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 the high-temperature technology (turbine blades for aeronautics, engine valves for automobiles...) due to their 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 growth of an Al2O3 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 than 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 SO2
- Temperature conditions (isothermal, thermocyclic)

Fluorination process optimisation

How much halogen at the surface?

Simplified model for the halogen effect

Enrichment of the subsurface
F-profile well defined

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 the alloys by halogens.

Fluorination process optimisation

Enrichment of the subsurface
F-profile well defined

Fluorine profile measurements before and after oxidation

Fluorination process optimisation

Lower F-concentration with chemical treatment

Ti, Nb-doping in the Al2O3-layer

Oxidation testing

Halogen parial pressure corridor for a positive effect [2]
Same boundaries even in presence of SO2
Form ion of sulphides at low pO2

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 SO2. 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^-6 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 optimisation of the fluorination process. It was observed that oxygen does less diffuse towards the alloy in presence of SO2 and reduces its sensibility to high temperature embrittlement.