Tracing Ca and F during Remelting of Titanium-Aluminides in ESR and VAR

J. Reitz, B. Friedrich
RWTH Aachen University, IME Process Metallurgy and Metals Recycling, Intzestrasse 3, 52056 Aachen, Germany

J. C. Stoephasius
TARGUS Management Consulting AG, Dechenstraße 7, D-40878 Ratingen, Germany

ABSTRACT

Pressure electroslag remelting (PESR) of titanium and its alloys under a Ca-CaF_2-CaO slag has been under investigation as a suitable means for the refining and deoxidation of scraps and intermediates from alternative titanium winning processes. Little is known on the solution of Ca and F in the metal phase during ESR and less on the impact of these elements on properties of the remelted material. Modelling of calcium and fluorine activities in CaF_2-based slags suggest that a solution of Ca and F in the metal can be expected in the ppm range. This paper presents a review of the analytical techniques presently applied to precisely track traces of Ca and F in titanium and titanium aluminides.

INTRODUCTION

For the melting and refining of titanium aluminide alloy scrap originating from foundry returns or alternative production routes such as aluminothermic reduction, a novel processing route is presently under investigation. It combines vacuum induction melting (VIM) of γ-TiAl-alloys in CaO crucibles, subsequent deoxidation and refining by pressure electroslag remelting (PESR) and final refining via vacuum arc remelting (VAR) into one process chain.

The core process of this concept electroslag remelting (ESR) of titanium alloys under CaF_2-based fluxes has been investigated by various researchers in the western world [1][2][3][11] starting in the 1960s after earlier successful reports on the method in the Soviet Union. Trials were conducted with regard to pure titanium and alloys then and some contradictory results were obtained concerning the properties of the final metal. In spite of the positive experiences with ESR of titanium in the former USSR, the US and also Europe [6], the process never really competed with VAR on an industrial scale, although not much [2] was published on the mechanical properties and eventual shortcomings of titanium alloys obtained by ESR. However, ESR of titanium alloys is presently still operated on a scientific level, while ESR of steels and superalloys is state of the art on an industrial scale, well understood and accepted.

ESR resembles VAR - nowadays the standard process for refining titanium alloys - in that the remelting takes place in a water-cooled copper crucible. In contrast to VAR, that crucible hosts a molten slag or sometimes called flux. The tip of a consumable electrode dips into the flux and melts when the slag reaches the melting point of the electrode material due to Joule heating by electrical currents. Because of the difference in density between metal and slag, metal droplets travel through the slag and a liquid metal bath collects below, which solidifies and continuously builds up an ingot with a controlled microstructure and smooth surface. Non-metallic inclusions with density equal or lower than the slag phase are being absorbed by the slag and due to large interfacial area, slag-metal reactions are likely to occur with fast kinetics, hence ESR is an effective refining process.

For the ESR of titanium Nafziger [1] identified CaF_2 in an intensive study as the most suitable flux because it exhibits low vapour pressures, good availability, suitable electrical and physical properties and prevents oxygen contamination of the metal due to a minimum of oxide components which would be reduced by the titanium melt otherwise. Unlike other molten salts (e.g. Na-Al-Fluorides applied in aluminium electrolysis) CaF_2 offers complete miscibility with calcium metal in the liquid range [8] which adds interesting refining possibilities in ESR: Dissolution of metallic calcium in the flux allows deoxidation and enhanced purification of the metal phase (e.g. removal of nitride inclusions) which has successfully been demonstrated by Ryabtsev et.al. [4] very recently. The term “active” or “reactive” ESR-slag was introduced for such a reducing slag system.

One major challenge however in the application of Ca-reactive slags, and possibly the reason why Ca-reactive ESR was not applied in earlier research lies in the evaporation of Ca from the slag at the melting temperatures of titanium alloys. This effect can be kinetically suppressed by melting under inert gas overpressure, leading to pressure electroslag remelting (PESR) as a promising process presently under investigation at RWTH Aachen.

