Research for Sustainable Technologies

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Stiftung bürgerlichen Rechts

A. Donchev, M. Galetz

The fluorine effect for the high temperature oxidation protection of Ti-based alloys – A thermodynamic approach

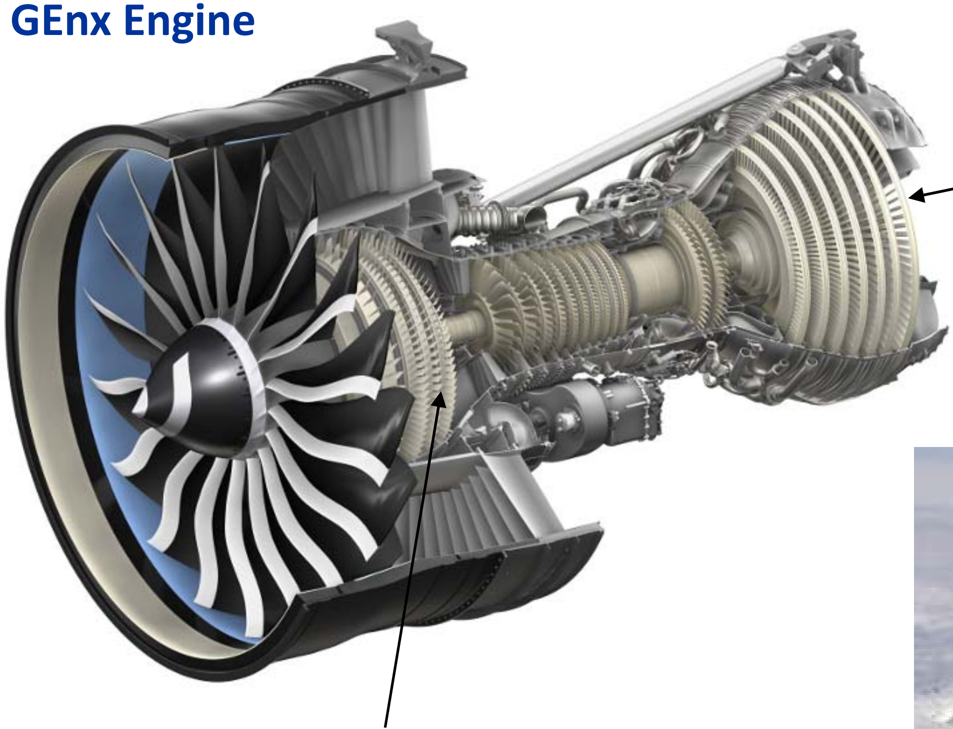
GTT Workshop, July 1st. 2016

Materials
Chemical Engineering
Biotechnology

Motivation

Use of Ti-based light weight materials to increase the efficiency of e.g. jet engines.

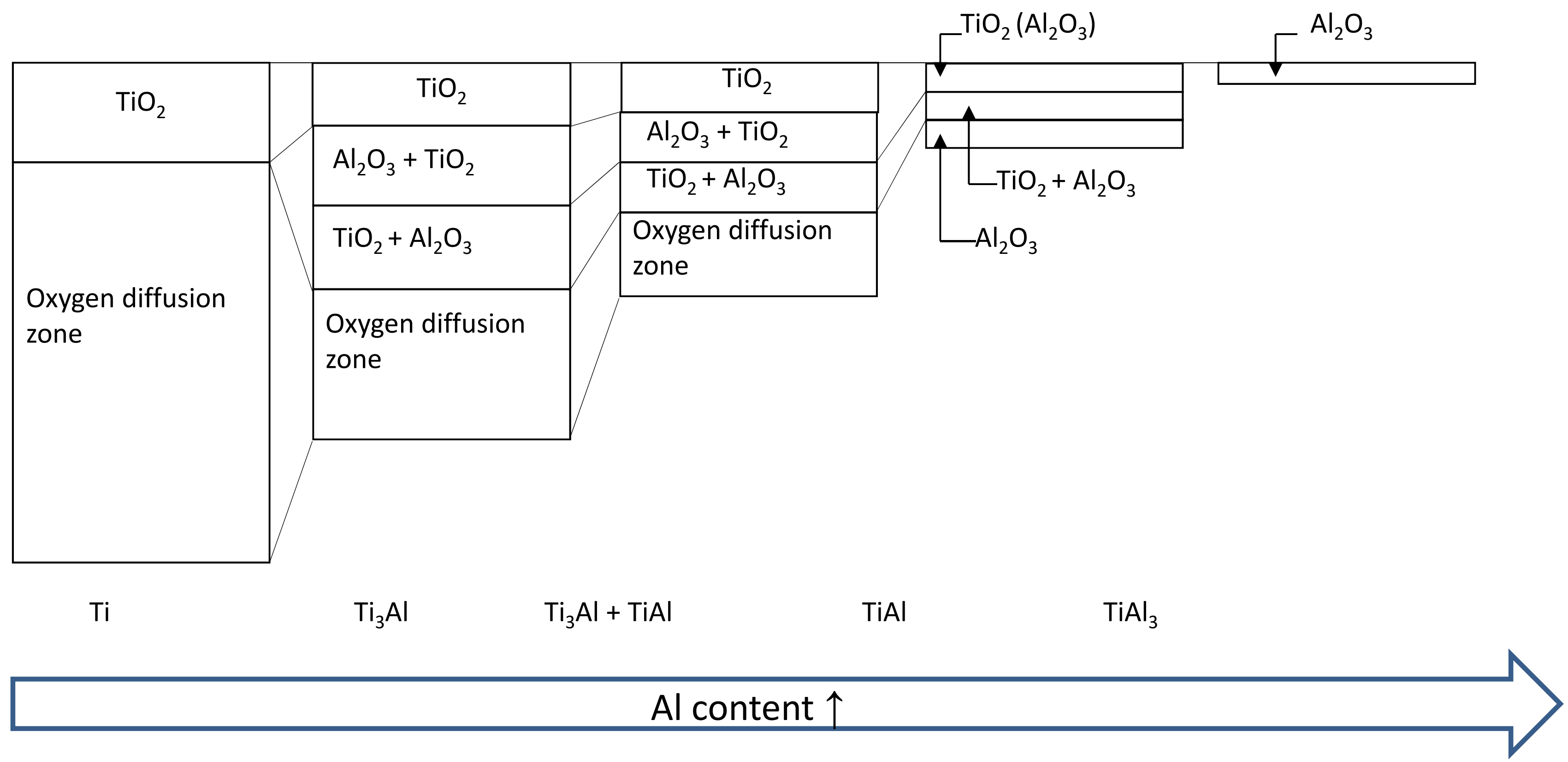
GEnx Engine



TiAl low pressure turbine blades used in the last two stages (T < 700°C) ρ ca. 4 g/cm³

Ti low pressure compressor blades (T < 500°C) ρ ca. 4.5 g/cm³

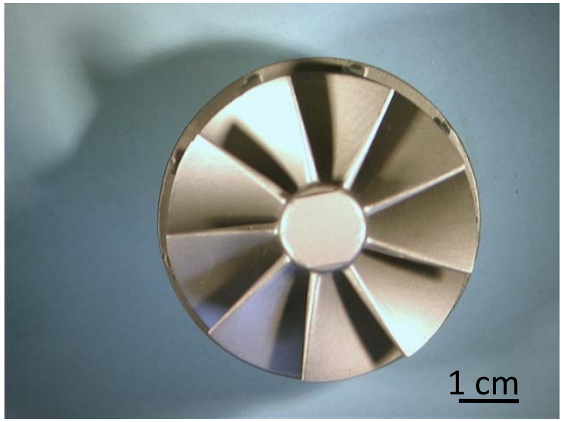
Oxidation of Ti-Alloys and Titanium Aluminides



Scheme of the oxide layers and the oxygen diffusion zone on titanium and titanium aluminides
(J.L. Smialek et al.; Mat. Res. Soc. Symp. Proc. 364(1995)1935)

⇒ Embrittlement by oxygen inward diffusion, mixed scale non-protective!

