



The Potential of Refractory Alloys for Solar Applications



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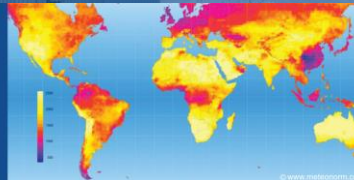
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September 27 - October 1, 2021
Online Event

27th SolarPACES Conference



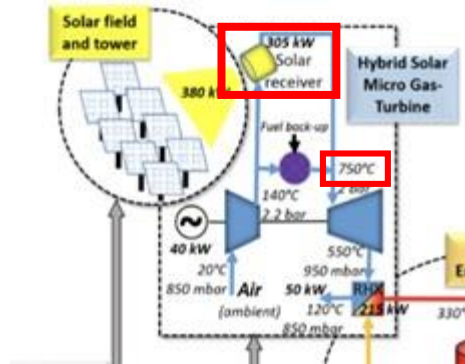


Context

Research hypotheses

Objectives

Improving current solar receivers



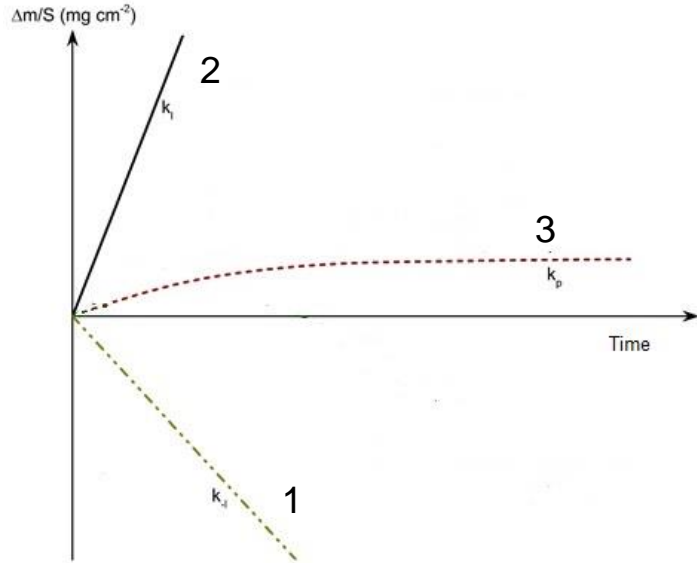
Solar loop developed in the frame of the POLYPHEM project

In CSP plants with solar tower system:

- The maximal temperature of the heat transfer fluid : 1000 K (due to the limitations of the currently used Ni-based alloys for the solar receiver)
 - Increasing this working point would request materials that stand:
 - Thermal cycling
 - Oxidation
- ...above 1100 K, without significant degradation of their radiative properties

Oxidation kinetics

Three different behaviors



1. Gaseous compounds (ex: MoO_3) : linear mass loss

$$\frac{\Delta m}{S} = -k_{-l} \cdot t$$

2. Solid oxide layer with fast diffusion of the oxydant through it (ex: TiO_2) : linear mass gain

$$\frac{\Delta m}{S} = k_l \cdot t$$

3. Solid oxide layer with diffusion-controlled growth of the oxide layer (SiO_2 , Al_2O_3) : semi-parabolic kinetic

$$\frac{\Delta m}{S} = k_p \cdot \sqrt{t}$$

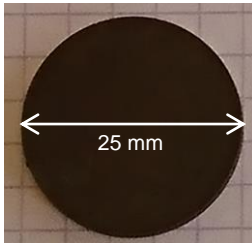
=> Interest of Si or Al to reduce the oxidation in time

Proposed solution

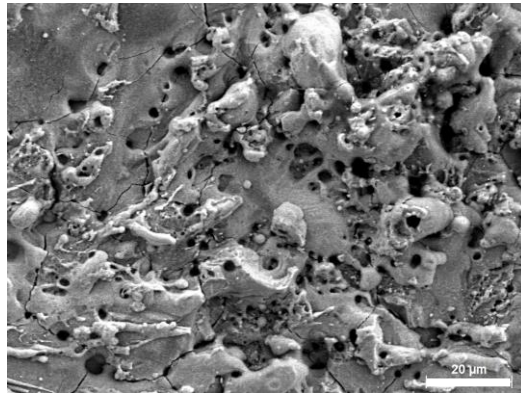
Refractory alloys Mo-Si-Ti

Investigations performed on Mo-20Si-52.8Ti (at.%) (MST)

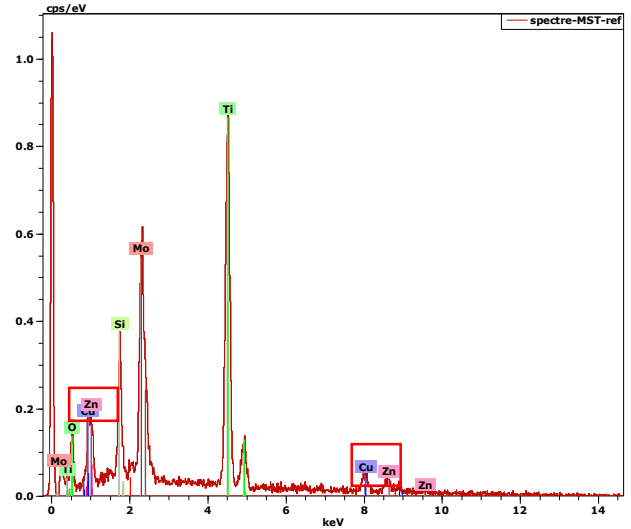
- Combining endurance to thermal cycling, spectral selectivity and oxidation resistance (Si).
- Oxidation performed using muffle furnace (6h, continuous) and solar furnace (2h divided into 8 cycles)