It can be assumed that a molten titanium alloy in contact with a CaF_2 flux could dissolve measureable quantities of fluorine. When calcium is applied for deoxidation of the melt, also a certain solution of calcium, to the extent of the solubility product between oxygen and calcium (formation of CaO), can be expected [13]. Upon solidification, solubilities may change compared to the liquid phase and in case of reduced solubility, precipitation of calcium and fluoride compounds of the matrix metal can be expected. On top of that, little is known on the effect of dissolved Ca and F on the properties of titanium and titanium aluminides, yet assumptions are that these elements would proof to act disadvantageous on mechanical properties. On the other hand, recent research on titanium aluminides has shown positive effects of fluorine surface treatment on high temperature corrosion behaviour [5] if exactly the correct amount of fluorine is achieved in the surface. In order to maintain this “halogen effect” on at long time service under high temperature conditions bulk fluorination of titanium aluminium alloys to a certain extent might even prove to be technically interesting.

This paper presents first investigations for a basic research project with the aim to correctly trace the elements fluorine and calcium in titanium alloys along the proposed process chain, with a strong focus on the application of PESR for the melting of titanium and it's alloys, as well as their possible removal by subsequent VAR. The present publication starts with a review on available solubility data and possible analytical methods and shows first attemps to analyse F and Ca in PESR remelted γ-TiAl obtained in lab-scale experiments.

FUNDAMENTALS

SOLUBILITY OF FLUORINE IN TITANIUM

Solubility of fluorine in a liquid titanium melt in equilibrium with a CaF_2 flux can be modelled using simple thermochemical calculations based on the assumption that at process temperatures necessary for ESR of titanium and it's alloys (1600°C – 1800°C) CaF_2 decomposes (eq. 1) and atomic fluorine radicals react readily with the metal by formation of the most simple titanium fluoride TiF (eq. 2) which then dissolves in the melt (eq. 3). This is in analogy to the generally accepted dissolution mechanism for oxygen as TiO.[1]

$$(CaF_2) = \{CaF\} + \{F\} \quad \text{with } \Delta G_{R,1} \qquad \text{(eq. 1)}$$

$$(Ti) + \{F\} = \{TiF\} \quad \text{with } \Delta G_{R,2} \qquad \text{(eq. 2)}$$

$$\{TiF\} = [TiF]_{Ti} \quad \text{with } \Delta G_{R,3} \qquad \text{(eq. 3)}$$

For the observed conditions with metallic calcium dissolved in the active slag and hence substantial vapour pressures of Ca above the melt, the further decomposition of CaF can to be taken into account (eq. 4)

$$\{CaF\} = \{F\} + \{Ca\} \quad \text{with } \Delta G_{R,4} \qquad \text{(eq. 4)}$$

A summary equation (eq. 5) is obtained, which can be expressed by the law of mass-action as (eq. 6) where the equilibrium constant K depends on the sum of the free enthalpies for the single reactions $\Delta G°_{R,total}$ and temperature by an Arrhenius term:

$$\{CaF_2\} + 2\,(Ti) = 2\,[TiF]_{Ti} + \{Ca\} \text{ with } \Delta G_{R,total} \qquad \text{(eq. 5)}$$

$$K = \frac{a^2(TiF)\cdot p(Ca)}{a(CaF_2)\cdot a^2(Ti)} = e^{-\frac{\Delta G^0_{R,total}}{RT}} \qquad \text{(eq. 6)}$$

with the total free enthalpy of reaction given by

$$\Delta G_{R,total} = \Delta G_{R,1} + 2 \times \Delta G_{R,2} + 2 \times \Delta G_{R,3} + \Delta G_{R,4} \quad \text{(eq. 7)}$$

Making the assumption that TiF activity in titanium melts for small concentrations follows Raoult's law and hence fluorine dissolves ideally in the titanium melt, with an activity coeffecent $f_{TiF} = 1$, the equilibrium concentration of fluorine in the metal can be expressed in atomic percent because $x(F) = x(TiF)$. This can be obtained from (eq. 6) as a function of CaF_2 and Ca activity in the slag. Fluorine concentration in wt.% is then obtained by the ratio of the molar mass M_F of fluorine and the average molar masses of the titanium alloy as (eq 8):

$$w(F) \approx \frac{M_F}{\tilde{M}_{Alloy}} \cdot a(Ti) \cdot e^{-\frac{\Delta G^0_{R,total}}{2RT}} \sqrt{\frac{a(CaF_2)}{p(Ca)}} \qquad \text{(eq. 8)}$$