Destruction of TiAl-Components



Before HT-exposure

After 100h at 1050°C in air

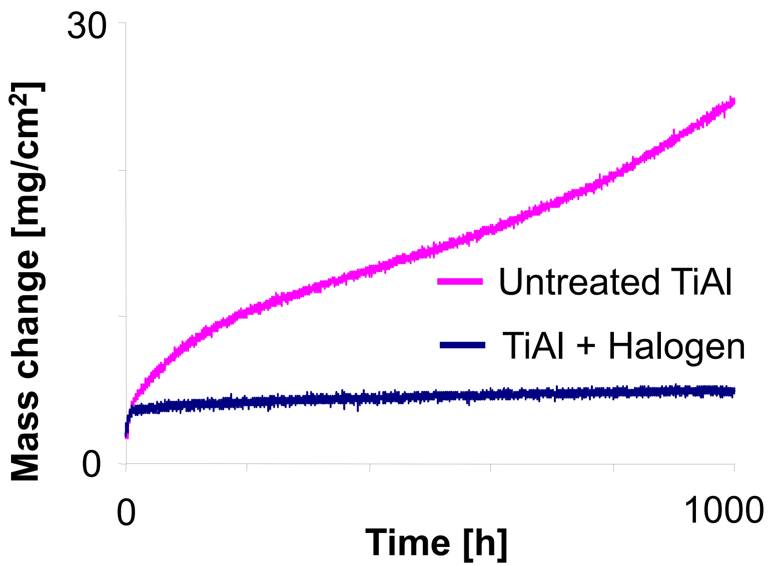
After 1200h at 1050°C in air

Insufficient high temperature stability

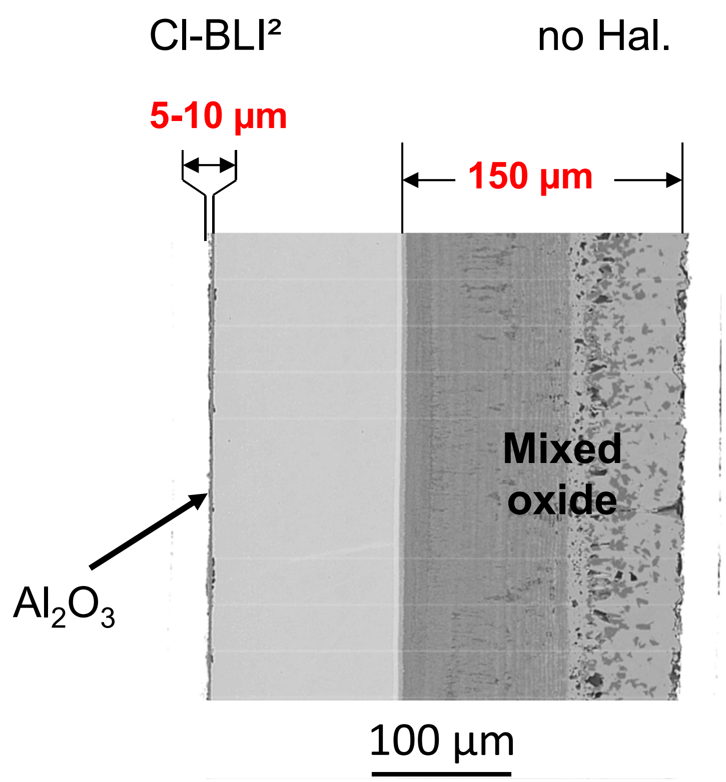
⇒ **<u>Improvement of the oxidation resistance necessary!</u>**

The Halogen Effect

TiAl, 900°C, 1000 h, air



Thermogravimetric data



SEM-image of a TiAl-sample implanted on the left side with Cl

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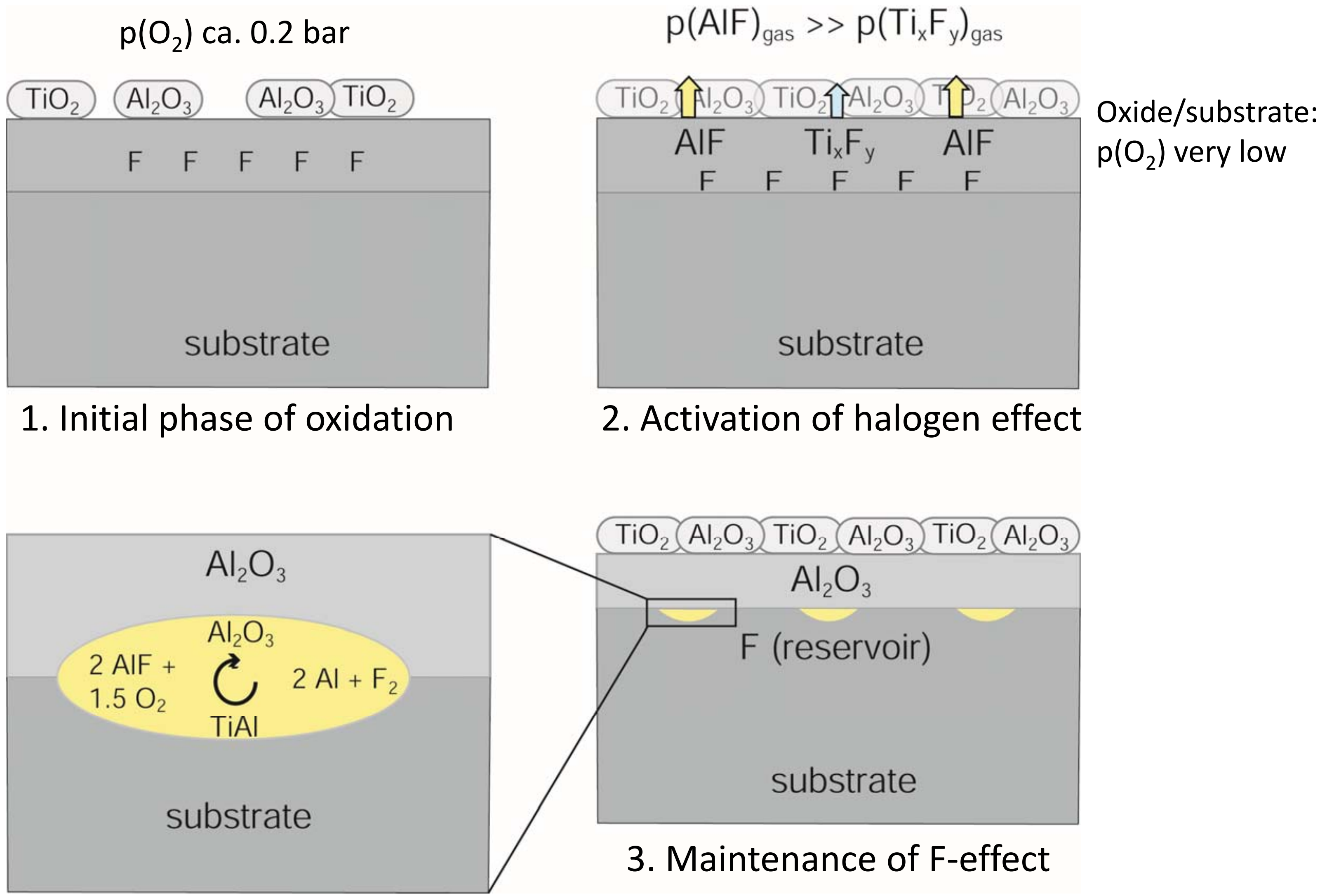
Mechanism



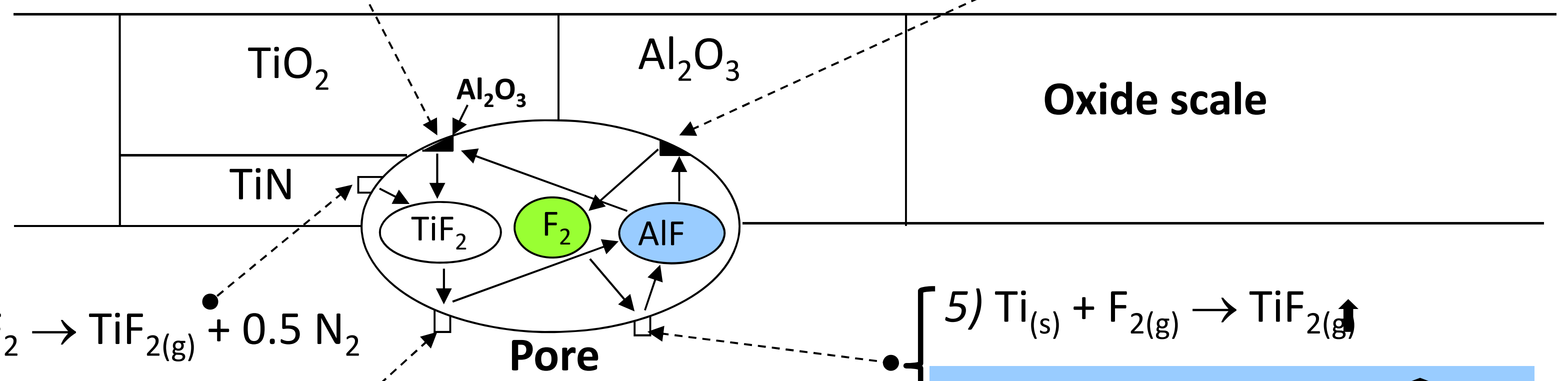
p(O2) ca. 0.2 bar
TiO2
Al2O3
Al2O3
TiO2
F F F F F
substrate
1. Initial phase of oxidation
p(AlF)gas >> p(TixFy)gas
TiO2 Al2O3 TiO2 Al2O3 TiO2 Al2O3
AlF TixFy AlF
F F F F F
substrate
2. Activation of halogen effect
Oxide/substrate:
p(O2) very low
Al2O3
Al2O3
2 AlF +
1.5 O2
2 Al + F2
TiAl
substrate
TiO2 Al2O3 TiO2 Al2O3 TiO2 Al2O3
Al2O3
F (reservoir)
substrate
3. Maintenance of F-effect

Reactions

1a) $3\ TiO_2 + 4\ AlF_{(g)} \rightarrow 2\ Al_2O_3 + 2\ TiF_{2(g)} + Ti_{(s)}$

1b) $3\ TiO_2 + 4\ AlF_{(g)} \rightarrow 2\ Al_2O_3 + TiF_{2(g)} + 2\ TiF_{(g)}$

2) $2\ AlF_{(g)} + 1.5\ O_2 \rightarrow Al_2O_3 + F_{2(g)}$



3) $TiN_{(s)} + F_2 \rightarrow TiF_{2(g)} + 0.5\ N_2$

4) $2\ Al_{(s)} + TiF_{2(g)} \rightarrow 2\ AlF_{(g)} + Ti_{(s)}$

5) $Ti_{(s)} + F_{2(g)} \rightarrow TiF_{2(g)} \uparrow$

6) $2\ Al_{(s)} + F_2 \rightarrow 2\ AlF_{(g)} \uparrow$

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Reactions of TiAl

$$Al_{(TiAl)} + 0.5\ F_2 \rightarrow AlF_{(g)}\ ;\ \Delta G°_{900°C} = -\ 3.57 \times 10^5\ (J/mol)$$

$$Al_{(TiAl)} + 0.5\ Cl_2 \rightarrow AlCl_{(g)}\ ;\ \Delta G°_{900°C} = -\ 1.48 \times 10^5\ (J/mol)$$

$$Al_{(TiAl)} + 0.5\ Br_2 \rightarrow AlBr_{(g)}\ ;\ \Delta G°_{900°C} = -\ 9.85 \times 10^4\ (J/mol)$$

$$Al_{(TiAl)} + 0.5\ I_2 \rightarrow AlI_{(g)}\ ;\ \Delta G°_{900°C} = -\ 6.19 \times 10^4\ (J/mol)$$

$$Ti_{(TiAl)} + 0.5\ F_2 \rightarrow TiF_{(g)}\ ;\ \Delta G°_{900°C} = -\ 1.92 \times 10^5\ (J/mol)$$

$$Ti_{(TiAl)} + 0.5\ Cl_2 \rightarrow TiCl_{(g)}\ ;\ \Delta G°_{900°C} = +\ 2.77 \times 10^4\ (J/mol)$$

$$Ti_{(TiAl)} + Cl_2 \rightarrow TiCl_{2(g)}\ ;\ \Delta G°_{900°C} = -\ 2.68 \times 10^5\ (J/mol)$$

$$Ti_{(TiAl)} + 0.5\ Br_2 \rightarrow TiBr_{(g)}\ ;\ \Delta G°_{900°C} = +\ 5{,}09 \times 10^4\ (J/mol)$$

$$Ti_{(TiAl)} + Br_2 \rightarrow TiBr_{2(g)}\ ;\ \Delta G°_{900°C} = -1{,}81 \times 10^5\ (J/mol)$$

$$Ti_{(TiAl)} + 0.5\ I_2 \rightarrow TiI_{(g)}\ ;\ \Delta G°_{900°C} = +\ 1{,}10 \times 10^5\ (J/mol)$$

$$Ti_{(TiAl)} + I_2 \rightarrow TiI_{2(g)}\ ;\ \Delta G°_{900°C} = -1{,}23 \times 10^5\ (J/mol)$$

Reactions of MeX (X = F, Cl, Br, I)

$4\ AlF_{(g)} + 3\ O_2 \rightarrow 2\ Al_2O_{3(s)} + 2\ F_2$; $\Delta G°_{900°C} = -\ 1.19 \times 10^6$ (J/mol)

$4\ AlCl_{(g)} + 3\ O_2 \rightarrow 2\ Al_2O_{3(s)} + 2\ Cl_2$; $\Delta G°_{900°C} = -\ 2.03 \times 10^6$ (J/mol)

$4\ AlBr_{(g)} + 3\ O_2 \rightarrow 2\ Al_2O_{3(s)} + 2\ Br_2$; $\Delta G°_{900°C} = -\ 2.22 \times 10^6$ (J/mol)

$4\ AlI_{(g)} + 3\ O_2 \rightarrow 2\ Al_2O_{3(s)} + 2\ I_2$; $\Delta G°_{900°C} = -\ 2.53 \times 10^6$ (J/mol)

$2\ TiF_{(g)} + 2\ O_2 \rightarrow 2\ TiO_{2(s)} + F_2$; $\Delta G°_{900°C} = -\ 1{,}09 \times 10^6$ (J/mol)

$TiF_{2(g)} + O_2 \rightarrow TiO_{2(s)} + F_2$; $\Delta G°_{900°C} = -\ 7{,}93 \times 10^4$ (J/mol)

$2\ TiCl + 2\ O_2 \rightarrow Cl_2 + 2\ TiO_{2(s)}$; $\Delta G°_{900°C} = -\ 1.53 \times 10^6$ (J/mol)

$TiCl_{2(g)} + O_2 \rightarrow TiO_{2(s)} + Cl_2$; $\Delta G°_{900°C} = -\ 4{,}69 \times 10^5$ (J/mol)

$2\ TiBr_{(g)} + 2\ O_2 \rightarrow 2\ TiO_{2(s)} + Br_2$; $\Delta G°_{900°C} = -\ 1{,}57 \times 10^6$ (J/mol)

$TiBr_{2(g)} + O_2 \rightarrow TiO_{2(s)} + Br_2$; $\Delta G°_{900°C} = -\ 5{,}56 \times 10^5$ (J/mol)

$2\ TiI_{(g)} + 2\ O_2 \rightarrow 2\ TiO_{2(s)} + I_2$; $\Delta G°_{900°C} = -\ 1{,}69 \times 10^6$ (J/mol)

$TiI_{2(g)} + O_2 \rightarrow TiO_{2(s)} + I_2$; $\Delta G°_{900°C} = -\ 6{,}13 \times 10^5$ (J/mol)

Al-Flux

Necessary amount of Al calculated from the parabolic rate constant

(1) $J_{Al}^{ox} = \frac{1}{48}\left(\frac{k_p}{t}\right)^{\frac{1}{2}} \qquad \frac{\text{mol Al}}{\text{cm}^2 \cdot \text{sec}}$

K_p = 5×10^{-13} $g^2/cm^4 \cdot sec$ at 900°C so after 60 sec of oxidation

J_{Al}^{ox} = 2×10^{-9} $mol/cm^2 \cdot sec$

Deduced from the kinetic gas theory for AlX (X = hal.) the flux is as follows

(2) $J_{AlX} = J_{Al} = 44.3 \frac{P_{AlX}}{(M_{AlX}T)^{\frac{1}{2}}} \qquad \frac{\text{mol Al}}{\text{cm}^2 \cdot \text{sec}}$

with p_{AlX} = partial pressure and M_{AlX} = molar weight.

In the case of AlCl (2) turns into $J_{Al} = 0.164 P_{AlCl} \frac{\text{mol Al}}{\text{cm}^2 \cdot \text{sec}}$

The fluxes must be equal $J_{Al}^{ox} = J_{Al}$ ($2\times10^{-9} = 0.164 P_{AlCl}$)

$\Rightarrow \boxed{P_{AlCl}^{min} = 1\times10^{-8} \text{ atm}}$

Pressure $\leftrightarrow$ k_p

T [°C]	$k_p(Al_2O_3)$ [g^2/cm^2s]	P_{AlCl}^{min} [atm]	$P_{Cl_2}^{min}$ [atm]
700	1×10^{-15}	5×10^{-10}	2.5×10^{-10}
800	5×10^{-14}	4×10^{-9}	2×10^{-9}
900	5×10^{-13}	1×10^{-8}	5×10^{-7}
1000	1×10^{-12}	2×10^{-8}	1×10^{-8}
1100	8×10^{-12}	5×10^{-8}	2.5×10^{-8}

Parabolic rate constants and necessary minimum amounts /partial pressures of AlCl and Cl_2, respectively.

FactSage Results I (F)

Excerpt of the tabular output from the Equilib menu: T = 900°C

Compound	Pressure / bar	Compound	Pressure / bar	Compound	Pressure / bar
AlF	3.1416 E-08	AlF	3.1416 E-07	AlF	3.1416 E-06
Al_2O	4.0640 E-09	Al_2O	4.0640 E-09	Al_2O	4.0640 E-09
Al	6.5253 E-10	Al	6.5253 E-10	Al	6.5253 E-10
AlF_2	5.6573 E-17	AlF_3	1.9990 E-14	AlF_3	1.9990 E-11
Ti	8.8189 E-17	AlF_2	1.4258 E-14	AlF_2	1.4258 E-12
Al_2	5.6573 E-17	AlFO	5.1448 E-16	TiF_3	4.7494 E-14
AlFO	5.1448 E-17	TiF	5.0519 E-16	TiF_2	2.4699 E-14
TiF	5.0519 E-17	TiF_2	2.4699 E-16	AlFO	5.1448 E-15
AlF_3	1.9990 E-17	Ti	8.8189 E-17	TiF	5.0519E-15
TiF_2	2.4699 E-18	Al_2	5.6573 E-17	Ti	8.8189 E-17
TiO	2.7096 E-19	TiF_3	4.7494 E-17	Al_2	5.6573 E-17
N_2	1.0000 E-15	N_2	1.0000 E-15	N_2	1.0000 E-15
O_2	1.0000 E-37	O_2	1.0000 E-37	O_2	1.0000 E-37
F_2	1.0000 E-44	F_2	1.0000 E-42	F_2	1.0000 E-40

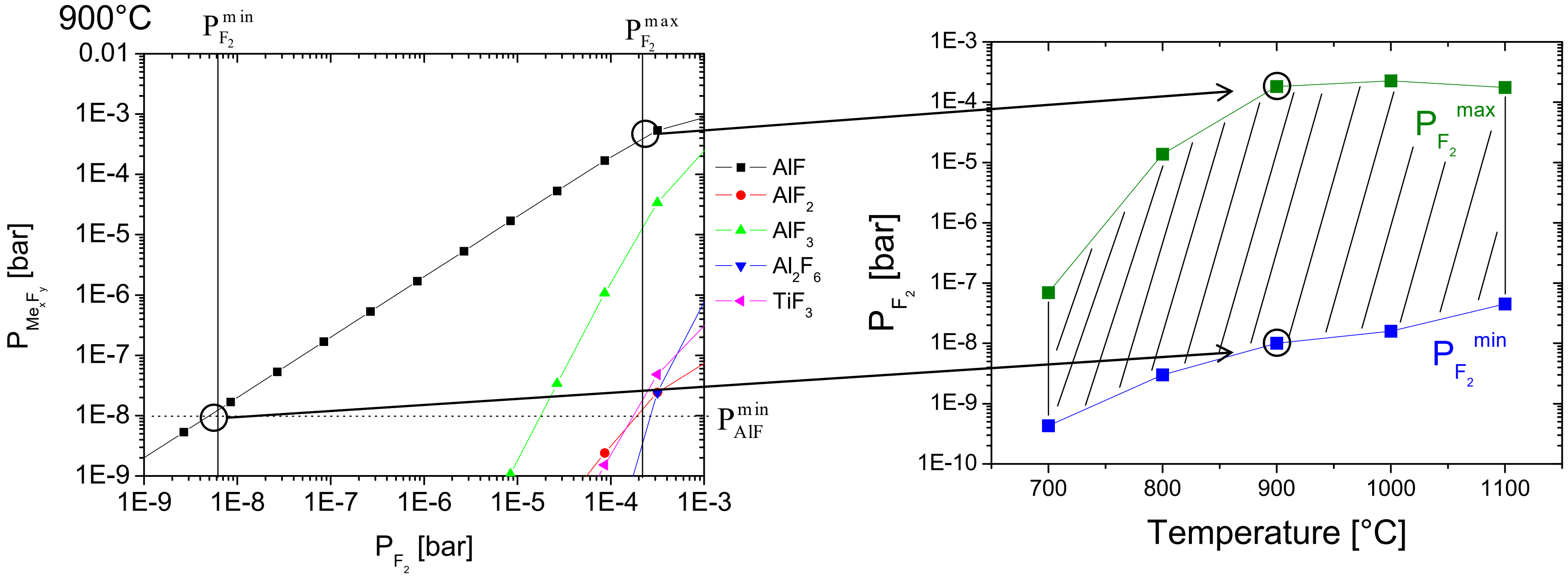
FactSage Results II (Cl)

