Closing The Material Cycle of Titanium – Thermochemical and Experimental Validation of a New Recycling Concept

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Abstract

Due to high scrap generation in the processing of semi-finished and final products made of titanium and titanium alloys, recycling shows a great potential to substitute titanium sponge, economize the titanium market and to apply secondary low cost titanium in new applications. This article deals with the development of a new recycling process using scrap, downgraded at present, as an input source. This process is an innovative combination of industrialized processes like Vacuum Induction Melting (VIM), Metallothermic Desoxidation, Electro Slag Remelting (ESR) and Vacuum Arc Remelting (VAR).

The primary melting of scrap is done by VIM using specialized ceramic linings and includes pre-deoxidization. A second step is final deoxidization by chamber-ESR using a continuously activated Ca-reactive slag. The third processing step is VAR, in order to remove small slag inclusions as well as dissolved Ca and to allow for hydrogen degassing. For each process step the according equipment, the metallurgical challenges and opportunities are pointed out and the way to make use of them within the process route is described. An intensive thermochemical modeling on refractory reactions with liquid titanium and titanium alloys, on the involved deoxidization by calcium master alloys and by the active ESR slag, as well as for the removal of excess Ca and H in VAR is conducted before semi-pilot scale tests are done at IME. These trials are assisted by fundamental investigations of the liquid phases' thermophysical properties like conductivity, density and viscosity. Further investigations on the kinetic behavior of nitride dissolution are conducted in parallel by Electron Beam Melting (EBM).

The paper will present the results of theoretical modeling as a basis for laboratory and semi-pilot scale experiments at IME in Aachen for the production of 100 kg VAR-ingots from 100 % scrap.

Introduction

Raw materials (e.g. titanium sponge respectively aluminum and master alloys) for the production of Ti and Ti alloys have to be very clean due to limited metallurgical refining possibilities within the well-established production route by vacuum arc melting and re-melting (VAR) or cold hearth electron beam melting (CHEBM). For this reason high quality standards are set for raw materials 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.

As shown in figure 1, high metal losses occur during the processing to semi-finished and end products.

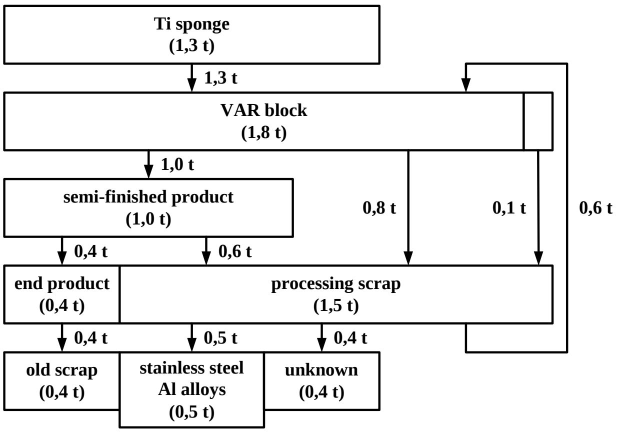

Figure 1: titanium mass flow and scrap amount [1]

Starting from a 1.8 t titanium block made by VAR melting of titanium sponge, 1.0 t of semi-finished products are produced. Normally just about 0.4 t of end products can be yielded within further processing of the semi-finished products. In the worst case material output is only about only 10 % of semi-finished products in case of complex mechanically produced final construction parts. [1]

60 % of the processing scrap is downgraded by use in non structural applications (i.e. as alloying material in steel and aluminium industry). Starting from an annual worldwide tonnage of Ti sponge of 110.000 t in 2006 [2], more than 76.000 t scrap for recycling to low cost titanium is available. According to figure 1, further more than 33.000 t of old scrap accumulate worldwide.

The main aim for a sustainable recycling process is to keep the expensive titanium metal in a closed loop at an economic level, achieved by the use of well established industrialized processes with satisfactory refining potential.

