock share of scrap in accordance with the desired maximum oxygen concentration. Another drawback is the small volume of the metal that is molten at one time during all titanium remelting processes except for the cost-intensive ISM. This requires either mono-fraction feedstock or multiple remelting steps in order to achieve homogenous material. Therefore, only clean, classified in-house scrap can be used for conventional recycling, leaving aside the dirty mixed scrap. A market analysis in 2006 revealed that



more than half of the available scrap is downgraded to master alloys like ferrotitanium and therefore permanently lost for the titanium cycle (Figure 2). It can be assumed that this share mainly consists of non-classified, highly contaminated turnings and scrap from used parts. While utilization of this cheaper scrap share as 100 % feedstock results in a substantial cost reduction, the conventional recycling process is not suitable for this due to restrictions regarding refining and homogenization. However, ferrotitanium can also be produced by aluminothermic reduction of iron and titanium oxides, resulting in a ferrotitanium alloy with up to 30 % titanium content. Thus, competition on low-class scrap with steel and superalloys industries, enhancing higher scrap prices, could be avoided.

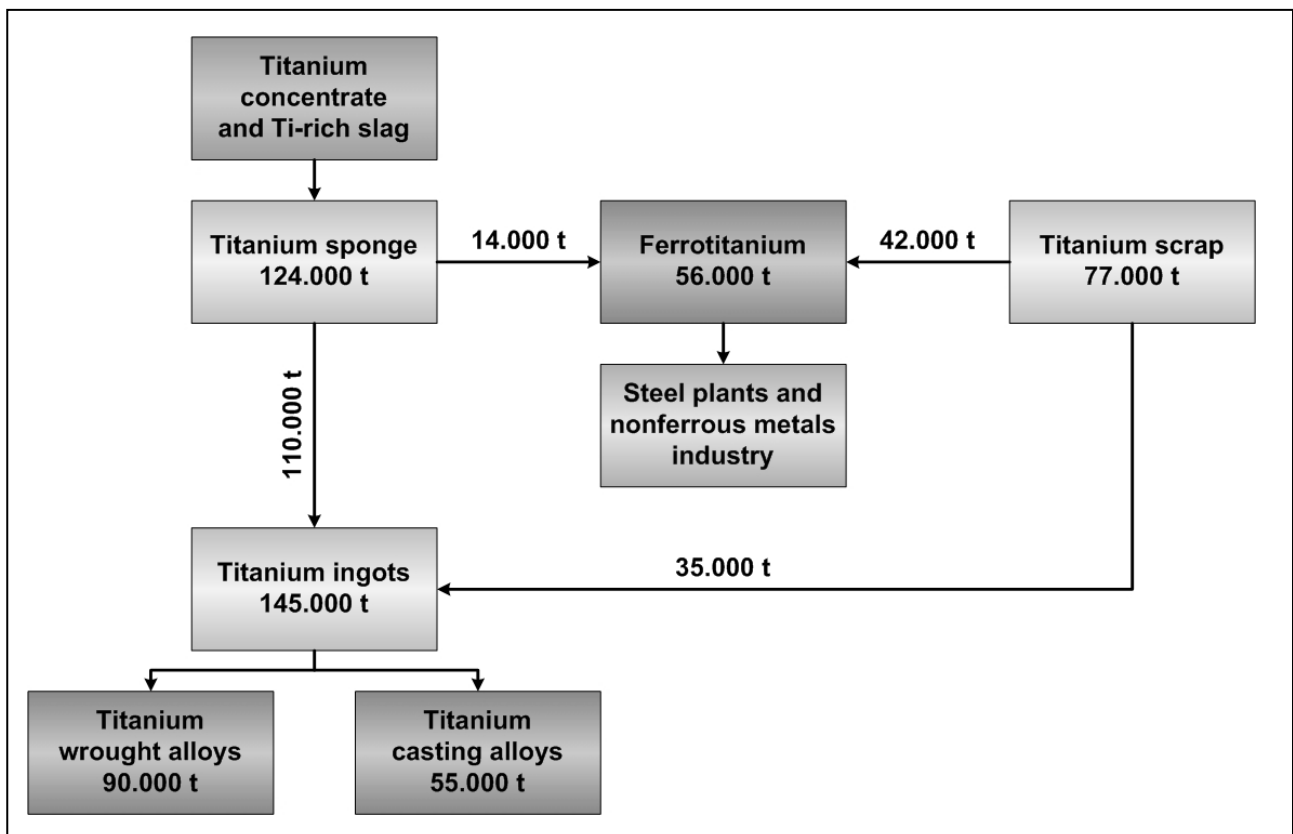


Figure 2: Flow chart of titanium production [6]

The IME recycling process is designed to handle 100 % low-grade scrap feedstock in order to allow considerable cost benefits. Hence, the proposed process could support the market entry for titanium in mass applications.

2 The IME Recycling Process

As shown in Figure 3, the IME recycling process route consists of three main steps: Conditioning, vacuum induction melting and vacuum arc remelting. Although the process route is designed to handle scrap from various sources, in order to estimate the overall refining potential the process scheme is exemplarily illustrated with low-grade turnings, being the worst case scenario regarding



contamination and processing behaviour. Other scrap qualities can easily be introduced into the process at a later point in time, e.g. clean scrap turnings after washing or bulk scrap after briquetting.

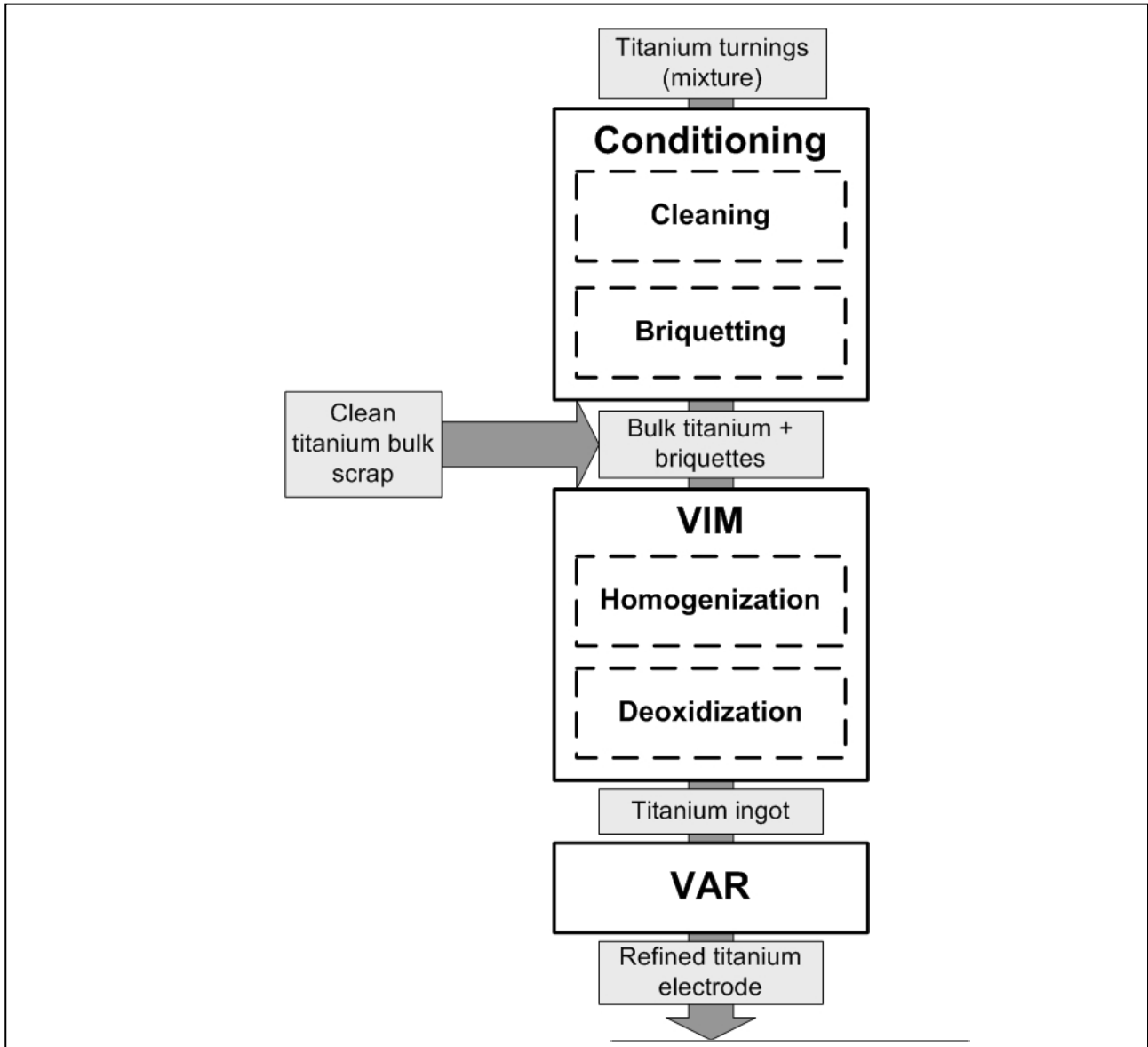


Figure 3: Flow chart of the IME recycling process

2.1 Conditioning

The main goals of conditioning are reducing impurities that come along with the scrap and compacting of loose scrap in order to ensure a sufficient energy input during vacuum induction melting. In the present investigation, different batches of scrap turnings were acquired from a revert supplier: Turnings with bulky and corkscrew-like shape and clustered fine turnings.



The alloys were chosen under the following considerations: On one hand, the alloy should be representative with regard to total market share. Having a market share of more than 50 % [7], this applies best to the Ti-6Al-4V alloy. On the other hand, the alloy mix should cover a high number of potential elements in titanium alloys. Ti-6Al-2Mo-4Zr-2Sn-Si is an alloy that not only ideally completes the range of alloying elements but also fits the demand of widespread utilization. Furthermore, the differing shape of swarf permits to evaluate its impact on the contamination with lubricants and the briquetting parameters. Chemical analysis of both batches show the following results:

Table 1: Chemical analysis of titanium turnings

	V wt.-%	Fe wt.-%	Mo wt.-%	Nb ppm	Sn wt.-%	Si ppm	Zr wt.-%	Al wt.-%	C wt.-%	O wt.-%	Ti wt.-%
Ti-6-4	0,09	0,11	1,81	982	1,92	104	3,84	5,72	0,20	0,20	bal.
Ti-6-2-4-2	3,80	0,24	0,24	294	0,001	73	0,012	5,89	4,16	0,58	bal.

As a first step of the conditioning, drying of the turnings was performed at 120 °C for evaporation of water, which is a major component of commercially used lubricants. In order to remove the remaining oil-based lubricant components, the turnings were washed in ethanol, then again dried at 100 °C. Subsequently, both turning qualities were mixed and then compressed to compacts of approximately 300 g each at a density of 1.5 kg/dm³. Although this accounts for only one third of the theoretical density, it is sufficient for a satisfactory energy input during vacuum induction melting. The necessary applied force for briquetting depends on the fine/bulky turnings ratio, ranging from 150 t for 100 % bulky turnings to 50 t for 100 % fine turnings. A fine-to-bulky ratio of 2:1 was chosen for further processing, taking into account the higher market share of Ti-6Al-4V. As final conditioning step, the briquettes were heated to a temperature of 400 °C. According to a thermogravimetric analysis of the swarf, this assures the removal of remaining organic compounds.

2.2 Vacuum Induction Melting

A vacuum induction furnace consists of a vacuum chamber and a water-cooled copper coil that is lined with appropriate refractories. The conductor is powered by an alternating current and therefore induces an alternating magnetic flux in the batch, in turn inducing an eddy current. This current leads to conductive heating of the metal. Additionally, the so-called Lorentz force from the alternating electro-magnetic field accelerates charged particles perpendicularly to magnetic field and velocity of the particles. Consequently, intensive stirring and homogenization of the melt takes place. The flexibility regarding atmosphere control and the excellent homogenization due to inductive stirring make VIM a valued process in high purity alloy synthesis, where narrow tolerances are required. Despite its advantages, VIM has not been applied to titanium remelting so far. This is reasoned by the lacking stability of conventional refractories towards titanium. The Ellingham diagram (Figure 4) plots the standard free energy for the formation of selected oxides. Thus, first evidence regarding the thermochemical stability of refractories towards titanium can be obtained. As can be



identified, only a few oxide-based ceramics exhibit sufficient thermochemical stability above the melting temperature of titanium, including CaO, ZrO₂ and Y₂O₃.

While only CaO and Y₂O₃ proved to be stable towards Ti-6Al-4V in a lab scale test, CaO was chosen due to the following considerations: Calcium is a far more efficient deoxidizing agent than yttrium, utilization of the corresponding oxide as crucible material for VIM should stabilize the crucible. Moreover, calcium refining is feasible, whereas yttrium concentration can not be diminished during the IME recycling process.

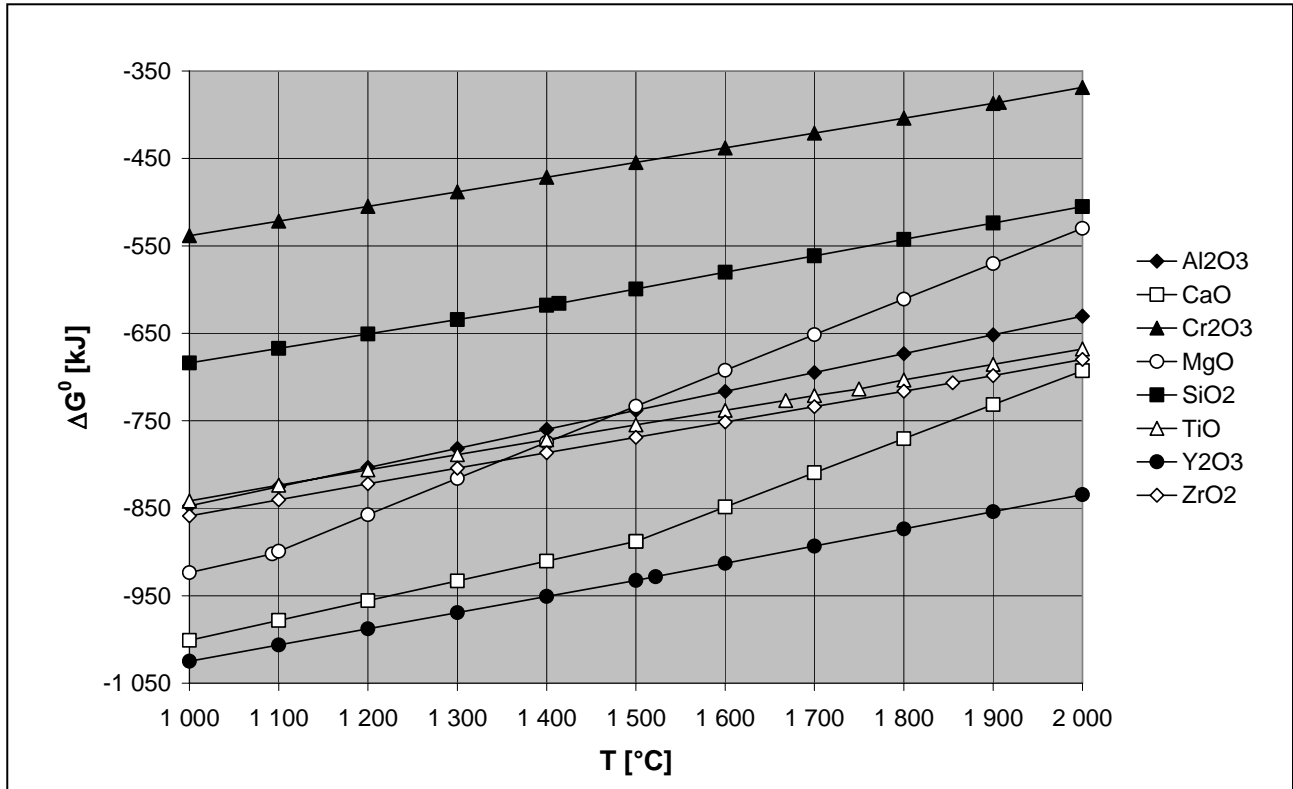


Figure 4: Standard Gibbs energies of formation $\Delta G^0(T)$ of crucible oxides versus titanium (+II) oxide (FactSage, Data: SGPS)

In the IME recycling process, vacuum induction melting in a CaO crucible is carried out in order to melt down the batch and to achieve a homogenous composition. In a second step, CaAl₂ is added for deoxidization of the melt. Unfortunately, melting titanium in ceramic crucibles suffers from the decomposition of the refractory oxides which leads to the decomposition of the crucible and an increase of the oxygen and calcium concentration in the melt.

To counteract the oxygen pickup, a deoxidizing process step is introduced in order to reduce the oxygen concentration to the required levels. As pure calcium has a boiling point of 1484 °C [8], excessive mass loss related to evaporation is diminished by melting under elevated pressure and using the intermetallic CaAl₂ phase instead of pure calcium. The melting point of CaAl₂ is significantly higher than for pure calcium (1079 °C versus 842 °C, [9]) and therefore retards melting down of the deoxidizing agent when dipped into the melt. Consequently, CaAl₂ can be introduced into the



melt instead of floating on the melt, subsequently reacting to calcium in dissolved and gaseous state:



me = titanium alloy

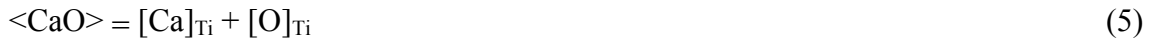


Afterwards, calcium reacts with the dissolved oxygen, forming CaO:



Due to the lower density of CaO compared to the melt and the intense stirring during VIM, the oxide particles are floated to the surface. Following the melt flow, they are transported to the edge, where they can cluster at the refractory walls.

As the oxygen concentration in titanium is directly connected to the calcium concentration via the solubility product, measures have to be taken in order to prevent the melt from new oxygen pickup from the crucible:



The law of mass action returns:

$$K = \frac{a_{[\text{Ca}]_{\text{Ti}}} \cdot a_{[\text{O}]_{\text{Ti}}}}{a_{\langle \text{CaO} \rangle}} \quad (6)$$

K = equilibrium constant ; $a_{[\text{Ca}]_{\text{Ti}}}$ = activity of Ca in Ti; $a_{[\text{O}]_{\text{Ti}}}$ = activity of O in Ti; $a_{\langle \text{CaO} \rangle}$ = activity of solid CaO

Therefore, additional calcium has to be batched in order to thermochemically stabilize the melt. Tsukihashi et al. have experimentally validated this approach, measuring calcium and oxygen concentrations of titanium in a CaO crucible at various temperatures [10]. According to their results, concentrations at 1750 °C can be estimated as:

$$-1,75 \cdot (\text{wt.}\%)^2 = -0,019(c_{\text{O}} + 0,3991 \cdot c_{\text{Ca}}) \quad (7)$$

c_{O} = oxygen concentration in titanium in wt.-%; c_{Ca} = calcium concentration in titanium in wt.-%

Although CaAl_2 is used instead of Ca in order to minimize mass losses, melting under vacuum or atmosphere pressure still induces massive evaporation of calcium. This leads to several challenges: First of all, a stable calcium level in the melt has to be maintained in order to prevent the melt from oxygen pickup. With high calcium losses during melting, the holding time for homogenization has to be reduced to the absolute minimum. Therefore, ensuring homogenous deoxidizing and minimizing deoxidizing agent losses have to be balanced. On the other hand, handling of the melt is severe-



ly hindered since gaseous calcium impairs the visibility, making it difficult to cast. Furthermore, calcium is highly reactive, so that special care has to be taken while cleaning the furnace from calcium powder.

According to [11], the partial pressure of calcium can be described as:

$$\ln p_{Ca} = 25,7691 - 20283,9T^{-1} - 1,0216 \ln T \quad (8)$$

p_{Ca} = partial pressure of pure calcium [Torr], T = temperature [K]

On the other hand, formation of bubbles in the titanium melt is only possible if the partial pressure exceeds the sum of process pressure, metallostatic pressure of the melt and capillary pressure at bubble formation, determined by the following formula:

$$p_{Ca} \geq p_P + \rho \cdot g \cdot h + \frac{2 \cdot \sigma}{r_B} \quad (9)$$

p_{Ca} = partial pressure of pure calcium [Pa]; p_P = process pressure [Pa]; ρ = density of titanium alloy [kg/m^3]; g = gravitational constant [m/s^2], h = distance from bubble to melt surface [m]; σ = surface energy of titanium melt [N/m] r_B = bubble radius [m]

In order to avoid boiling of the melt, the necessary process pressure can hence be calculated for pure calcium:

$$p_P \geq p_{Ca} - \rho \cdot g \cdot h - \frac{2 \cdot \sigma}{r_B} \quad (10)$$

Worst case boundary conditions are given for $h \rightarrow 0$ and $r_B \rightarrow \infty$. Therefore, minimum process pressure at 1700 °C should be:

$$p_P \geq p_{Ca} = 3.05 \text{ bar} \quad (11)$$

Consequently, the application of a process pressure of $p_P > 3.05$ bar during melting should efficiently hinder boiling of the melt and therefore contribute to the reduction of calcium evaporation.

2.3 Vacuum Arc Remelting

A vacuum arc furnace is basically composed of a vacuum chamber and a water-cooled copper mould. In order to melt the electrode, a direct current is applied between electrode and ground plate, causing an electric arc. Heated by the arc, drips start to form at the bottom of the electrode, fall down, accumulate in the mould and form a new ingot. Further descriptions can be found in pertinent literature.

During VAR, elements with high partial pressure can be removed due to the low process pressure. Supplementary, local superheating from the electric arc promotes the evaporation of volatile elements. This process can be characterized by:



$$[TiX]_{me} = (Ti) + \frac{1}{n} \{X_n\} \quad (12)$$

X = O, N, H with n = 1, 2; me = titanium alloy

Thus, the corresponding equilibrium constant is:

$$K = \frac{a(Ti)_{me} \cdot (p\{X_n\})^{1/n}}{a[TiX]_{me}} \quad (13)$$

$a(Ti)_{me}$ = activity of titanium in me; $a[TiX]_{me}$ = activity of TiX in me; $p\{X_n\}$ = partial pressure of X_n

By using thermochemical modelling tools as FactSage, the success of such a process can be predicted: At 1850 °C, partial pressures of $<3,4 \cdot 10^{-21}$ Pa O_2 respectively $<2,2 \cdot 10^{-11}$ Pa N_2 have to be reached in order to undercut 2500 ppm for oxygen and 300 ppm for nitrogen (Data: FS53). VAR is therefore not capable of removing nitrogen and oxygen from titanium. On the other hand, hydrogen concentration in titanium is estimated with the following formula within a temperature range of 1655 °C to 1800 °C

$$\log c = \frac{1}{2} \cdot \log p - 2,0 + \frac{2460}{T} \quad (14)$$

c = hydrogen concentration in Ti [at%], p = hydrogen partial pressure [Torr], T = temperature [K], [12]

According to this equation, a hydrogen partial pressure of 0.01 mbar is sufficient to decrease the hydrogen concentration below 3 ppm at 1850 °C.

According to thermochemical calculations, calcium should be successfully removed during VAR due to the high temperatures and the continuous evacuation of the vacuum chamber. In addition, the removal of calcium is supported by the condensation of evaporated calcium at the water-cooled copper mould, as thereby thermochemical equilibrium between the gaseous calcium and solved calcium in the melt can not be attained and hence partial pressure of calcium in the gas phase is lowered. Anyhow, a re-dilution of calcium into the melt seems possible.

3 Refining Assessment

In order to evaluate the refining potential of the IME recycling process, an input/output analysis is made. Figure 5 identifies all potential sources and sinks for the relevant elements.

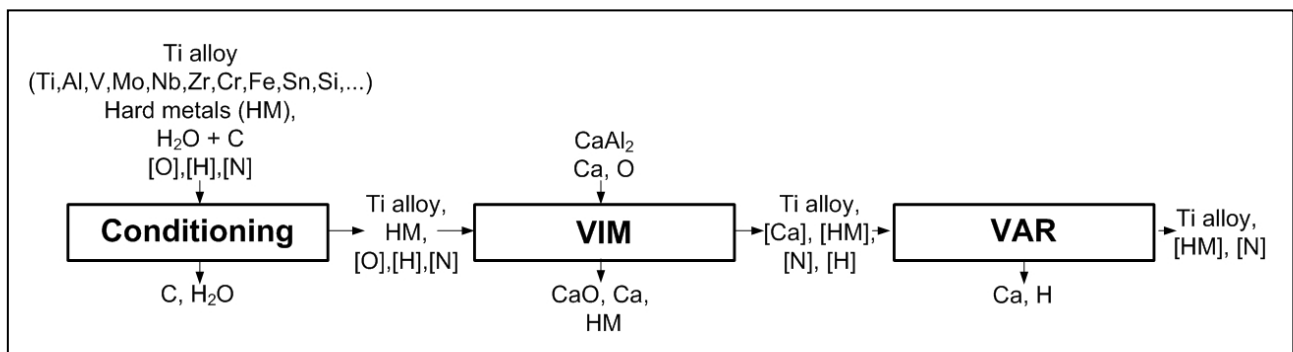


Figure 5: Summary of potential in- and outputs during the recycling process

3.1 Interstitial Elements

Titanium features a high affinity as well as a high solubility for interstitial elements such as oxygen, carbon, nitrogen and hydrogen. Together with iron, these elements also define the commercial titanium grades 1-4, with oxygen, nitrogen and carbon being alpha phase stabilizers that increase the strength of titanium when added in small concentrations. However, higher concentration levels can lead to the formation of so-called high interstitial defects (HID), inclusions that consist of hard brittle alpha phase enriched in nitrogen, oxygen and carbon. Furthermore, hydrogen can cause embrittlement through formation of hydride phases in the titanium matrix. [13]

Nitrogen is mainly introduced into the process via surface nitrated scrap. In lack of a stronger nitride forming element than titanium and taking into account that the process pressure for effective nitrogen distillation is not within reach, it has to be stated that refining of nitrogen is limited to dissolution of nitride inclusions during VIM and VAR. Fortunately, entry levels are manageable: With typical contents of 300 ppm, they consistently undercut the maximum levels of titanium grades 1-4.

Carbon is primarily picked up from lubricants that adhere to the turning surface. Depending on the surface to volume ratio, the concentration can exceed 5 wt.-% for highly contaminated scrap. Several drying steps in combination with ethanol washing reduce carbon concentrations during conditioning below 0.15 wt.-%. Given that further reduction is desired, an additional vacuum distillation step at 400 °C with a pressure of 1 mbar should ensure further decrease of carbon contamination to 0.05 wt.-%.

As water is a major component of lubricants, hydrogen is introduced likewise into the process in large quantities. Fortunately, the share of up to 5 wt.-% can be considerably reduced by drying the turnings at 120 °C. The remaining dissolved hydrogen that has generally been picked up at high temperatures and high pH-levels [2] and can be treated by VAR: At process pressures below 0.01 mbar and temperatures above 1700 °C, the solubility of hydrogen in titanium is < 10 ppm, therefore the hydrogen concentration can be reduced to acceptable limits.

Due to elevated temperatures during machining, turnings exhibit a comparably thick oxide layer. Taking the high surface-to-volume ratio into account, this leads to considerable contamination,



while the dissociation of the CaO crucible increases the oxygen levels even further. Thereby, maximum concentrations of 20,000 ppm can arise. However, the addition of CaAl₂ as deoxidizing agent during VIM not only inhibits the dissolution of the crucible, but also reduces the initial oxygen concentration below 1,500 ppm.

3.2 Tramp Metals

Since the feedstock is a mixture of different titanium alloys, the main source for alien elements is the feedstock itself. Furthermore, calcium is picked up from the dissolution of the crucible and, jointly with aluminium, the admixture of the CaAl₂ deoxidizing agent.

The necessary calcium addition is calculated from the shares for direct deoxidizing and stabilizing the melt against new oxygen pickup. Moreover, excess calcium is added to compensate for evaporation losses:

$$m_{\text{Ca}} = m_{\text{Ca, deox}} + m_{\text{Ca, sat}} + m_{\text{Ca, excess}} \quad (15)$$

m_{Ca} = total calcium addition; $m_{\text{Ca, deox}}$ = calcium mass share to deoxidize the melt; $m_{\text{Ca, sat}}$ = calcium mass share to stabilize the melt; $m_{\text{Ca, excess}}$ = calcium mass share to counter evaporation losses

According to calculations made in chapter 2.1, the total calcium input accounts for approximately 2.5 wt.-% to deoxidize and stabilize a titanium alloy with an initial oxygen concentration of 20,000 ppm and a final concentration of 1,500 ppm. Despite operating under pressure, a considerable fraction evaporates already during VIM. Owing to its high vapour pressure, calcium can subsequently be diminished to values under the lower detection level of the atomic absorption spectrometer by keeping the process pressure during VAR below 0.005 mbar.

Hard metals are unlikely to be detected as constant impurity but rather as singular incidents from cutting tool contamination. Nevertheless, they are undesirable because of the so-called high density inclusions (HDI) they form. Depending on the size, small hard metal particles can dissolve during VAR and VIM. Moreover, remaining particles can be retained in the crucible through a currentless sedimentation period before casting.

However, apart from elements with significantly higher vapour pressures than titanium, this process route offers no refining ability towards other elements of common titanium alloys as Al, V, Mo and Zr. Table 2 summarizes expected levels of contamination and gives an overview of the IME recycling process refining potential.



Table 2: Refining evaluation of the recycling process

Elements	Expected values	Refining capability	Refining procedure
Tramp elements (Al, Fe, V, Mo, etc.)	Up to 10 wt.-% each	-	-
Ca	2.5 wt.-%	< AAS detection limit	VAR
H	Up to 5 wt.-% (H ₂ O)	< 3 ppm	Drying, VAR
N	300 ppm	-	Dissolving
C	Up to 5 wt.-%	< 500 ppm	Cleaning, vacuum distillation
O	Up to 2 wt.-%	< 1500 ppm	Deoxidizing during VIM
Hard metals	Singular incidents	-	Dissolving during VIM + VAR, Sedimentation

4 Conclusions

The IME recycling process offers a high flexibility regarding feedstock material, thus enabling the substitution of titanium sponge and classified clean scrap by inexpensive low-grade scrap. The key feature of this approach is the introduction of vacuum induction melting as process step. With this, the whole batch is homogenized in a single melt and efficiently refined, particularly with respect to the highly sensitive oxygen values. Therefore, a large fraction of production costs is economized by applying the IME recycling process, resulting in not only higher cost-competitiveness for the produced titanium, but also contributing to efforts concerning the reduction of energy consumption and therefore the carbon footprint.

However, due to this high flexibility, the produced alloy will not be able to meet current alloy specifications. Table 3 shows the comparison between the specifications of the well-known titanium grade 4 and Ti-6Al-4V alloys [13] and the final composition of the secondary alloy from the IME process. Additionally, the last column indicates the worst-case scenario for each element, based on 15 common titanium alloys [7]. Extensive cleaning and deoxidizing during vacuum induction melting ensure compliant concentrations regarding the crucial oxygen and carbon levels. However, due to the wide range of possible alloying elements and the very limited refining capabilities for them, even small shares of differing alloys in otherwise mono-fraction feedstock will inhibit meeting the specifications. With the lack of a distinct specification, market entry will be severely restricted, if not impossible, for such a secondary titanium alloy.



Table 3: Comparison of common alloy specifications with secondary IME alloy

	Titanium grade 4	Ti-6Al-4V	IME secondary alloy	Worst case for single element
Al wt.-%		6	7.04	6
V wt.-%		4	2.39	15
Mo wt.-%			0.69	11.5
Cr wt.-%			-	6
Zr wt.-%			1.19	6
Nb wt.-%			0.03	0.7
Fe wt.-%	0.5	0.3	0.24	2
Sn wt.-%			0.75	4.5
Si wt.-%			0.15	0.35
O wt.-%	0.4	0.2	0.15	-
N wt.-%	0.05	0.05	0.03	-
H wt.-%	0.015	0.0125	< 0.001	-
C wt.-%	0.1	0.1	0.05	-
Ti wt.-%	bal.	bal.	bal.	100

Simple adoption of the worst-case scenario from Table 3 would result in an unlimited number of possible element combinations, making the identification of a narrow range of physical and chemical properties impossible. Therefore, a new approach is necessary: A new specification could be based on the estimated share of titanium alloys within the low-grade scrap, allowing moderate variations for each element.

To anticipate such a share, the following aspects have to be taken into account: Total market share, buy-to-fly ratio and extent of classification. The Ti-6Al-4V alloy can serve as an example: This alloy dominates the market with a >50 % share, it can be assumed that a large amount is used in high-volume applications, e.g. aerospace. Since this increases chances for a closed-loop recycling process, the expected share in a low grade feedstock would be significantly below 50 %.

Nevertheless, such a preliminary specification draft has to be optimized in terms of physical properties. Intensive benchmarking and structure analyses within the potential alloying element matrix should result in further restrictions regarding the element band width, ultimately giving a low-cost multi-purpose secondary titanium alloy. Flying and rotating applications like aerospace and turbine blades require a critical combination of physical properties (e.g. high strength at high temperatures)



that are barely satisfied by a secondary alloy under these circumstances. However, various applications could profit from a cheaper titanium alloy, such as automotive, health care or chemical engineering, where titanium is not yet established due to cost considerations.

5 References

- [1] USGS: Mineral Commodity Summaries (2011); United States Geological Survey; Reston; VA; USA; page 172-173
- [2] Lütjering, G.; Williams, J. C. (2010): Titanium. 2nd. [Berlin, New York]: Springer, page 51 & 168
- [3] Moeller, E. (Hg.) (2008): Handbuch Konstruktionswerkstoffe. Auswahl, Eigenschaften, Anwendung; München; Hanser; page 475
- [4] Gungor, M. N.; Imam, M. A.; Froes, F. H. (2007): Innovations in titanium technology. Proceedings of a symposia; TMS 2007 Annual Meeting & Exhibition; Orlando, Florida, USA; Warrendale, Pa: TMS; page 6
- [5] Kraft, E. H.; (2003); Summary of Emerging Titanium Cost Reduction Technologies; Oak Ridge, TN.; Oak Ridge National Laboratory, page 7
- [6] Angerer, G.; Erdmann, L.; Marscheider-Weidemann, F.; Scharp, M.; Lüllmann, A.; Handke, V.; Marwede, M. (2009); Rohstoffe für Zukunftstechnologien. Einfluss des branchenspezifischen Rohstoffbedarfs in rohstoffintensiven Zukunftstechnologien auf die zukünftige Rohstoffnachfrage; 2., überarb. Aufl.; Hg. v. Fraunhofer ISI. Karlsruhe; page 265
- [7] Peters, M.; Leyens, C. (2002); Titan und Titanlegierungen 3., neu bearb. Aufl.; Weinheim: Wiley-VCH; page 23
- [8] Smithells, C. J.; Gale, W. F.; Totemeier, T. C. (2004); Smithells metals reference book. 8th ed.; Amsterdam, Boston; Elsevier Butterworth-Heinemann; page 14.1
- [9] Predel, B.; in: Landolt-Börnstein - Group IV; Vol. 5, Springer-Verlag Heidelberg,
- [10] Tsukihashi, F.; Hatta, T.; Tawara, E. (1996): Thermodynamics of calcium and oxygen in molten titanium and titanium-aluminum alloy. In: *Metall and Materi Trans B* 27 (6); page 967–972.
- [11] Köhler, M., Engell, H.-J. , Janke, D.(1985); Excess pressure refining of steel melts using metallic calcium; In: Proceedings 8th International Conference Vacuum Metallurgy; Linz/Austria, Eisenhütte Österreich; page 851-68.
- [12] Becker, H.; Zwicker, U. (1976); IVa Metalle – Titan, in: Gase und Kohlenstoff in Metallen – Zweiter Teil: Daten; Springer Verlag; page 397
- [13] Donachie, M. J. (2000); Titanium. A technical guide; 2nd. ed.; Materials Park, OH; ASM International; page 14