Excerpt of the tabular output from the Equilib menu: T = 900°C

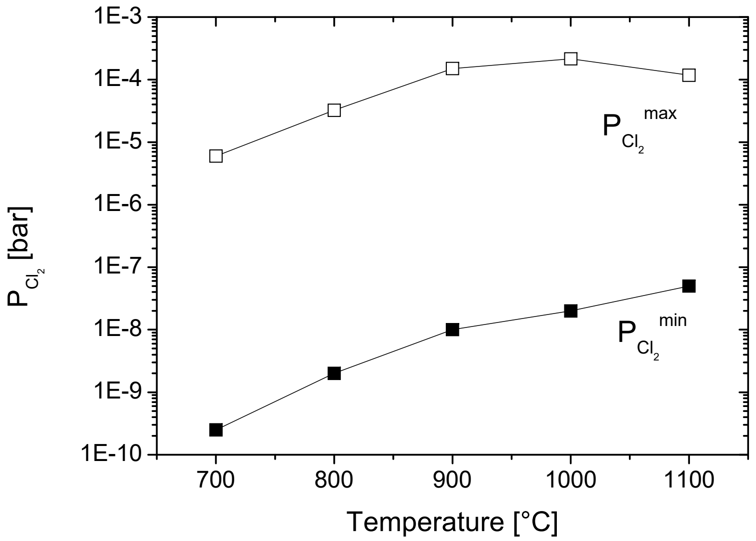
Compound	Pressure / bar	Compound	Pressure / bar	Compound	Pressure / bar
AlCl	1.5092 E-08	AlCl	1.5092 E-07	AlCl	1.5092 E-06
Al_2O	4.0640 E-09	Al_2O	4.0640 E-09	Al_2O	4.0640 E-09
Al	6.5253 E-10	Al	6.5253 E-10	Al	6.5253 E-10
$AlCl_2$	1.2392 E-15	$AlCl_2$	1.2392 E-13	$AlCl_2$	1.2392 E-11
Cl	3,5274 E-16	$AlCl_3$	9.4609 E-15	$AlCl_3$	9.4609 E-12
Ti	8.8189 E-17	Cl	3,5274 E-15	$TiCl_2$	1.1376 E-13
Al_2	5.6573 E-17	$TiCl_2$	1.1376 E-15	Cl	3,5274 E-14
$TiCl_2$	1.1376 E-17	Ti	8.8189 E-17	$TiCl_3$	7.8854 E-15
$AlCl_3$	9.4609 E-18	TiCl	8.1550 E-17	Ti	8.8189 E-17
TiCl	8.1550 E-18	Al_2	5.6573 E-17	Al_2	5.6573 E-17
TiO	2.4699 E-18	$TiCl_3$	7.8854 E-18	AlClO	7.4107 E-18
N_2	1.0000 E-15	N_2	1.0000 E-15	N_2	1.0000 E-15
O_2	1.0000 E-37	O_2	1.0000 E-37	O_2	1.0000 E-37
Cl_2	1.0000 E-26	Cl_2	1.0000 E-24	Cl_2	1.0000 E-22

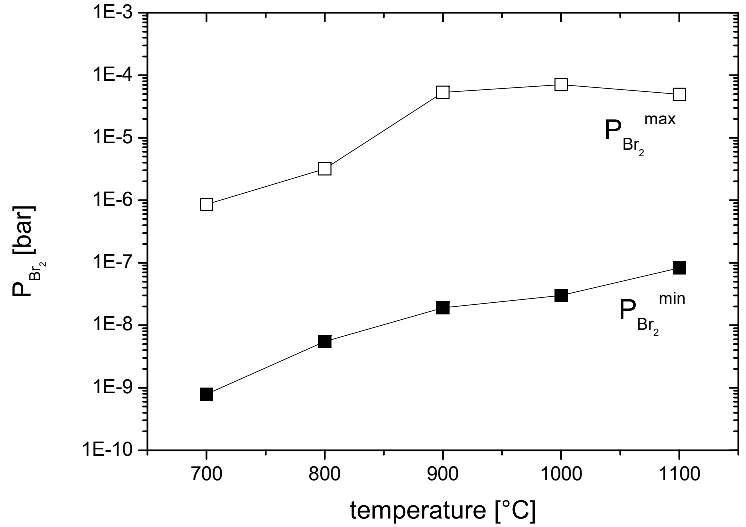
Fluorine Pressures

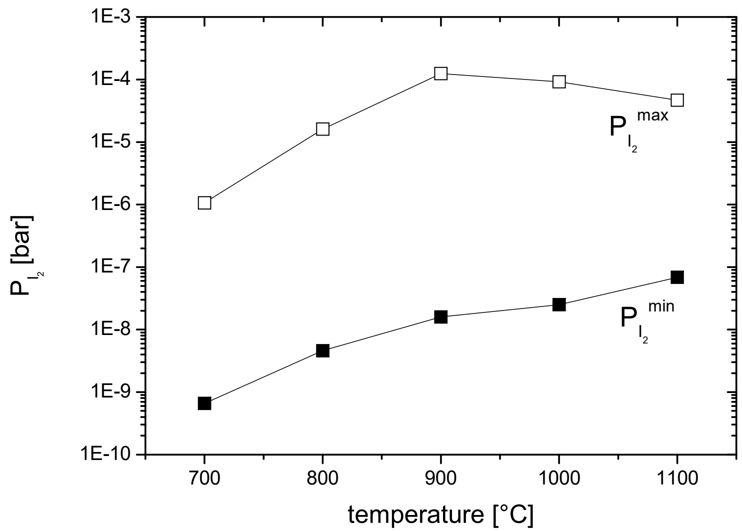
Conditions at the metal/oxide interface (low partial pressures of oxygen and nitrogen)