*As-received sample
(ϕ 25 mm, th. 2 mm)*



*As-received samples
SEM image (SE mode) at the center*

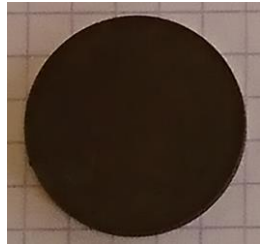


*As-received samples
Surface EDS analysis*

Results

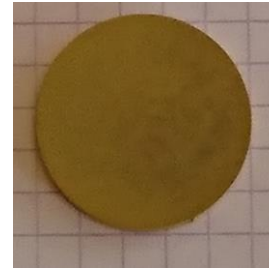
Oxidation in muffle and solar furnace

Oxidation in muffle furnace (6h at 1400K) Picture and mass change



As-received sample
 $m_i = 8.5484 \text{ g}$

6 h in air at 1400 K



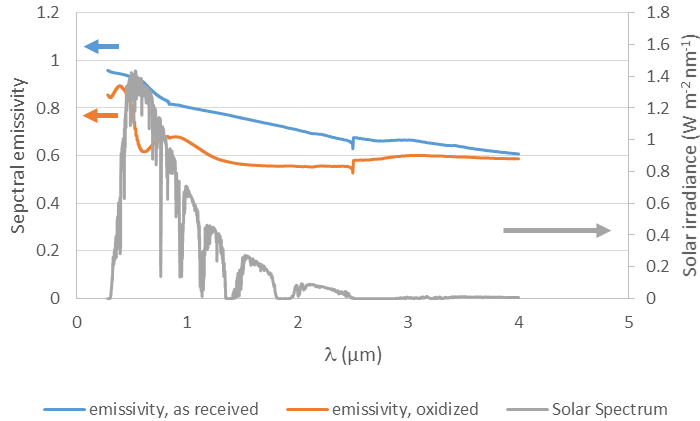
Oxidized sample
 $m_f = 8.5342 \text{ g}$

Mass change : - 2,89 mg cm⁻² after 6h oxidation

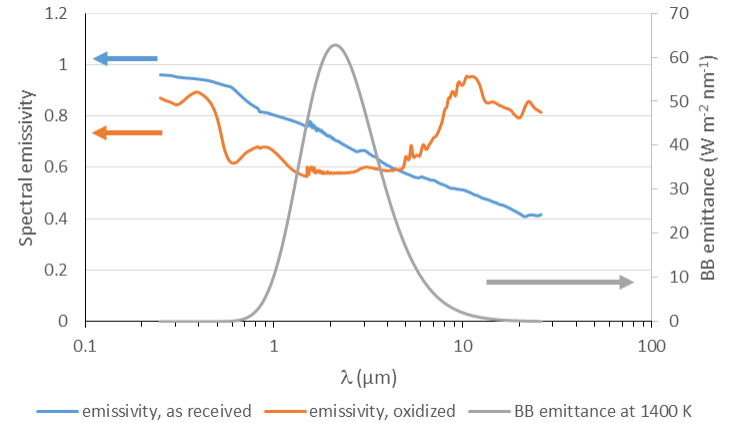
- Mass loss probably due to the volatilization of MoO₃

Oxidation in muffle furnace (6h at 1400 K)

Comparison of spectral emissivities (RT)



*Spectral emissivities, Visible – NIR range
(RT measurement with Perkin Elmer Lambda 950)*



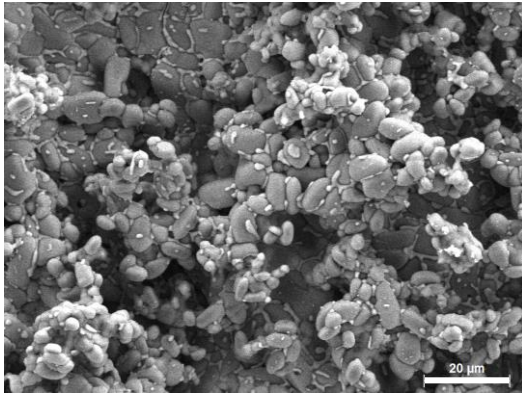
*Spectral emissivities, Visible – NIR - IR range
(RT measurement with Perkin Elmer Lambda 950 + SOC 100)*

In the 0.25-5 μm range:

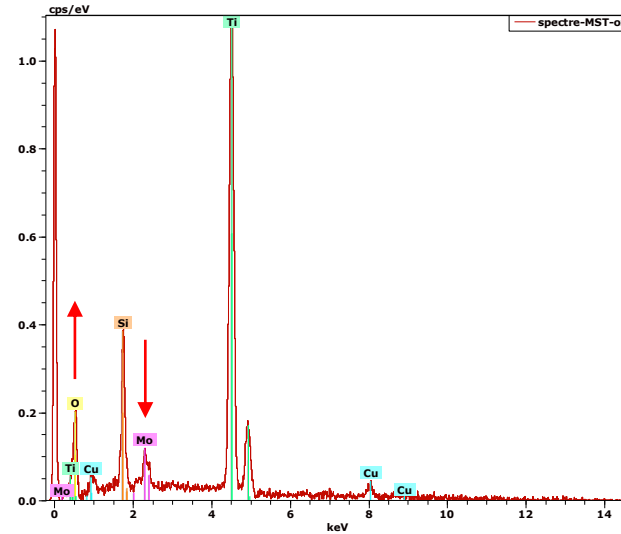
- Lower spectral emissivity for the oxidized sample
 - