Oxidation resistance improvement of TiAl alloys by the halogen effect in industrial environments

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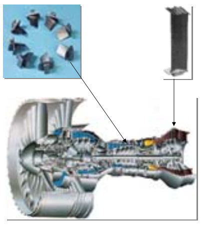
Introduction



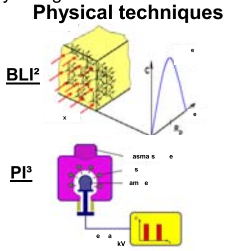
The alloys on the basis of TiAl open up new possibilities in he high-temperature technology (turbine blades for aeronautics, engine valves for automobiles...) due to heir mechanical characteristics at high temperatures. However their use at temperatures above 700 °C is limited by their oxidation resistance. In order to improve the oxidation resistance, fluorination of the alloy can be accomplished by surface modification by halogens. The halogen effect improves the oxidation resistance by promoting of growth of an Al_2O_3 protective layer. It has been shown that the halogen effect was effective for alloys with aluminium content higher than 35 at.% [1]. The goal of this project is to examine the potential of the halogen effect for alloys with Al-contents less han 48 At. % for complex industrial environments as a function of the following parameters:

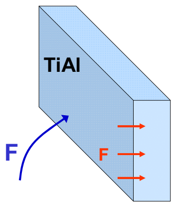
- Influence of the fluorine treatment (dipping, spraying, gas phase, implantation)
- Atmospheres: effect of moisture and SO_2.
- Temperature conditions (isothermal, thermocyclic)

How to modify the alloy surface by halogens ?

Physical (Beam-Line-Ion-Implantation BLI² or Plasma-Immersion-Ion-Implantation PI³) and chemical techniques (gas phase, F-containing polymer spraying, dipping into F-based solutions) may be used to enrich the surface or subsurface of he alloys by halogens.

Physical techniques

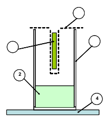




Chemical techniques

spraying

gas phase [3]

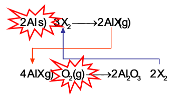


Enrichment of the subsurface
F-profile well defined

Enrichment of the subsurface
and/or surface

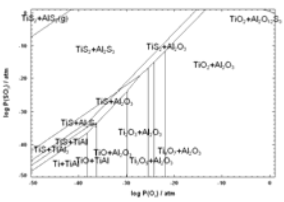
How much halogen at the surface ?

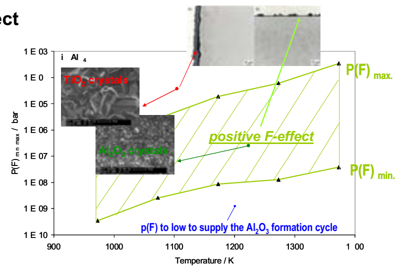
Simplified model for the halogen effect



with X = F, Cl, Br, I

Al-Ti-S-O stability diagram at 900 °C



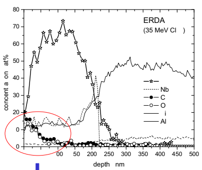


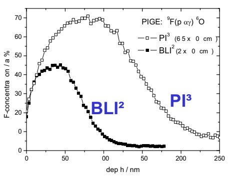
Halogen partial pressure corridor for a positive effect [2]

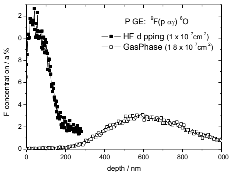
Same boundaries even in presence of SO_2.

Forma ion of sulphides at low pO_2

Fluorination process optimisation

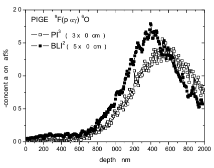


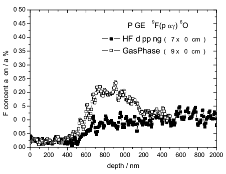


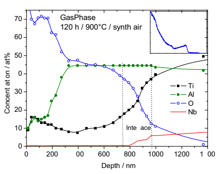


PI³ H, C, O at the surface

Fluorine profile measurements before and after oxidation
Fluorination process optimisation



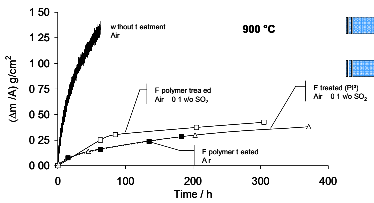




Lower F-concentration with chemical treatment

Ti, Nb-doping in the Al_2O_3-layer

Oxidation testing

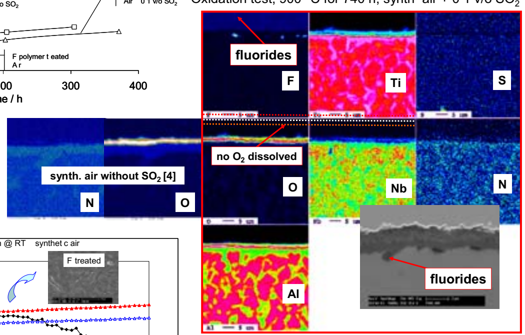


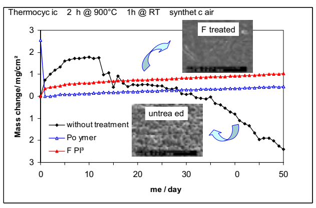
Halogen par ial effec ive even in presence of sulphide

Oxygen dissolution in the alloys seems to be suppressed with SO_2.

S barely detectable in the oxide layer

Oxidation test, 900 C for 740 h, synth air + 0 1 v/o SO_2





Halogen partial effective even in thermocyclic conditions

Conclusions

Chemical and physical fluorination techniques were found to be effective to improve the oxidation resistance of TiAl alloys in isothermal and thermocyclic conditions even in presence of SO_2.Thermodynamic predictions showed that under sulphur-based atmospheres encountered in industrial environments, the formation of either aluminium sulphide or titanium sulphide in the oxide scale is expected if the oxygen partial is lower than 10^{15} atm. However sulphur could be only barely detectable in the oxide layer. Using non destructive methods the fluorine profile were measured before and after oxidation and was used as an assessment tool for the op imisation of the fluorination process, It was observed that oxygen does less diffuse inwards the alloy in presence of SO_2 and reduces its sensibility to high temperature embrittlement.

References: /1/ P Masset, S Neve, H -E Zschau, M Schütze, Materials and Corrosion, 59(7) (2008) 609-618 /2/ P J Masset, M Schütze, Adv Eng Mater , 2008, Adv Eng Mater , 10(7) (2008) 666-674, /3/ P J Masset, M Schütze, ECS Trans 11 (15) (2008) 37-48, /4/ P J Masset, M Laurent, M Schütze, Defect and Diffusion Forum, 289-292 (2009) 397-404