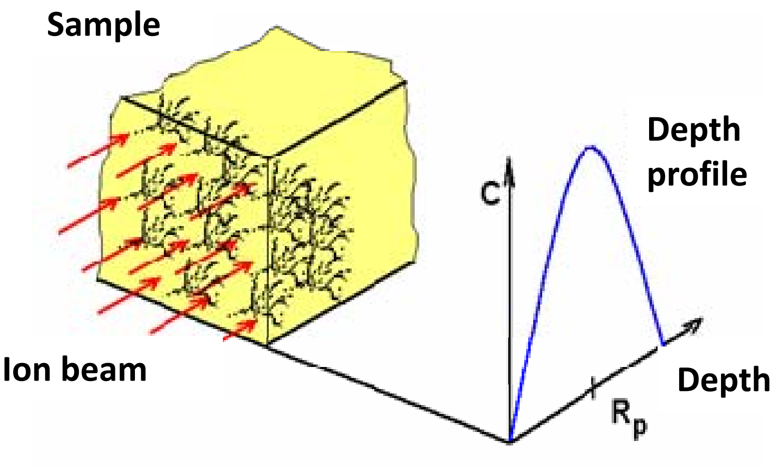
Limits of the Cl-, Br- and I-Effect



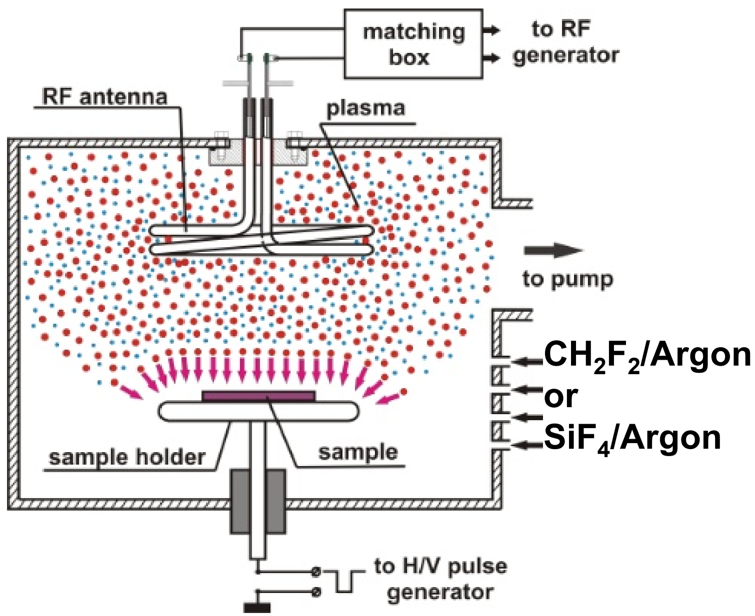




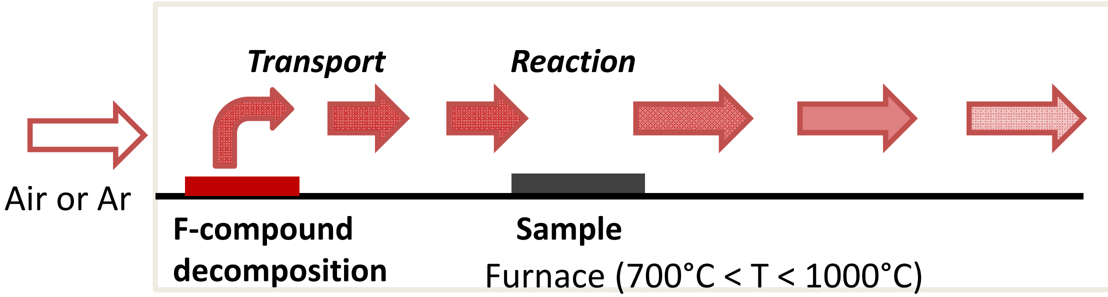
Fluorine Applications



Beamline ion implantation



Plasma immersion ion implantation



Gas phase process

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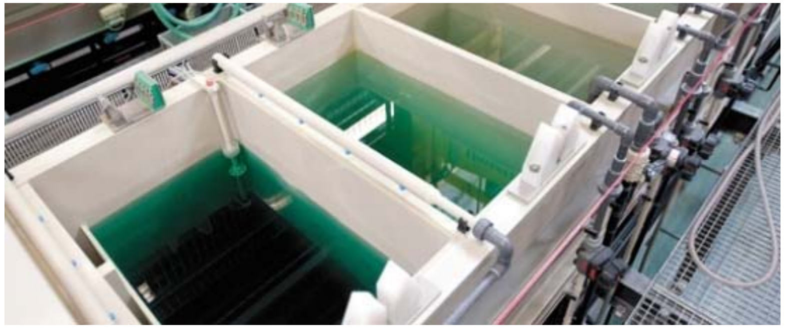
Liquid Fluorine Applications

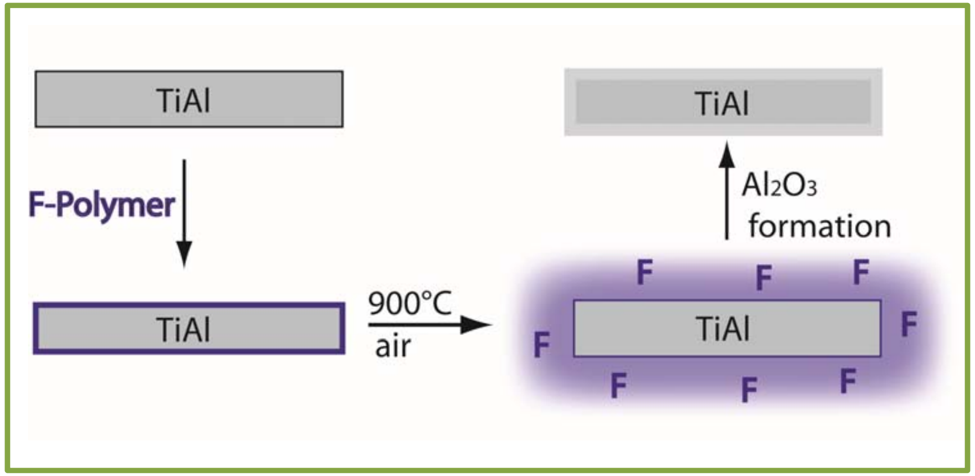


Spraying **Painting**

of F-containing compounds:
F-polymer spray or suspension, F-paste

Dipping

in F-containing acids, e.g. $HF_{(aq.)}$



Activation process at elevated temperatures

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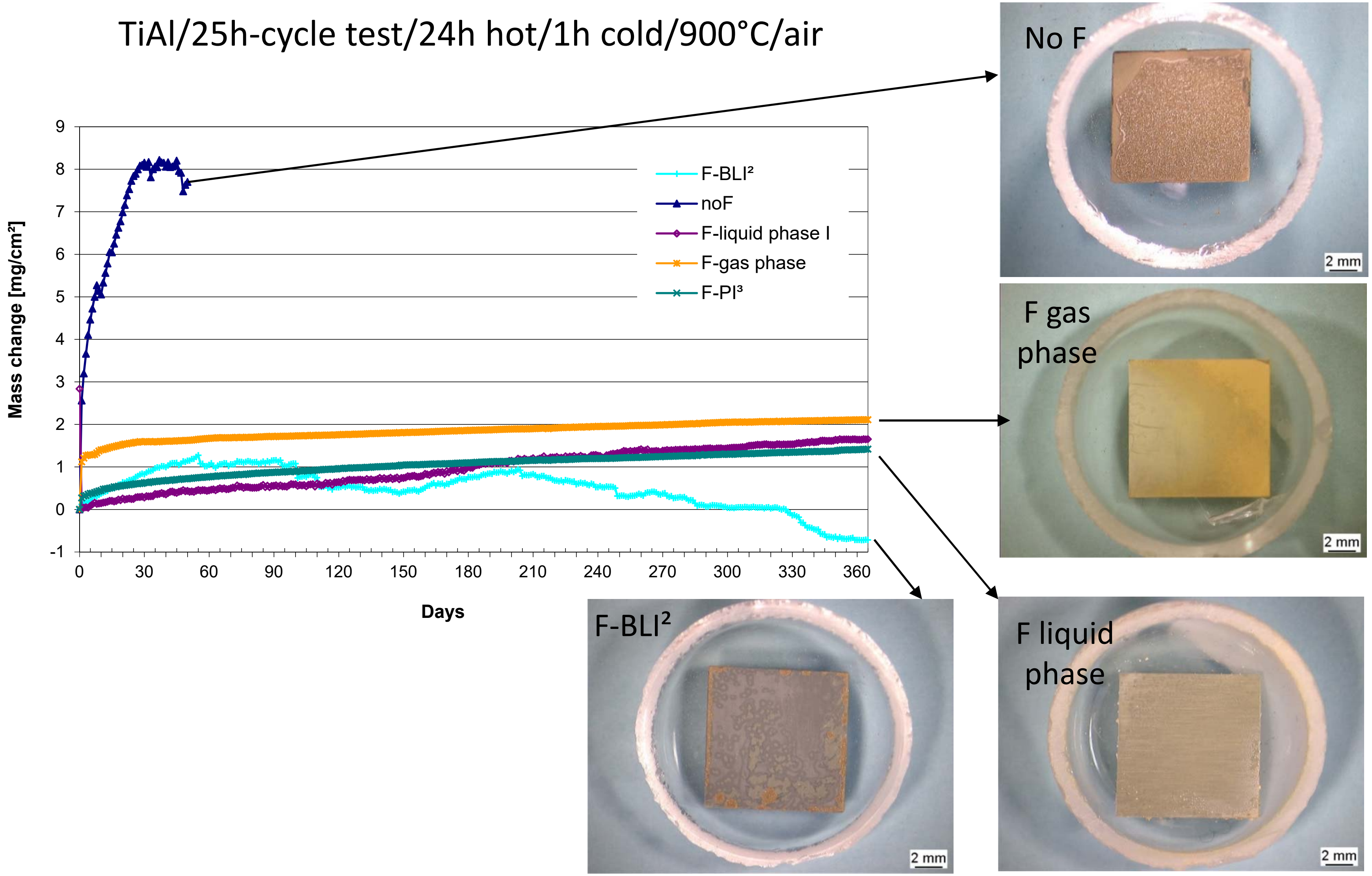
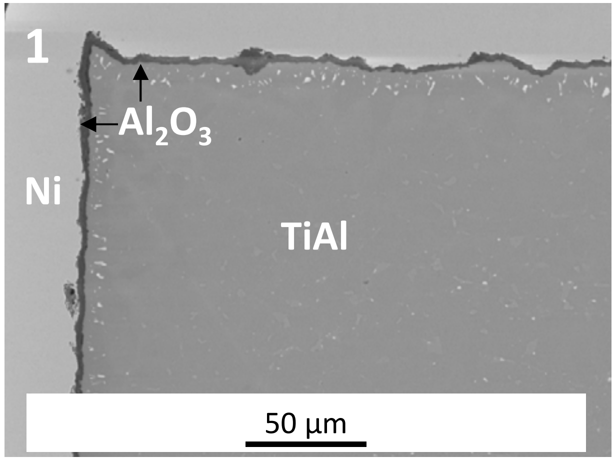
Long Term Stability of the Fluorine effect

TiAl/25h-cycle test/24h hot/1h cold/900°C/air



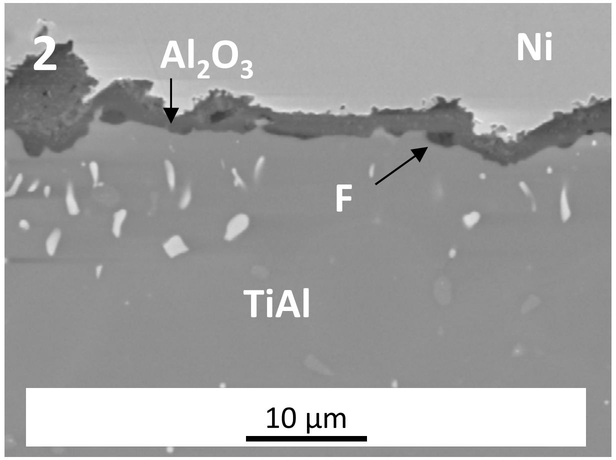
Proof of Fluorine

TiAl + F-PI³/25h-cycle test/24h hot/1h cold/900°C/8760h/air



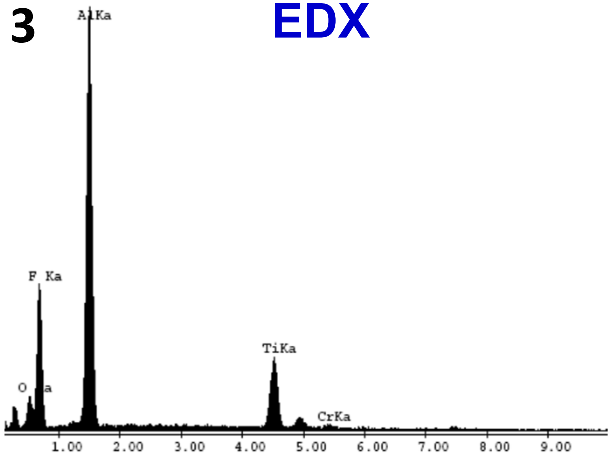
1) SEM-image of one edge

2) SEM-image of the Al_2O_3-layer



3

EDX



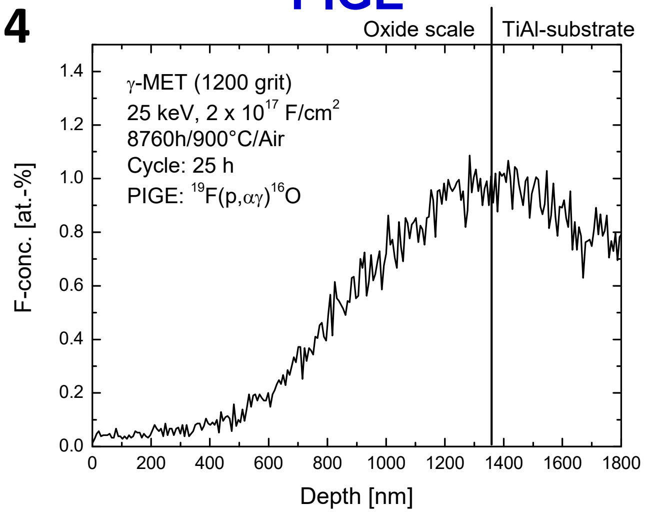
Proof of F by

3) EDX

4) PIGE

4

PIGE



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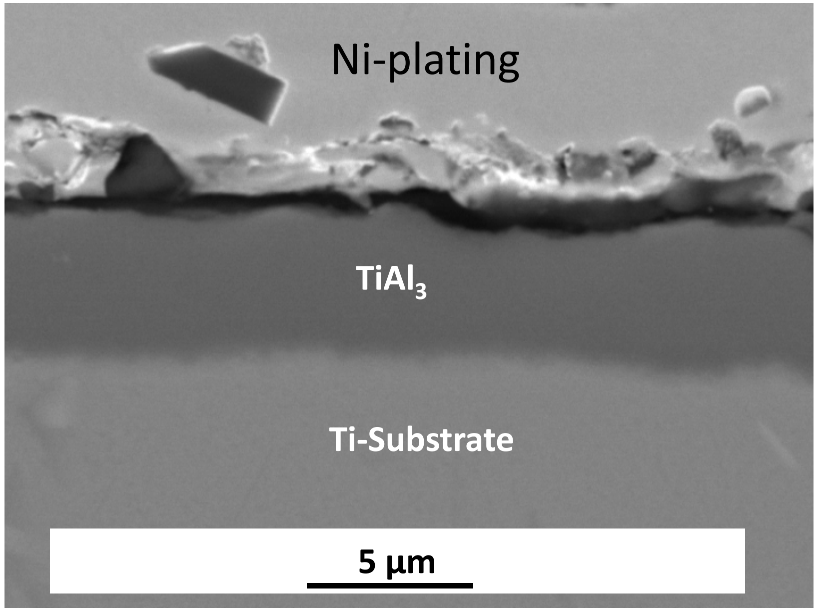
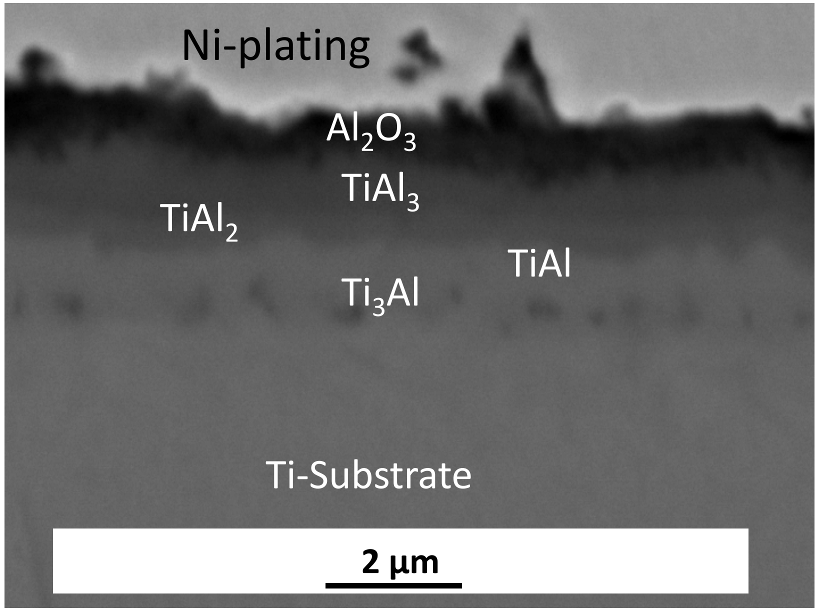
Results for Ti-Alloys



$TiAl_3$-layer after pack process



After fluorination and oxidation at 600°C for 120 h in air

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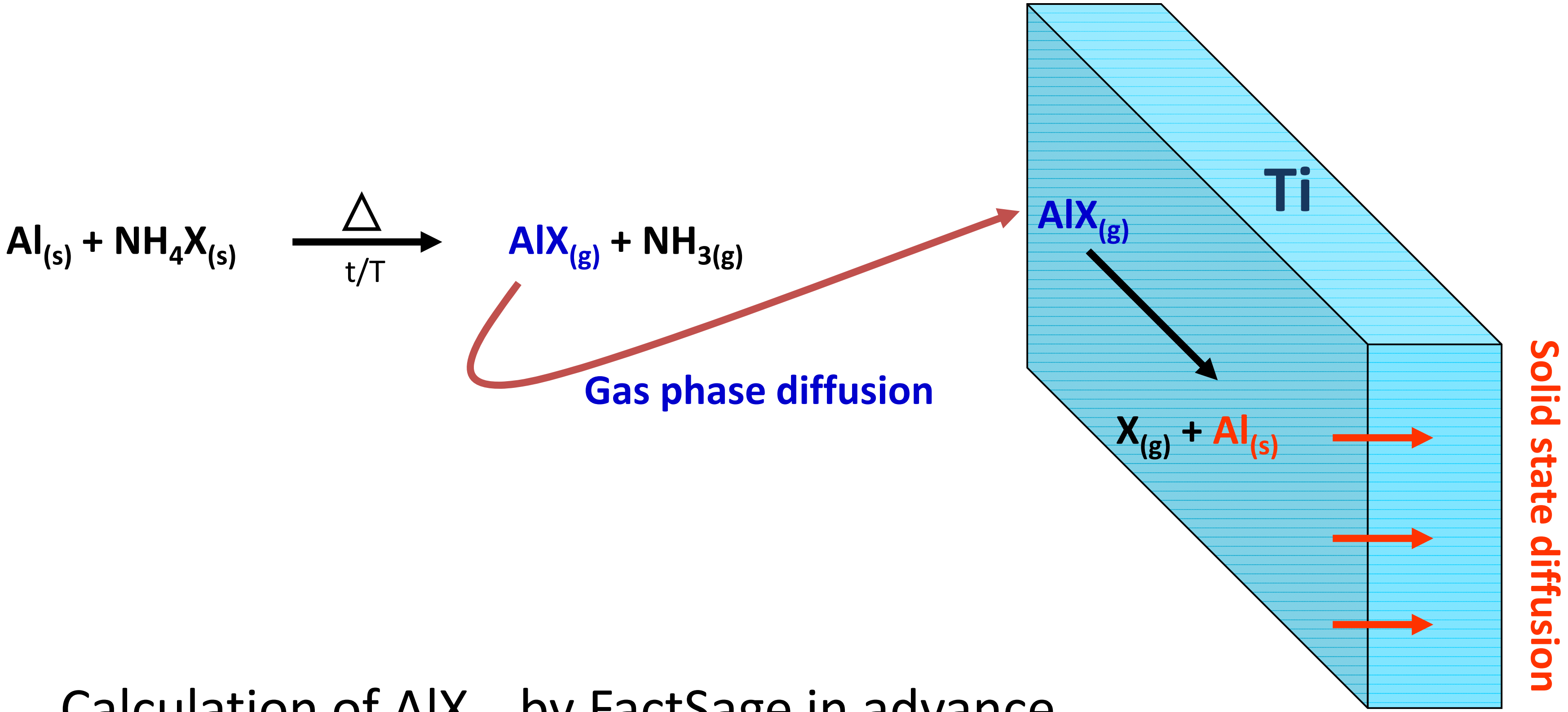
Powder Pack Process of Aluminum

Precursors: e.g. Al, Ti_xAl_y, Cr_yAl_x
Activators: e.g. NH_4Cl, $H(NH_4)F_2$, AlF_3
Filler: Al_2O_3

Temperature: 500 - 600°C
Gas: Ar
Time: 1-5 hours



Calculation of $AlX_{(g)}$ by FactSage in advance.

Conclusions

- Thermodynamic calculations have revealed the halogen effect process windows
- The halogen effect works at temperatures above 700°C by changing the oxidation mechanism from mixed oxide scale formation to protective alumina formation
- Fluorine is the best doping halogen
- The F-effect works for all technical TiAl alloys with an Al-content ≥ 40at.%
- The F-effect works also for technical Ti-alloys after Al-enrichment

Thank you for your attention !!!