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Improving the oxidation resistance of refractory metals via aluminum diffusion coatings and halogen effect

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High Temperature Materials

Improving the Oxidation Resistance of Refractory Metals via Aluminum Diffusion Coatings and Halogen Effect

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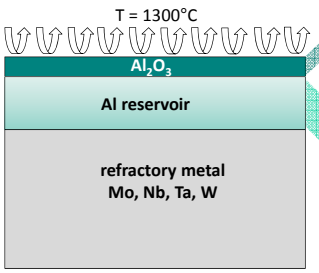
Introduction

Research on high temperature applications such as gas turbine engines, reformer systems, turbochargers or various power plant components [1] focuses on increasing the efficiency which is achieved by increasing the temperature. Refractory metals offer higher working temperatures than Ni-based superalloys due to their high melting points and comparable mechanical properties. However, refractory metals suffer from low oxidation resistance at elevated temperatures. Meeting this challenge, aluminum diffusion layers were manufactured on the refractory metals molybdenum, niobium, tantalum and tungsten using pack cementation process with the aim to form protective Al_2O_3 scales during oxidation. The oxidation kinetics of the coated samples are investigated via thermogravimetric analysis (TGA) for up to 100 h at 1300°C in synthetic air. The halogen effect is used to enhance the protective Al_2O_3 layer formation and thereby increase the materials resistance against high temperature oxidation. The importance of optimization of the halogen treatment depending on the substrate material is demonstrated on tantalum.

Coating System



TGO:
- oxidation protection
- diffusion barrier

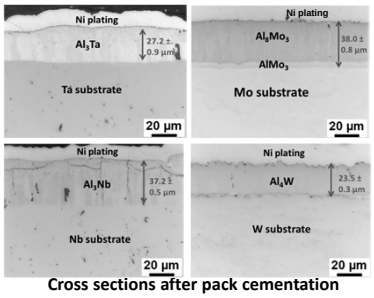
BC:
- Al reservoir to form and maintain the oxide layer

Schematic of the target protective layer system for refractory metal

Pack Cementation Process

- Diffusion coating process
- Substrate is embedded in powder mixture (1 wt.% Al, 1 wt.% NH_4Cl, 98 wt.% Al_2O_3)
- Heated for 8h @ 1000°C

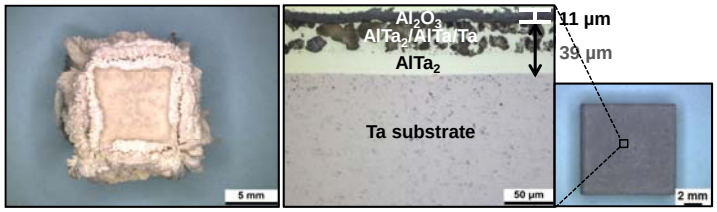
→ Homogeneous intermetallic layers with high aluminum contents are formed



Cross sections after pack cementation

The Fluorine Treatment on Tantalum

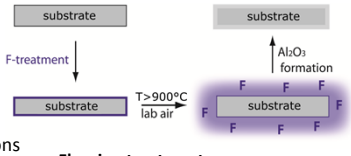
Oxidation of aluminized and additional fluorine treated tantalum substrates for **40 h @ 1300°C in synthetic air**



single F-treatment **double F-treatment**

- competition between Al_2O_3 and Ta_xO_y formation
- similar to TiAl alloys the amount of fluorine is a critical factor [2]

Halogen effect:
- Halogen treatment enhances protective Al_2O_3 scale formation during oxidation
- Good oxidation protection by Al_2O_3 because of its very low permeability for O, N, H, and metal ions
- Fluorine superior to other halogens (+F)



Fluorine treatment process

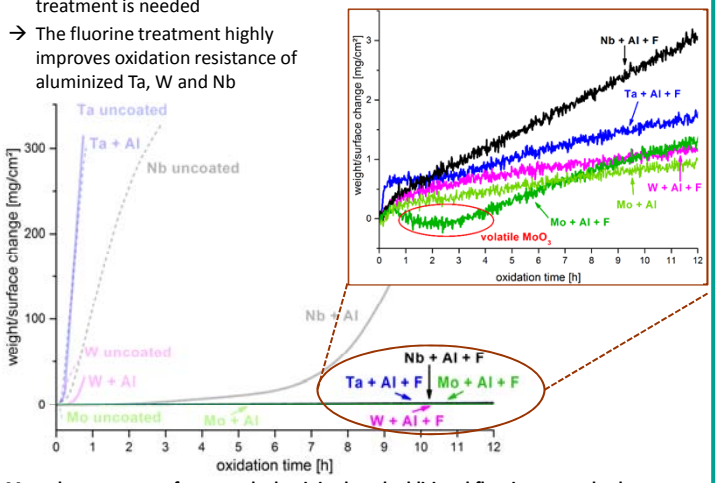
Effect of Aluminizing and Halogen Treatment on Oxidation

12 h @ 1300°C in synthetic air

- Uncoated substrates show destructive oxidation
- Substrates with an Al-diffusion surface layer:
  - formation of protective Al_2O_3 surface layer on Mo
  - mixed oxide formation on W, Ta, Nb
- Coated samples with halogen treatment:
  - low mass gains for all substrates
  - formation of protective Al_2O_3 layer on Mo and Ta

→ Volatile MoO_3 themselves promote Al_2O_3 formation, no additional fluorine treatment is needed

→ The fluorine treatment highly improves oxidation resistance of aluminized Ta, W and Nb

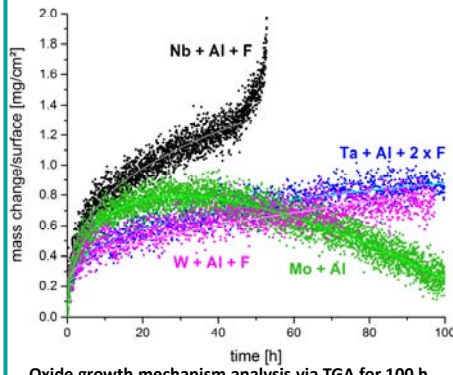


Mass change curves of uncoated, aluminized, and additional fluorine treated substrates

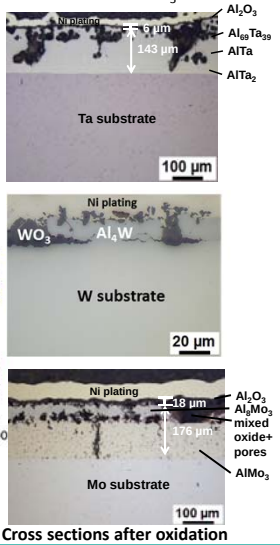
Isothermal Oxidation for 100 h

100 h @ 1300°C in synthetic air

- Aluminized and double fluorine treated Ta:
  - shows sub-parabolic oxidation kinetics
  - forms a dense and protective Al_2O_3 layer
  - a high aluminum reservoir remains in the subsurface region
- Aluminized Mo:
  - shows paralinear oxidation kinetic due to the volatility of its oxides
  - local oxide spallation causes destructive oxidation → volatile MoO_3 is formed
- Aluminized and fluorine treated Nb and W:
  - develop no protective Al_2O_3 layer



Oxide growth mechanism analysis via TGA for 100 h



Cross sections after oxidation

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[1] J. R. Nicholls, K. A. Long, N. J. Simms, Sheir's Corrosion, ed. By T. J. A. Richardson, (Elsevier, Oxford, 2010), 2532 - 2555
[2] A. Donchev, B. Gleeson, M. Schütze, Intermetallics **11** (2003)