Recycling Concept

The principle of the recycling process developed at IME in Aachen is shown in figure 2. The concept consists of three main processes: VIM, ESR and VAR

In spite of the well-known chemical aggressiveness of titanium and titanium alloys in molten state, scrap melting is conducted in conventional vacuum induction furnaces using refractories. This ensures economy due to strongly increased energy efficiency compared to high sophisticated vacuum metallurgy utilising water-cooled copper moulds (CHEBM) or crucibles (Induction Skull Melting). Only with induction melting the best possible homogenisation can be achieved, as the entire material reaches jointly a fully liquid status.

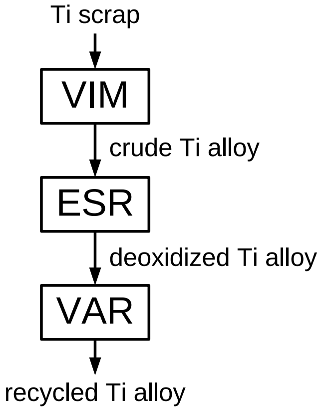

Figure 2: titanium recycling concept at IME in Aachen

Following figure 2 at first scrap is charged into a VIM-furnace and molten under inert gas (argon) atmosphere. The charge consists of sorted scrap and as required of master alloys (e.g. Nb-Al, Cr-Al, V-Al). Due to oxygen pick-up during melting, VIM comprises pre-deoxidization of the melt either using a Ca-Al master alloy or yttrium metal. Solid CaO or Y_2O_3 is floated up and accrues at the crucible wall, excess calcium respectively yttrium is partly dissolved in the melt to keep the equilibrium constitution. The homogeneous melt is cast into a water-cooled copper mould to obtain a segregation free electrode for ESR.

The main challenges concerning the VIM process are:

- oxygen pick-up, target is max. 5.000 ppm in the VIM-cast electrode
- melt contamination by dissolved metals originating from reduced ceramic metal oxides or precipitations
- melt contamination by non metallic inclusions caused by ceramic particles
- melt contamination by dissolution of desoxidation metals (Ca, Y)
- crucible lifetime

Slag removal and final deoxidization is served by electro slag re-melting.

Finally a second re-melting is done by VAR in order to remove dissolved Ca and smallest non metallic inclusions from the alloy as well as to adjust directional solidification of the re-melted block.

Vacuum Induction Melting (VIM)

The application of conventional VIM offers the following advantages:

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

Disadvantageous in case of titanium-alloys is the unavoidable contamination (i.e. oxygen pick-up from applied oxide ceramics as crucible material) during melting due to ceramic-melt interactions. To evaluate the chemical and thermal stability of refractories, thermochemical modeling is applied. Target is the calculation of the thermochemical equilibrium (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 on searching for the minimum of total Gibbs energy G_{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. For calculation the software tool FACTSAGE® is used:

$$\alpha <Me_mO_n> + (X) = \alpha\text{-}\delta <Me_mO_n> + (XMe_{m\cdot\delta}O_{n\cdot\delta}) \qquad (1)$$

$<Me_mO_n>$…solid crucible material (e.g. Al_2O_3)

(X)…liquid Ti or Ti/TiAl alloy

δ…extent of reaction, δ [0, α]

Figure 3 and 4 show the results of the thermochemical modeling in case of unalloyed titanium respectively binary γ-TiAl (50 at.% Al) and pure alumina (Al_2O_3) as crucible material.

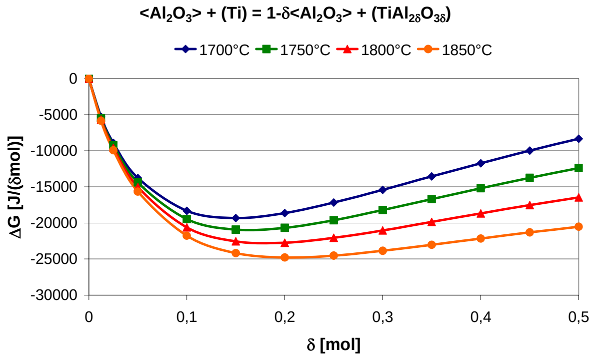

Figure 3: $\Delta G_R = f(\delta, T)$ in case of liquid unalloyed titanium versus pure Al_2O_3

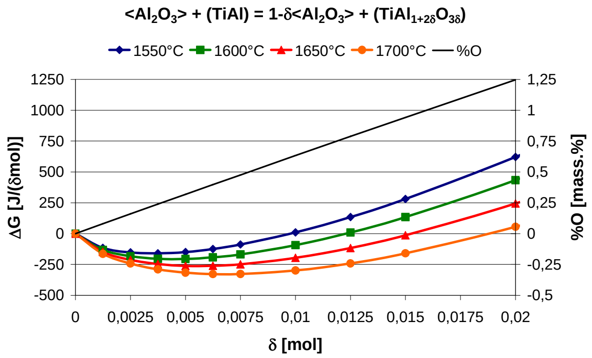

Figure 4: $\Delta G_R = f(\delta, T)$ in case of liquid binary g-TiAl (50 at.% Al) versus pure Al_2O_3

As it is seen in figure 3, there is no equilibrium reached within the considered extend of reaction. The total amount alumina will be dissolved in titanium and the final oxygen content is only limited by the dissolved mass of oxide. In case of binary titanium aluminide an equilibrium is reached and the corresponding oxygen content of the melt depends on temperature.

Via experimental work in laboratory scale, the thermochemical modelling is validated and the stability of commercial refractories is investigated to identify possible fields of application. Positive results are evaluated in case of yttria (Y_2O_3) and calcia (CaO) as crucible material for titanium melting.

Because of unavoidable oxygen pick-up during melting, a so called direct pre-deoxidisation is employed. This is realized by dipping a Ca-Al master alloy or yttrium metal directly into the melt. In case of g-TiAl alloys even a final deoxidisation within the VIM process is possible. Qualitative reaction equations are given below.

$$\{Ca\} + [O]_{melt} = \langle CaO \rangle \tag{2}$$

$$[Ca]_{melt} + [O]_{melt} = \langle CaO \rangle \tag{3}$$

$$2\,[Y]_{melt} + 3\,[O]_{melt} = \langle Y_2O_3 \rangle \tag{4}$$

$\{gaseous\}$ $[dissolved]$ $\langle solid \rangle$

Figure 5 shows the between calcium and oxygen content in liquid TiAl, $TiAl_3$ and Ti in contact with pure calcia (activity of CaO is one).

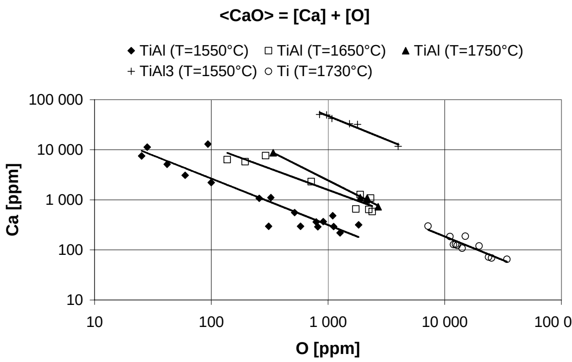

Figure 5: Dependency between Ca and O content in molten TiAl, $TiAl_3$ and Ti [3]

As it can be seen in figure 5, TiAl and Ti show virtually the same equilibrium constant K for reaction (3). Whereas Ti shows significantly lower Ca contents and hence higher oxygen contents. As already mentioned in case of g-TiAl alloys, final deoxidization by VIM is conceivable to save the ESR process.

Figure 6: VIM-cast TiAl electrode (∅ 105 mm, L 750 mm, mass approx. 25 kg)

Electroslag Re-melting (ESR)

In electroslag re-melting (ESR) a metal billet (electrode) is continuously molten by contact with a defined liquid slag. Only a small part of the ingot is liquid at a certain time and shortly after resolidified. As a major benefit of ESR, solid inclusions with melting points above that of the base-metal will float or eventually dissolve in the slag, depending on their density and chemical properties. Concerning the treatment of titanium alloy scraps, it has been shown that the dissolution of high melting TiN inclusions is possible during ESR [5],[6].

In addition to the removal of inclusions, chemical reactions such as desulphurisation, desoxidation, alloying or removal of accompanying elements can occur at fast rates at the liquid-liquid phase-boundary between the metal and the slag. Furthermore, if melting under inert-gas is applied (so called I-ESR or chamber-ESR), an oxygen and nitrogen pickup from the atmosphere can be avoided. Thus the ESR process is nowadays in the transfer to more reactive alloy systems like titanium based materials, chromium and certain intermetallics.

The fact, that only a very small part of the bulk electrode is being melt at a time, may be noted as a disadvantage of the process. This is unlike to other metallurgical melting operations where usually the full content of a crucible is molten, allowing for mixing and homogenisation before casting. Because mixing in the solid state does not take place, it is crucial in ESR to reach stationary process conditions in terms of melting rate, temperature and especially in terms of slag-metal equilibria, in order to receive a homogeneous ingot.

Chemical reactions in ESR, like desoxidation, are thermochemically controlled by the oxygen potential of the slag-phase. A proven method to influence the oxidation potential in return is the addition of reactive metals, like Ca, Mg, Si, Al or rare earth metals. Own thermochemical calculations have shown, that even the desoxidation of titanium, a metal with remarkably high oxygen affinity, is possible by chamber-electroslag remelting using reactive Ca-CaF_2-slags and an inert atmosphere [8]. To ensure a uniform oxygen content with respect to the full length of an ingot, oxygen potential in the slag has to be carefully controlled and adjusted during the whole melting process. Due to the current lack of industrialized methods for online-measurement, suitable to deliver reliable data under the harsh remelting conditions, the Ca-content of the slag has to be levelled using mass-balance calculations, heat data documentation in an expert system and continuous feeding of desoxidation agents accordingly. A quasi-equilibrium process model has been developed at the IME, Aachen to deliver charging rates and process control parameters necessary to ensure constantly low oxygen contents during the ESR treatment of recycled titanium material. Because the Ca vapour-pressure in the slag is near one atmosphere, the model also accounts for calcium evaporation [7].

ESR melting at IME also aims to treat γ-TiAl alloys, originating from scrap and even from aluminothermic reduction (ATR). After pre-desoxidation via VIM, the final oxygen content is adjusted in the ESR-process using Ca-reactive slags. To meet specifications significantly below 800 ppm for castable alloys, Ca is applied as a reducing agent in the slag, according to the following reaction (5):

$$\begin{aligned}&\mathrm{TiAl}_{\varphi-2\left(\frac{2-x}{3}\right)}\mathrm{O}_x + x\,\mathrm{Ca} + \kappa\,\mathrm{CaF_2Ca_\gamma CaO_\delta} \xrightarrow{\vartheta}\\ &\mathrm{TiAl}_{\varphi-2\left(\frac{2-x}{3}\right)}\mathrm{O}_{x\cdot(1-\xi)} + \kappa\,\mathrm{CaF_2Ca}_{\gamma+\frac{x(1-\xi)}{\kappa}}\mathrm{CaO}_{\delta+\frac{x\cdot\xi}{\kappa}}\end{aligned} \qquad (5)$$

where ξ is the extend of reaction (desoxidation), κ the molar ratio of slag-phase to metal-phase; γ the molar Ca/CaF2-ratio in the slag; δ the molar CaO/CaF2-ratio in the slag [8].

An almost 100% desoxidation degree can only be reached with extremely low CaO contents, while thermochemical calculations for ATR-type material using a Ca-CaO-CaF_2 system modeled in FactSage^{TM} suggest that a 99% desoxidation (aiming at 100 ppm O) should be possible throughout the full scale of CaO solubility of the slag by adjusting the Ca content accordingly. Figure 7 shows the necessary Ca-content respecting the increasing CaO contents in the slag in the form of oxygen-equi-concentration-lines at different temperatures. sufficient to treat TiAl materials down to 800 ppm oxygen.

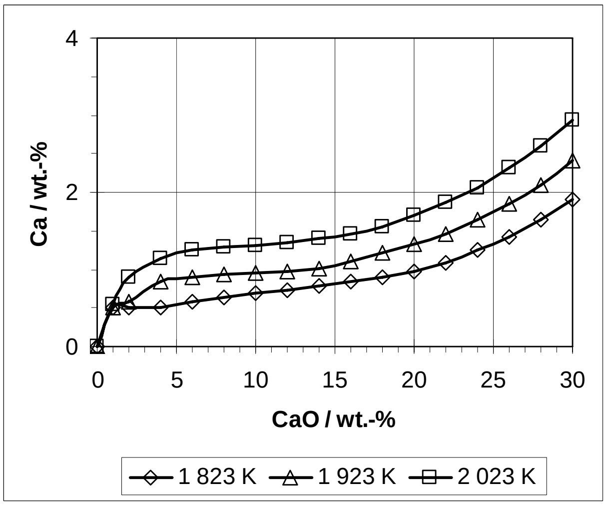

Figure 7:Necessary Ca-content in a Ca-CaF_2-CaO-slag to deoxidize γ-TiAl containing 1,5% O down to 800 ppms, depending on CaO content and the temperature of the slag

As mentioned above, only a partial amount of the total metal is in the molten state at a time and gets into contact with the slag in ESR, so that the above reaction can occur. Thus over the entire process, the slag will be enriched by the desoxidation product CaO and depleted of Ca, hence the thermochemical equilibrium will shift to the left side of the equation, decreasing the efficiency of desoxidation over time. The result would be a non-homogeneous ingot in terms of oxygen content. Thus, from a thermochemical point of view, Ca-activity has to be increased continuously and well controlled during the process, e.g. by adding over-proportionally more metallic calcium. Additionally the CaO-activity has to be decreased, e.g. by diluting the solution through the addition of CaF_2.

As to date no method is available for on-line measurement of the slag's oxygen potential and no tools for adjustment by adding desoxidation agents accordingly, a calculation system was developed to assist in process control for the desoxidation of the named materials. Using given conditions for the start-up phase (e.g. slag composition, metal-content in starting mixture, system pressure, etc.), the control system calculates the melting progress in discrete steps and assumes chemical equilibrium in each step. It accounts for the solution of Calcium in the metal, for the amount of Ca consumed for desoxidation, for the amount of Ca evaporated, for the increase of CaO in the slag and successively for the necessary increase of metallic Ca concentration in the slag to compensate for the higher oxygen potential of CaO.

Figure 8 shows the result of such calculation for the melting of a γ-TiAl-electrode with a diameter of 110 mm and 1325 mm in length. The electrode's oxygen concentration was analysed to be 1,59% using the gas-extraction method. The ESR crucible applied has a diameter of 178 mm at the base-plate and 159 mm at its rim and measures 880 mm in height. The initial CaO-content of the applied batch of WACKER 2052 slag (>97,5% CaF2) was determined to be 1,17%.

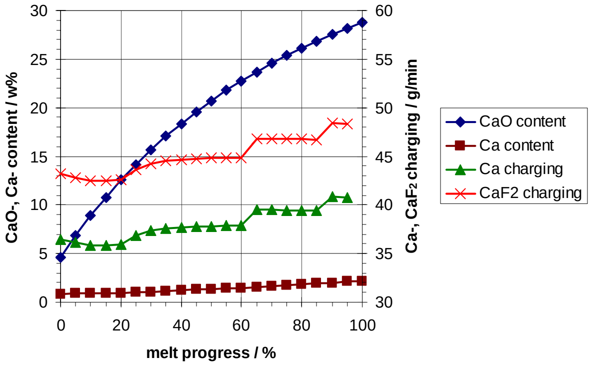

Figure 8: Evolution of Ca and CaO concentration in the ESR slag during melting of oxygen containing γ-TiAl and necessary feed rates for Ca and slag

Melting results in 25 kg ingots of a γ-TiAl alloy, with homogeneous, directional solidification microstructure, and an oxygen content <800 ppm. Macro segregations, macro size slag inclusion and voids that could have been previously introduced during VIM-melting and casting are removed.

Calculations indicate, that the fluorine pick up in the material should only be only in the range of a few ppm due to the Ca content of the slag that reduces fluorine activity tremendously. On the contrary, significant amounts of Ca (>300ppm) will be dissolved in the solidified metal. The influence of Ca on the mechanical properties of γ-TiAl are still to be determined but generally Ca is expected to have negative effects on the material quality. Additionally, ESR is assumed to increase the amount of small non-metallic inclusions <10 µm, while though larger inclusions are removed [9].Thus, a subsequent vacuum arc remelting becomes necessary to ensure for superior material properties by further removing smallest inclusions and by evaporation of the desoxidation agent from the metal.

Vacuum Arc Re-melting (VAR)

The final process step of the IME-recycling-process is vacuum arc re-melting of the deoxidized ESR blocks, The objectives are to remove dissolved calcium and hydrogen and to adjust directional solidification inside the re-melted VAR block. The Ca-distillation and H-degassing can be expressed by following reactions:

$$[Ca]melt = \{Ca\} \qquad (6)$$

$$2\,[H]_{melt} = \{H_2\} \qquad (7)$$

{gaseous} [dissolved]

Figure 9 shows the modelling results for Ca removal via distillation using VAR.

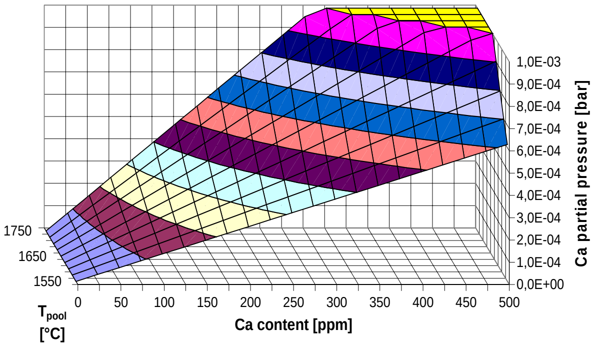

Figure 9: Ca partial pressure as a function of VAR pool temperature and Ca-content in binary g-TiAl

As it is seen in figure 9, even at low overheat (assumed melt temperature of 1550°C correspond to 25°C overheat in case of binary TiAl) of the melt and moderate vacuum conditions (<1 mbar), Calcium removal per distillation to values less than 100 ppm is easily possible. In case of Ti the Ca vapor pressure at process temperature is even higher and the Ca content in re-melted metal is therefore much lower.

During VAR the removal of smallest non-metallic-inclusions (NMI) can be expected. Even though dissolved nitrogen cannot be removed, it is nevertheless homogeneously distributed after this triple-melt recycling process. To confirm this concept, trials concerning the dissolution kinetics of TiN contaminations in Ti-6Al-4V are conducted by electron beam melting (EBM). Monolithic titanium nitride specimen are made by powder sintering c.p. titanium powder and TiN powder are blended using a ball mill, pressed into compacts and sliced into pieces of about 50 mm. The small blocks are sintered using an induction furnace. After sintering, the nitrogen, oxygen and the carbon content is analyzed and TiN dissolution kinetics tests are carried out using the 60 kW EB furnace operated at IME:

The specimens are inserted in a rectangular arrangement of prepared holes on the cross-section of a Ti-6Al-4V ingot. The ingot with the TiN specimen is loaded into the crucible, firstly preheated using 0.1-0.2 A current for 30 minutes and finally treated by a predefined beam power. During the melting process, the molten pools' top surface temperature is measured using an infrared quotient-type pyrometer and fiber optics. Results of fundamental research on nitride-dissolution kinetics will be reported in an upcoming paper.

Figure 11: loaded water-cooled crucible and optical fibre measurement set-up

Physical Properties of ESR Slags

To adjust and optimize metallurgical processes detailed information on physical properties of metals and slags like density, conductivity and viscosity is necessary. Especially in case of ESR, uncommon slag systems which are essential for the mentioned ESR refining step are not well explored and deserve closer attention. Parallel to the process development work, systematical investigation in a specialized lab [10] for the determination of thermophysical properties of molten phases takes place in Aachen.

For the ***density*** measurement the hydrostatic weighing method based on Archimedes' principle is used. A submerged tool is effected by the buoyancy of the volume of liquid it displaces. The result is that the tool weighs less in a liquid media than in air. It is necessary to know exactly the volume of the submerged tool, as well as its density dependence on the temperature. The density of the melt is calculated as

$$\rho_m - \rho_a = \frac{m_a - m_m}{V} \qquad (8)$$

where ρ_m and ρ_a are the densities of the melt and air, m_a and m_m the weights of the specimen in air and in the melt and V is the volume of the specimen at the corresponding temperature. Figure 10 shows exemplary the results of measuring a pure CaF_2 ESR slag compared to literature values. More information will be published soon in a separate article [11].

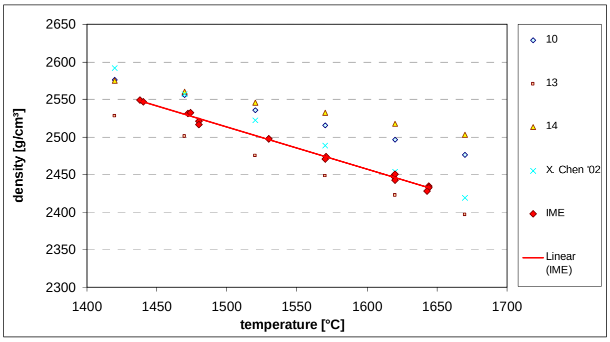

Figure 10: Density of liquid CaF_2 as function of temperature

For the measurement of the ***surface tension*** a gas/liquid meniscus is produced at a capillary submerged in a liquid media. The pressure in the capillary is increased up to the bubble detachment from the orifice. The pressure in the capillary is continuously recorded. Using the maximum bubble pressure, the surface tension can be calculated from the following relation that is derived from the Laplace equation, where P_{max} is the maximum occurring gas pressure inside the capillary, σ the surface tension and the term $\rho \cdot g \cdot h$ is the hydrostatic pressure of the melt.

$$P_{max} = \frac{2\sigma}{r} + \rho g h \qquad (9)$$

The viscosity is measured using a plate oscillated by an primary coil and the corresponding output signal from an secondary coil is recorded. If the plate is immersed in a liquid sample, the oscillation characteristics of the specimen changes with respect to amplitude, phase and frequency due to the viscosity forced friction. The method uses various assessment modes depending on the viscosity range. The principle of measurement applied at IME in Aachen is based on the so called “Vibration or Amplitude Method”, which can be used for liquids with viscosities up to 10 Pa·s. The final determination of the viscosity value results from a calibration curve, which is made by measuring fluids with known viscosities and densities. The mathematical model used for evaluation of the signals results in formula (10), in which A represents the amplitude of vibration, ρ the density and η the viscosity of fluid as well as C1 and C2 the constant parameters related to the actually used measuring system.

$$\sqrt{\rho \cdot \eta} = \frac{C_1}{A} + C_2 \qquad (10)$$

For this method the density of the fluid must be known.

Summary / Outlook

IME developed and successfully proved an innovative recycling concept for titanium scraps. It is based on a VIM homogenization in ceramic crucibles accepting a significant oxygen pick up. Subsequently VIM and ESR is used for deoxidization and VAR for final refining and consolidation. The process allows for treatment of various scrap types (flexibility) and for correcting the initial melt composition.

The entire recycling concept has been realized for γ-TiAl alloys at this time. VIM melting/deoxidization of Ti-6Al-4V scrap has been successfully conducted in laboratory scale. For semi-pilot trials yttria crucibles (useful volume 8 L) are made by investment casting techniques.

Final investigations on NMI particularly with regard to fluoride inclusion due to ESR process slag will be conducted in near future.

Calcium is almost completely removable by VAR, dissolved metallic yttrium not. In this case it has be mentioned, that many restrictions are presently existing as no standards exist for low cost secondary titanium and titanium alloys, which could be used for structural application in automotive industry or other new opened applications fields. But such materials could substitute titanium sponge and economise the titanium market.

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