Karl-Winnacker-Institut

High Temperature Materials

Fundamentals of the long time oxidation protection of gamma-titanium aluminides at high temperatures by using the fluorine effect

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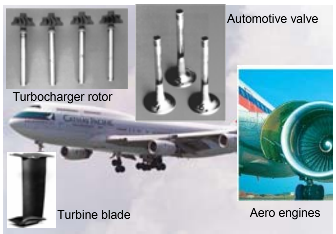
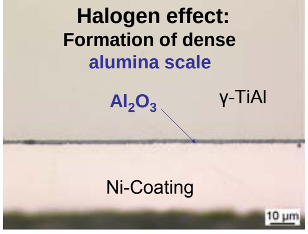
Motivation: Stability Parameter C^F_{max}

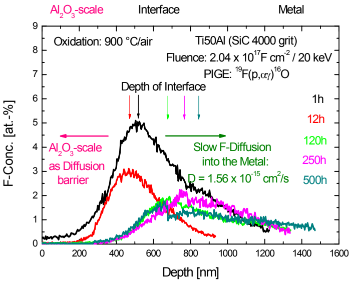
The insufficient oxidation resistance of γ-TiAl above 750°C can be improved dramatically by doping the surface with fluorine - e. g. using ion implantation or HF-treatment - forming a dense alumina scale on the surface. The fluorine maximum - located at the metal/alumina interface - is an essential parameter for the stability of oxidation protection. In this work the behaviour of the F-maximum during isothermal and cyclic oxidation was studied at 900°C and 1000°C and an analytical time-dependence was formulated. A multiple ion implantation was performed to enhance the fluorine reservoir at the metal/oxide interface. The F-depth profiles were obtained by using the non-destructive PIGE technique.



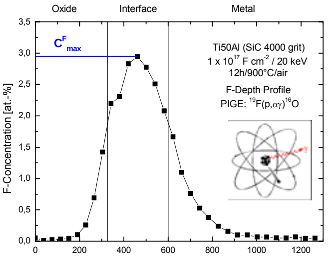
Applications of γ-Titanium Aluminides in High Temperature Technology.



F-implanted γ-TiAl-sample (10^{17} F cm^{-2}/ 20 keV) after oxidation (12h/900°C/air).



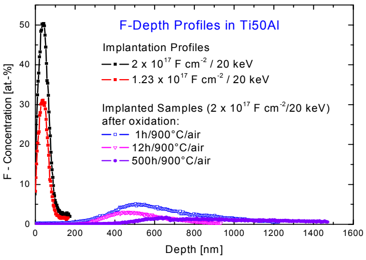
No F-loss to the surface and slow F-diffusion into the metal.



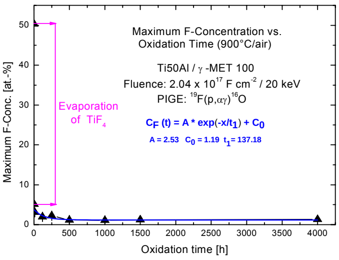
The maximum F-concentration C^F_{max} is defined as stability parameter.

Behaviour of C^F_{max} after single Fluorine Treatment

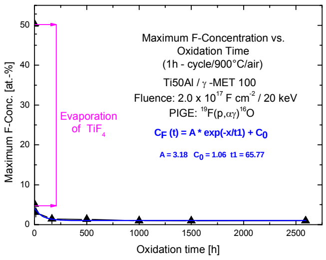
Within the first hours of oxidation a F-loss occurs from the surface. However, the dense alumina scale – once formed – acts as a diffusion barrier. At the same time slow F-diffusion into the TiAl occurs. An exponential function fits the time dependece of C^F_{max} revealing a relatively stable F-maximum of about 1 at.-% ensuring the F-effect.



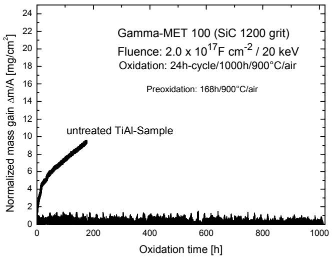
Time behaviour of the F-depth profiles during isothermal oxidation (900°C/air) depicts the high F-loss until formation of alumina scale.



Dependence of the F-maximum (2.04x10^{17} F cm^{-2} / 20 keV) during isothermal oxidation (900°C/air) is fitted by a decay function.

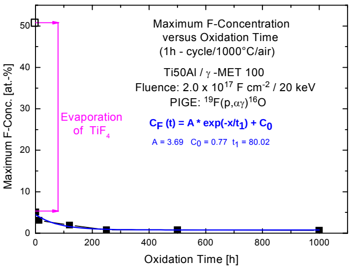


A decay function describes the time behaviour of C^F_{max} (2x10^{17} F cm^{-2} /20 keV) during cyclic oxidation (900°C/air).

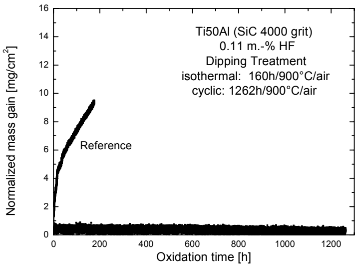


Mass gain vs. oxidation time after implantation (2x10^{17} F cm^{-2} /20 keV) during cyclic oxidation (900°C/air).

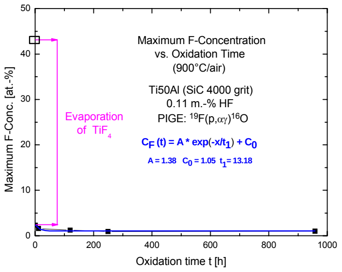
Cyclic oxidation simulates the service conditions of γ-TiAl alloys. The thermocyclic oxidation (1h-cycle/900°C/air) was performed up to 2600 h (900°C/air) and 1000h (1000°C/air). The F-maxima fitted by an exponential decay function predict a maximal F-amount of about 1 at.-% at the metal/oxide interface. Similar results have been found after treatment with diluted HF. In accordance with results obtained by metallography, SEM/EDX and thermogravimetric analysis (TGA) this F amount is condition for long time stability and a technical exploitation of the F-effect.



Even for cyclic oxidation (1h-cycle/ 1000h/ 1000°C/air) the F-maximum of implanted samples is described by a decay function.



TGA - curve after dipping in 0.11 m.-% HF and cyclic oxidation (24h-cycle/1262h/ 900°C/air).



The time dependence of the F-maximum after dipping in 0.11 m.-% HF and oxidation (958h/900°C/air).

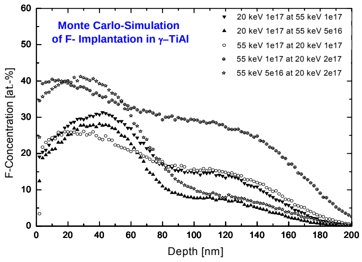
$$C_F\ (t) = A * \text{exp-}x/t1 + C_0$$

F-Treatment/Oxidation	Parameters		
	A	t_1	C_0
HF (900°C)	1.38	13.18	1.05
F-Implant. (900°C/isoth.)	2.53	137.18	1.19
F-Implant. (900°C/cycl.)	3.18	65.77	1.06
F-Implant. (1000°C/isoth.)	4.18	97.27	0.27
F-Implant. (1000°C/cycl.)	3.69	80.02	0.77

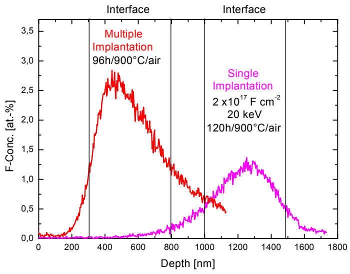
Table of parameters for the decay function describing the C^F_{max} – dependence showing a constant F-amount of about 1 at.-%.

Enhanced F-Reservoir by Multiple Ion Implantation

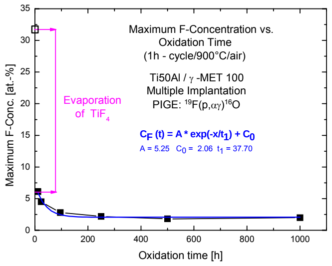
The F-reservoir at the metal/oxide-interface can be increased by multiple F-implantation. From the resulting F-profiles a lower growth of the alumina scale has been achieved.



F-depth profiles for several cases of multiple F-implantation simulated by using the Monte Carlo software code T-DYN.



F-depth profiles after isothermal oxidation (900°C/air) for multiple and single implanted TiAl-samples.



A decay function fits the time behaviour of C^F_{max} (multiple implantation) during cyclic oxidation (900°C/air).

$$C_F\ (t) = A * \text{exp-}x/t1 + C_0$$

F-Treatment/Oxidation	Parameters		
	A	t_1	C_0
F-Implant. (900°C/isoth.)	6.70	13.65	3.33
F-Implant. (900°C/cycl.)	5.25	37.70	2.06
F-Implant. (1000°C/isoth.)	5.41	59.03	1.37
F-Implant. (1000°C/cycl.)	4.80	76.34	1.23

Table of parameters for the decay function describing the C^F_{max} – dependence for multiple F-implantation.