For a pure titanium melt in contact with a pure CaF_2 flux, the activities of CaF_2 and Ti respectively would be unity. hence (eq. 8) simplifies so that the equilibrium concentration of fluorine in the melt can be expressed only as a function of the total free enthalpy (eq. 9):

$$w(F) \approx \frac{M_F}{M_{Ti}} \cdot e^{-\frac{\Delta G^0_{R,total}}{2RT}} \sqrt{\frac{1}{p(Ca)}} \qquad \text{(eq. 9)}$$

This illustrates that for high calcium partial pressures, as with the application of active slags, fluorine content in the metal should approach a temperature dependent minimum when calcium activity in the slag increases towards one. Furthermore, when comparing (eq. 8) and (eq. 9) is becomes obvious that in the ESR of titanium aluminides, when titanium activity is substantially reduced, equilibrium fluorine contents should be lowered relatively to pure titanium. When active slags are applied for deoxidation not only high calcium activities are achieved: the slag dissolves CaO as a product from the reaction between oxygen from the metal and calcium dissolved in the slag.

---

[1] Brackets denote compound or element in equation is () – liquid, {} – gaseous, $[]_x$ – dissolved in phase x

As a result, also the activity of CaF_2 will be reduced and therefore again the fluorine solubility in the metal (eq. 8).

Stoephasius [7] modelled the equilibrium concentration of fluorine in the metal following similar assumptions but including fluorine partial pressure in his expressions instead of calcium partial pressure. In an ideal, closed system the partial pressure of Ca is connected to fluorine concentration via equation 5 and it holds that x(Ca) = 2 x(F). For the case of pure titanium in contact with a pure CaF_2-slag at the melting point of the metal, a fluorine content in the range of 100 ppm was predicted from the calculation (figure 1) depending on the superheat of the slag while at only 0,5 wt% metallic calcium in an active slag which adds to the Ca vapour pressure (eq. 9), fluorine solution in the metal should be reduced by nearly two orders of magnitude.

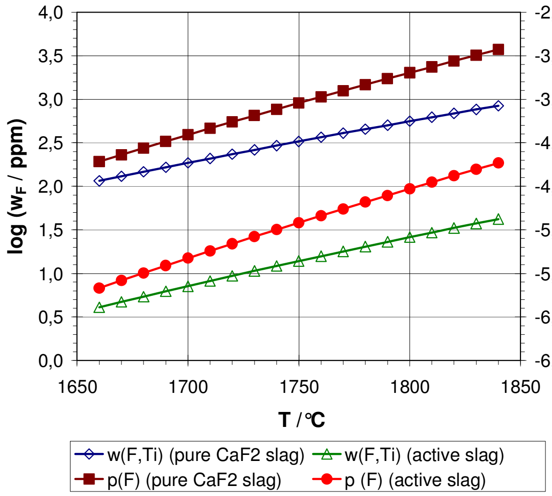

Figure 1: Expected fluorine concentration in titanium melt w(F,Ti) and fluorine partial pressure p(F) for pure CaF_2 slag and active slag containing 0,5 wt.% Ca.

Taking potential kinetic effects and the oxygen content of technically pure CaF_2 fluxes into account, this value seems quite reasonable in comparison with the 60 ppm reported by Scholz et al. [6] for ESR remelted cp. titanium. Nafziger [11] reports 90 ppm for samples obtained after remelting in a CaF_2 slag with addition of carbon a comparatively weak reducing agent. When stronger metallic reductants Y and Gd were added to the flux, fluorine was reported as not detectable for Y and only < 23 ppm for Gd. Trials with the straightforward approach to add Ca to the flux however were never published. When less stable fluorides MgF_2 (i.e. higher fluorine activity at same temperature) were added to the CaF_2 flux, fluorine contents up to 300 ppm were observed as could be expected.

REVIEW OF ANALYTICAL METHODS FOR DETERMINATION OF FLUORINE IN METALS

While the determination of calcium in metals is easily accessible by non-destructive analytical techniques like XFA, fluorine, given the low atomic order number cannot be readily analysed with standard spectroscopic laboratory equipment. XFA can principally detect fluorine but detection limits are above the theoretically expected levels. Lower detection limits could be achieved by ICP but that would require dissolution of the sample and also reaches limited accuracy when traces in the ppm range are to be investigated.

For the determination of fluorine in ESR samples in the 1970s Nafziger [11] used a specific ion-sensitive electrode method and reports uncertainties of the published values of 50%. In parallel microprobe analyses as a support to microscopy provided qualitative detection for fluorine. No fluoride grains could be found in VAR material while 1-5 µm grains containing fluorine were observed on the surface of ESR titanium. Because Ca was not detected by microprobe, these inclusions are suspected to be TiF_n or Ti-O-F.

A compact review of up to date analytical methods for fluorine detection in general is given by Yin et al. [10] They summarize the present state of developed analytical methods for different cases, from water to gases, organic materials and glasses. Their list groups publications on the available techniques into four major categories: electroanalytical methods, spectral analysis, chromatography and miscellaneous which they claim are methods mainly based on radio analysis.

In an more practical work, the solubility of fluorine in magnesium melts was examined by Aarstad at NTNU Trondheim in an attempt to find an alternative covering gas to SF_6 for the magnesium industry [9]. The work compares three analytical techniques to analyse fluorine in Mg samples obtained from different melting trials. The first method is called “SINTALYZER” and was originally developed by SINTEF for use in the aluminum industry, essentially the method is based on ion selective LaF electrodes. Metallic samples need to be dissolved in a buffer and the EMF of the electrode in the solution is determined. Calibration is done by adding controlled amounts of NaF to the solution.

As a second method samples were sent to an external laboratory for glow discharge mass spectrometry (GDMS). In GDMS the solid sample forms the cathode in an argon gas discharge or plasma and over time several atom layers are sputtered off the sample transferred to a separate plasma where they are ionized so that the ions can be separated in a mass spectrometer. GDMS is nearly matrix independent and does not require dissolution of the sample like in photometric or ion sensitive electrode methods. Because of the sputtering technique, also depth profiling is possible in contrast to these bulk methods.

With secondary ion mass spectrometry (SIMS) Aarstad applied a third analytical method. In contrast to GDMS, sputtering is done with a focused ion beam, consisting of, producing ionized secondary particles to be analyzed, again by mass spectrometry. As a conclusion of the results the author favours SIMS over the other methods because of two reasons: While the ion selective electrode delivered reasonable concentrations in the range of 10-100 ppm fluorine in Mg in a first measurement, these values could not be reproduced in a second batch. SIMS delivered excellent results in the same magnitude as "Sintalyzer" while samples analysed by GDMS showed the same dependency from melt temperature in the conducted experiments but fluorine concentration appeared to be an order of magnitude lower than with the other two methods. As a result SIMS was favoured in Aarstad's thesis because of better reproducibility and because the values superimpose neatly with what was obtained by "Sintalyzer".

A drawback in the application of SIMS however in comparison with GDMS is that obviously some matrix effects occur and calibration is necessary by samples doped with F^{19}, which cannot easily be obtained from titanium aluminides. The same holds for electron-probe surface mass spectrometry, which was applied by Lichtman et al. [14] for inspection of a TiF_4 surface layer on HF etched titanium ribbons.

Because of this and after intensive review of the available literature, GDMS is regarded as probably the best available technology for tracing fluorine in titanium and titanium aluminide samples obtained in our works and is therefore applied in the present study.

RESULTS FROM OBTAINED SAMPLES

In order to trace fluorine contamination throughout the proposed processing chain (VIM, PESR, VAR) a batch of spent sputter targets from binary γ-Ti50Al were melted via VIM and deoxidized by PESR as a second step. Samples were cut from the bottom, middle, and top region of the ingot with a grinding blade and then analyzed for their chemical composition with regard to oxygen content and metal concentration, with a special focus on the determination of calcium content.

While the focus of this paper is the determination of F and Ca in γ-TiAl, it should be noted that also the analysis of oxygen down to low ppm values is a matter of it's own. Ca was obtained by X-Ray fluorescence analysis (XFA) and the results are shown in table 1. Oxygen was analysed by hot-gas extraction on a Ströhlein ON-Mat 8500 (Lab 1) using Ni baskets and secondly on a LECO PCH 900 (Lab 2) under application of Ni-flux wires. While samples in Lab 1 were etched for one minute in a solution of HF:HNO3:H2O (1:4:10) to remove surface oxidation potentially resulting from sampling, samples at Lab 2 were not etched. Oxygen values from Lab 1 are in good accordance with the solubility product between Ca and O in γ-TiAl expected after ESR (compare [7],[13]) but are at the lower detection limit of the apparatus and method. There seems to be some contradiction to the values from Lab 2 which are more trustworthy with respect to the analytical method but contradict the trend in Ca content. These results are presently under reexamination by a third lab.

Table 1: Calcium is significantly measureable in samples obtained from PESR remelted γ-Ti50Al.

Sample	Ca /ppm	O /ppm	O /ppm
Top	660	100	274
Middle	1110	15	353
Bottom	1260	15	493

Based on the findings cited above for the available methods on fluorine detection, samples from the same remelted ingot were sent for GDMS analysis to an external lab. Analysis of the samples is still ongoing while this paper is due. Results can therefore only be presented at the conference.

In addition to bulk analysis REM micrographs were prepared from the same PESR ingot in order to trace eventual fluorine containing inclusions or grain-boundary segregations (figure 2). Inclusions in the size-range of 1-10 µm were found, mainly in the darker (Al-rich), late solidified γ-TiAl matrix and were hence regarded as precipitates. Two types of these could be identified by EDX one being a Mg-Ca-Al intermetallic (light gray) the other phase a Si-Al-Oxide (dark gray). However, no metal-fluoride precipitates could be found. As far as Ca is concerned, no measurable concentrations of Ca could be found by EDX in the solidified matrix material, but only observed in the mentioned Mg-Ca-Al precipitates.

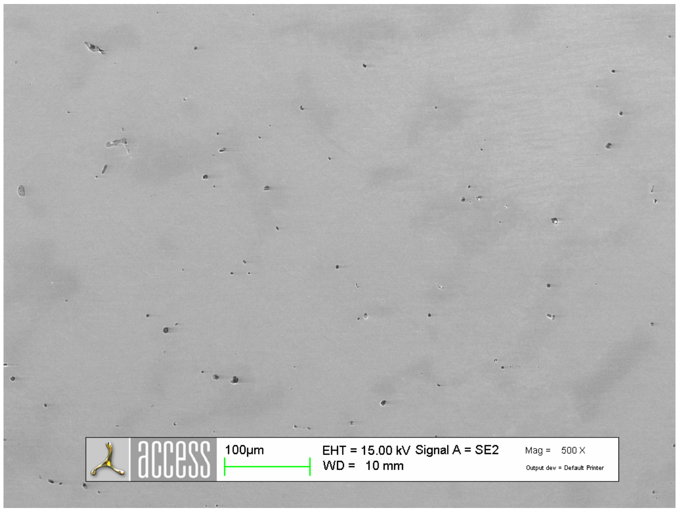

Figure 2: REM image of binary γ-Ti50Al remelted and deoxidized by PESR under active Ca-CaF_2 slag.

DISCUSSION

After concluding that fluorine can possibly be dissolved in titanium melts in concentrations ~ 100 ppm and that dissolution will reduced by two orders of magnitude when “active slags” containing metallic calcium are applied, an open question remains towards the solubility of fluorine in solid Ti. No studies in literature could be found up to now on the formation of TiF or other fluorine precipitates upon solidification, although some indications exists that titanium samples from ESR show somewhat reduced mechanical properties and exhibit fluorine containing inclusions in comparison with VAR remelted material [2] In a publication on electroslag welding of titanium sheets where CaF_2 is used as a flux, the authors [12] observed that the welded material has kept yield strength but shows slight deterioration in elongation and fracture toughness, which they explain by excessive grain growth during the welding. The question if segregations could be responsible for weaker mechanical properties is especially interesting with regard to titanium aluminde alloys where not only the formation of TiF but of $Ti_xAl_yF_z$ phases would theoretically be possible. However fluorine containing phases could not be identified by REM-EDX in the micrometer range and therefore the matter will be examined more in detail.

CONCLUSION

Electroslag remelting offers interesting potential for the refining and deoxidation of titanium and titanium aluminide alloys at the heart of a whole process chain in combination with vacuum induction melting and vacuum arc remelting. In ESR the metal comes into contact with a CaF_2 based flux and hence a certain pick-up of fluorine in the lower ppm range can be expected from theoretical calculations. The impact of fluorine and potential fluoride precipitation is not well examined and published, also because this element is not easily analysed by conventional laboratory equipment. Hence an effort was made to trace fluorine contents in ESR remelted titanium aluminide material in order to support further research on process development and microstructural observations.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the support of ACCESS e.V., Aachen, Germany for preparation and interpretation of the REM micrographs.

REFERENCES

1. R.H. Nafziger; “Slag compositions for Titanium Electroslag Remelting and Effects of Selected Melting Parameters”, in: Second International Symposium on Electroslag Remelting Technology, September 23-25 1969
2. C.E. Armantrout, R.H. Nafziger; “Development of Electroslag Melting Technique for Titanium: Selected Properties of Fabricated Material”; in: Proceedings of the Seventy-Third Annual Meeting of the American Foundryman’s Society, Volume 77, p. 353-359
3. B.E. Paton, B.I. Medovar, M.G. Benz, R.H. Nafziger, L.B. Medovar; “ESR for Titanium: Yesterday, Today, Tomorrow”; in: Proceedings of the 9th World Conference on Titanium, St. Petersburg, Jue 7-11 1999
4. M.G. Benz, A.D. Ryabtsev; “ESR as a Fast Technique to Dissolve Nitrogen-rich inclusions in Titanium”; in: Mat. Res. Innovat. 1999, p. 364-368
5. Schütze, M, Donchev, A; “Oxidationsschutz durch Fluorbehandlung”, in: Oberflächentechnik, 60 (2006) Nr. 12.
6. Scholz, H. et al.; “An Advanced ESR Process for the Production of Ti-Slabs”; in: Lütjering, G. and Albrecht, J. (Ed.): Ti-2003 Science and Technology, 2004, Wiley-VCH-Verlag, Weinheim, pp. 205-212
7. Stoephasius, J.C., Reitz, J., Friedrich, B.; “ESR Refining Potential for Titanium Alloys using a CaF2-based Active Slag”; in: Advanced Engineering Materials 9, No. 4, 2007; DOI: 10.1002/adem.200700009
8. B. D. Lichter, M. A. Bredig; “Solid and Liquid Phase Miscibility of Calcium Metal and Calcium Fluoride”; in: Journal of the Electrochemical Society, Vol. 112, Nr. 5, May 1965, p. 506ff
9. Aarstad, K; “Solubility of Fluorine in molten Magnesium”; doctoral thesis; NTNU Trondheim, Norway, May 2004
10. F Yin, Y Yao, CC Liu, ML Wena; “Developments in the analysis of fluorine; in: Fluoride Vol. 34 No. 2 114-125 2001
11. Nafziger, R.H.; “Electroslag melting of titanium and aluminium”; in: The Electroslag remelting process, 1976, U.S. Dept. of the Interior, Bureau of Mines
12. Devletian, Chen, Wood, Eagar, Caplan; “Fundamental aspects of electroslag welding of titanium alloys”; in: Recent Trends in Welding Science and Technology, ASM, 1990
13. Tsukihashi, F. et al.; “Thermodynamics of Calcium and Oxygen in Molten Titanium and Titanium-Aluminium Alloy”; in: Metallurgical and Materials Transactions B 27B (1996) December, pp. 967-972
14. D Lichtman and T R Kirst; “Electron-probe study of fluorine-contaminated titanium”, in: J Vac Sei Technol, 3, 1966, 224.