POTENTIAL OF CERAMIC CRUCIBLES FOR MELTING OF TITANIUM-ALLOYS AND GAMMA-TITANIUMALUMINIDE

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INTRODUCTION

Owing to their high reactivity, molten titanium and γ-titanium aluminides (γ-TiAl) are generally melted in water-cooled copper crucibles or hearths. Firstly, these processes are cost-intensive due to their low energy efficiency and secondly, they only have limited refining potential and typically no homogenization capability. Hence, a high quantity of titanium scrap cannot be recycled and becomes downgraded in non-structural applications like deoxidation of steel. To close the cycle of materials for titanium, an alternative recycling route with increased refining potential is under development at the IME in Aachen.

The process starts with consolidation and homogenisation by vacuum induction melting (VIM) and a first deoxidation in the molten state with Ca. Subsequently the produced ingot is processed via vacuum arc remelting (VAR) to remove hydrogen, excess calcium and non-metallic inclusions (NMI). If further deoxidation is necessary, additional electroslag remelting (ESR) with deoxidising slag components can be interposed prior to the VAR. Figure 1 illustrates the basic setup of the recycling route without ESR.

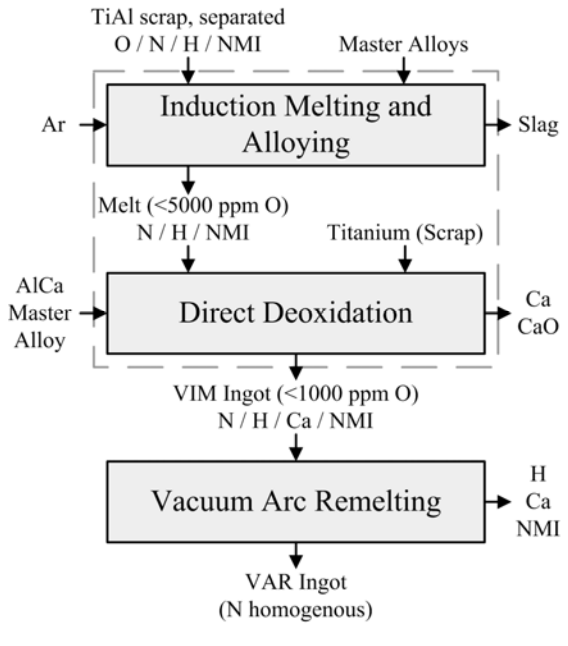

Fig. 1: TiAl recycling process at IME [1]

One of the main challenges to realize this recycling route was the selection of a suitable refractory for the VIM process. In summary, this paper presents the theoretical work as well as the experimental validation that were carried out in order to select such a material.

MATERIALS AND METHODS

Theoretical approach

In order to evaluate the most promising refractories for the melting of Ti-alloys a literature research was carried out. Furthermore, thermochemical calculations were conducted by means of FactSage 5.3 to obtain an indication for the degree of the expected interactions between melt and crucible. In a first step, $\Delta G°$ was calculated for several pure oxides in comparison to TiO [2], which was determined as the most stable oxide of titanium at temperatures between 1000 and 2000°C. Based on the results of this modelling a pre-selection of stable oxides was undertaken. Secondly, the reaction of different titanium alloys with the previously evaluated oxides was computed based on the Gibbs free energy, calculated for different combinations of alloys and oxides based on the reaction mechanism in equation (1).

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

$<Me_mO_n>$ stands for the employed refractory and (X) for the molten Ti/TiAl-alloy, which dissolves the solid oxide until the condition of equilibrium. As this model takes the dissolution and the associated shift of the equilibrium into account it is not only possible to predict the degree of the reaction but the theoretical content of oxygen and the metallic constituent in the melt as well.

Experimental work

The experimental work includes melting trials in a vacuum induction furnace in laboratory scale, the subsequent up scaling to pilot scale and the analysis of the cast ingots. As the aggressiveness of titanium-based alloys highly depends on their titanium content, Ti-6Al-4V and Ti-50Al (50 at.-% Al) were chosen as input materials to investigate the interaction with the crucible as examples for a conventional titanium alloy and for the new γ-TiAl material group. In both cases authentic revert material from industrial processes was used.

Laboratory scale melting trials

At the beginning, the most promising ceramics according to the literature research and the thermochemical calculations were tested in laboratory scale experiments. These trials took place in a high-frequency vacuum induction furnace with a nominal capacity of 10 kg steel and up to 40 kW melting power. The charges consisted of 300 to 600 g metal as the volume of the examined crucibles was approximately 0.3 l. Figure 2 illustrates the experimental setup.

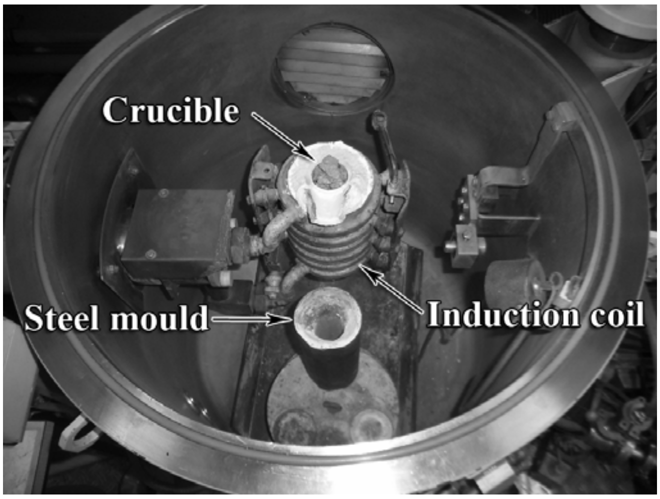

Fig. 2: Experimental setup of the laboratory scale trials

The material was charged into the crucible at room temperature, the furnace was then closed, evacuated below 10^{-3} mbar and flushed with argon twice to minimize the residual oxygen in the chamber. Melting took place under an argon atmosphere of 800 mbar to reduce the evaporation of refractory components or volatile alloying constituents. To avoid thermal shocks in the crucible, power was applied by degrees in steps of 2 kW/0.5 h. After detecting the first molten metal, the melting power was kept constant until all material was liquid. When clear melt was reached, the holding time was varied before casting the material into a cold steel mould (45 mm Ø). For Ti-6Al-4V the casting temperature was set between 1680 and 1800°C whereas for Ti-50Al between 1500 to 1650°C. Temperature measurements were carried out either by type B (Pt-6Rh/Pt-30Rh) or type C (W-5Re/W-26Re) immersion thermocouples which were enclosed by a casing made of 77 wt.-% Mo and 22 wt.-% Al_2O_3.

Pilot scale melting trials

The pilot scale melting trials were carried out in a vacuum induction furnace with a capacity of 100 kg steel and a nominal melting power of 150 kW. A crucible volume of 14 l allowed a charge weight of 28 kg and the melt was poured into a water-cooled copper mould (110 mm Ø). The general experimental setup and the execution of the trials were comparable to the laboratory scale experiments except that the melting power was increased by degrees in steps of 10 kW/0.5 h.

Examination of the recycled material

The laboratory scale ingots were crushed under air into pieces <0,1g which were analyzed by ICP-OES as well as hot gas extraction. This laborious sampling method was employed to avoid additional oxygen pickup due to the high temperatures during drilling. A correct oxygen analysis is of particular importance because the degree of the interaction between melt and crucible is generally rated by this value.

As the pilot scale material had to be further processed via vacuum arc remelting after sampling, five discs were cut out of each ingot. Out of each disc, a drilling core was extracted, crushed and analysed like the material from the laboratory scale trials.

RESULTS

Outcome of the literature research

As numerous publications concerning the melting of titanium alloys in ceramic crucibles are available, at this point only some of the essential findings will be presented.

Amongst others Kuang et al. [3] report the general feasibility of melting Ti-48Al-2Cr-2Nb in crucibles of Al_2O_3, MgO, CaO and MgO with an yttria-coating (~20 mm Ø). Whereas the oxygen level in the TiAl from the trials with CaO and the yttria-coated MgO is relatively low (2 400 and 1 550 ppm), the oxygen pickup from the Al_2O_3 and the pure MgO crucibles was significantly higher (9 500 and 9 600 ppm). Szkliniarz et al. [4] successfully employed Y_2O_3-stabilized ZrO_2 to melt Ti-48Al-2Cr-2Nb (2 900 ppm) as well as CaO (1 500 ppm) and Al_2O_3 (8 500 ppm). According to most sources, the stability of the investigated oxides can be described by the following sequence:

$$Y_2O_3 > CaO > ZrO_2 > Al_2O_3 > MgO$$

Results of thermochemical modelling

Figure 3 illustrates the dependence of ΔG° versus the temperature for the formation of above-mentioned oxides. The plots generally reflects the sequence above but the chart also points out that above 1 420°C TiO is more stable than MgO and Al_2O_3 and nearly as stable as ZrO_2. For that reason, a significant interaction is likely and therefore these oxides do not seem to be appropriate as crucible materials for melting of alloys rich in titanium. The Gibbs free energy of CaO and Y_2O_3 is considerably more negative than that of TiO what is the major requirement for an applicable refractory. But as an incrementing Al-content decreases the Ti-activity and such the aggressiveness of Ti-alloys, MgO, Al_2O_3 and ZrO_2. oxides might be suitable to melt γ-TiAl.

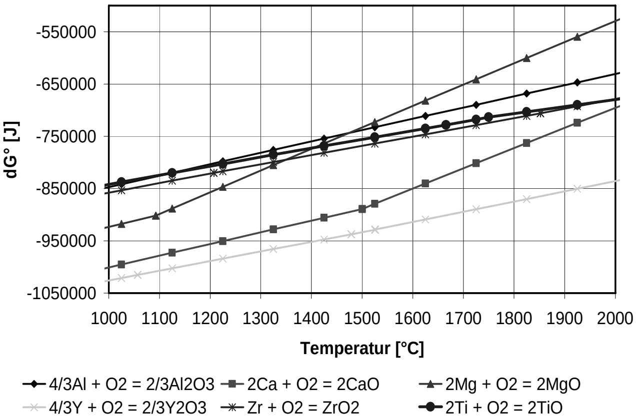

Fig. 3: ΔG° for several oxide formation reactions

As a consequence the Gibbs free energy was calculated for the reaction represented in equation (1) for those oxides with pure titanium in a closed system. In the case that equilibrium is reached without a complete dissolution of the refractory, the oxygen content in the melt was computed as well. Figure 4 exemplifies that in the case of CaO the equilibrium will be achieved prior to the full conversion of the refractory but even with a minimal superheat of 40°C the oxygen content nearly equals 5 wt.-%. Furthermore, heavy damage of the refractory has to be expected. As MgO and Al_2O_3 are even less stable, they will be completely dissolved by pure Ti. For the lack of thermochemical property data the oxygen content could not be calculated for Y_2O_3.

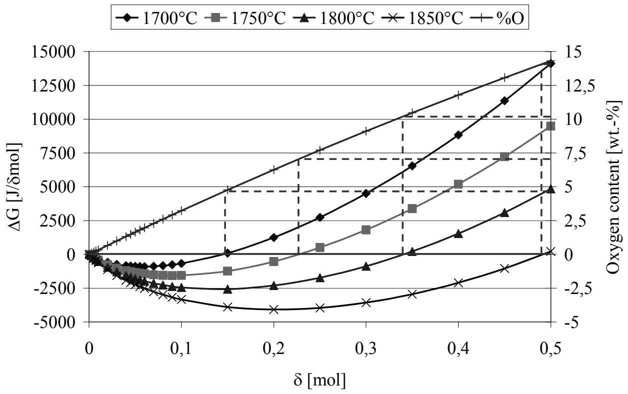

Fig. 4: ΔG and oxygen content for CaO reacting with Ti

The calculation for Ti-50Al was carried out analogically. As figure 5 illustrates, the Gibbs free energy is positive at all temperatures for the reaction with CaO and hence no significant interaction should occur. Whereas Y_2O_3 performs comparable to CaO, there are considerable reactions with Al_2O_3 and MgO and at 1550°C each leads to ~0.5 wt.-% oxygen in the molten metal.

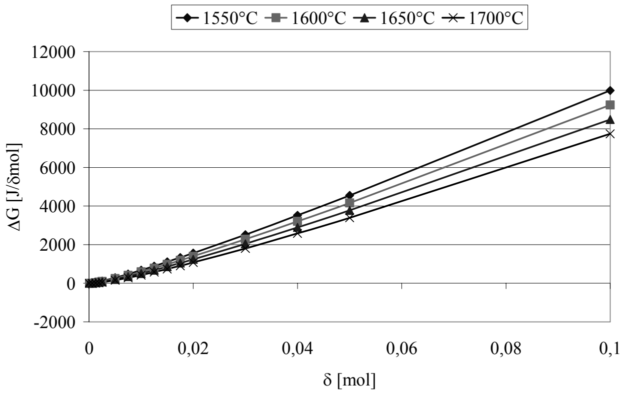

Fig. 5: ΔG plot for CaO reacting with Ti-50Al

Experimental test results of the laboratory scale trials

Following the theoretical work, commercial crucibles made of CaO, ZrO_2 and Al_2O_3 were selected to melt Ti-50Al in laboratory scale trials. In accordance to the theoretical results, the most intensive reaction can be observed for Al_2O_3, which leads to the formation of smoke and slag. The oxygen content increases from 0.07 wt.-% in the initial charge to 1.0 - 2.5 wt.-% in the final ingot. In the case of ZrO_2 only a small slag layer forms and the oxygen level stabilizes at 0.6 – 0.8 wt.-%. However, the zirconium content in the product rose to 2.1 – 3.1 wt.-% limiting the use of this refractory as the composition of the metal should not be altered significantly. With 0.25 – 0.35 wt.-% oxygen in the ingots CaO provides a satisfactory stability to melt γ-TiAl and due to the high vapour pressure of calcium the residual Ca-content doesn't exceed 0.05 wt.-% in the final ingot. As CaO was found to be sufficient to melt Ti-50Al, Y_2O_3 was not tested due to the high material costs of the ceramic. Table 1 summarizes the results for the laboratory scale trials.

Tab. 1: Contamination of Ti-50Al laboratory scale ingots after melting in various ceramic crucibles

Refractory	CaO	ZrO_2	Al_2O_3
Oxygen content /wt.-%	0.25 - 0.35	0.6 - 0.8	1.0 - 2.5
Ca/Al/Zr content /wt.-%	0.01 - 0.05	2.1 - 3.1	35.5 – 37.5

Parallel trials with Ti-6Al-4V showed that in the case of CaO, ZrO_2 and Al_2O_3 the reaction with the liquid metal causes a rapid dissolution of the crucible. Only Y_2O_3 provides enough thermochemical stability to melt this aggressive alloy with final levels of 0.5 – 1.0 wt.-% for oxygen and 0.3 – 0.5 % for yttrium.

Experimental test results of the pilot scale trials

In the pilot scale trials, CaO was tested vs. Ti-50Al and Y_2O_3 vs. both Ti-6Al-4V and Ti-50Al. As table 2 illustrates, the contamination of the ingots due to the dissolution of the oxide ceramics are in excellent correlation with the values from the laboratory scale experiments. Again, the calcium content is very low due to the high vapour pressure whereas the yttrium level in the final ingot is significant. Unexpectedly the oxygen content in TiAl is higher after melting in yttria than in lime despite the higher thermochemical stability of Y_2O_3. A possible explanation could be a difference in the wetting behaviour of both ceramics.

Tab. 2: Contamination of the pilot scale Ti-alloy ingots after inductive melting in ceramic crucibles

Alloy	Ti-50Al		Ti-6Al-4V
Refractory	CaO	Y_2O_3	Y_2O_3
Oxygen content /wt.-%	0.24	0.32	0.74
Ca/Y content /wt.-%	0.012	0.31	0.26

In addition to the chemical analysis of the ingots, one of the CaO crucibles was investigated after three melts of Ti-50Al. Macroscopically figure 6 shows that bottom and walls are considerably infiltrated by the melt but that the original shape of the crucible is maintained. That suggests that besides the mechanical infiltration of the ceramic no significant chemical reaction occurred.

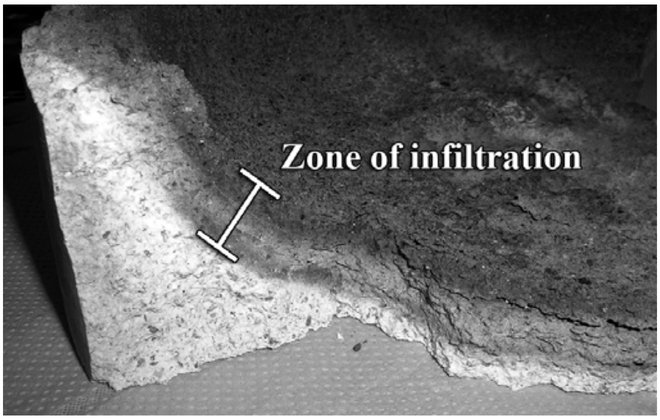

Fig. 6: Cross-section of an infiltrated CaO crucible

For a more detailed examination, several samples were cut out of this CaO crucible and investigated by the means of scanning electron microscopy (SEM). To compare the infiltrated zone with the original material further samples were taken from virgin areas, embedded in epoxy resin and grinded. Figure 7 illustrates the ceramic in the initial state. The bright regions represent pure lime grains, which are surrounded by the darker solidified CaO slurry.

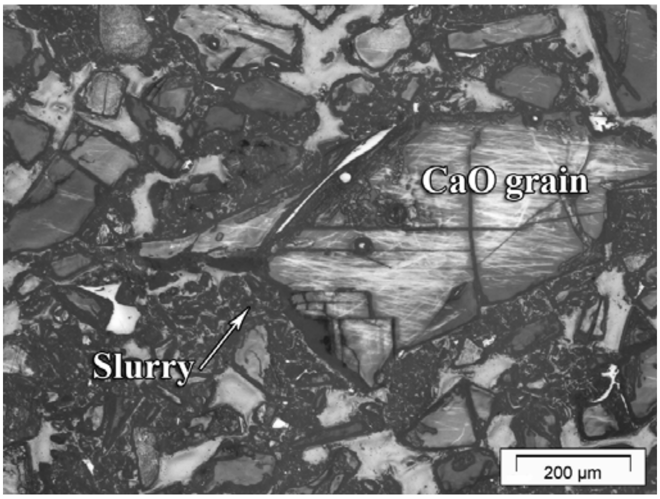

Fig. 7: CaO crucible in the initial state

On the micrograph of the infiltrated ceramic (figure 8) the bright areas represent metallic and the dark regions oxidic phases.

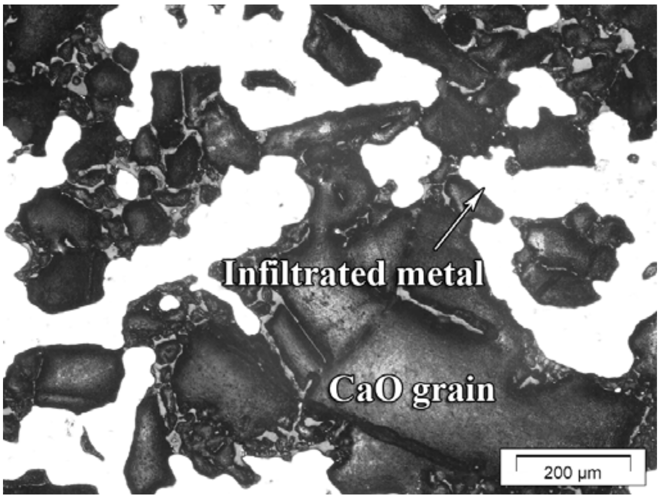

Fig. 8: CaO crucible after infiltration by Ti-50Al

Although both the grains and the slurry consist of nearly pure lime, only the latter seems to react significantly with the γ-TiAl. This can be explained by the smaller size of the CaO particles in the slurry, the associated higher specific surface and unknown binder components used by the supplier. A local chemical analysis of the metallic regions shows that the titanium content is significantly higher than in the alloy charge. That leads to the conclusion that lime preferentially reacts with the aluminium content of the melt to an undetermined but obviously very stable calciumaluminate. However, no new mixed phases containing Al and Ca could be detected and analyzed to support this thesis.

DISCUSSION AND CONCLUSION

Among the investigated oxides, only Y_2O_3 exhibits sufficient thermochemical stability in inductive crucible melting of Ti-6Al-4V without considerable damage of the ceramic. Whilst the oxygen content of 0.5 – 1.0 wt.-% is considered acceptable for numerous applications, the effect of 0.3 – 0.5 wt.-% Yttrium on the material properties has yet to be evaluated.

Owing to the reduced titanium activity in γ-TiAl, all investigated oxides were generally feasible to melt Ti-50Al. However, a significant contamination by oxygen in case of Al_2O_3 and zirconium in case of ZrO_2 advises not to use these oxides. In contrast, the application of CaO provides low oxygen contents of ~0.3 wt.-% and ultra low calcium levels below 0.05 wt.-% and is therefore the best available ceramic for melting of γ-TiAl.

As the integrated IME recycling concept allows an additional deoxidation with Ca in VIM or ESR, the oxygen level can be decreased even further below 600 ppm. Since this operation is associated with an extra pickup of calcium, subsequent remelting in VAR has to follow deoxidation to decrease the Ca content to an acceptable level.

Since the availability of the currently used CaO crucibles is very poor and prices are extremely high, a cheaper technology has to be developed and a supplier has to be found who manufactures crucibles or ceramic sinter masses in a larger scale. Firstly, this provides higher cost effectiveness and secondly, good disposability is a necessary requirement for an industrial application of CaO crucibles to melt γ-TiAl.

To ensure a successful transfer of the obtained results to more complex titaniumaluminides containing further reactive and costly elements like niobium and chromium, additional tests have to be carried out in the future.

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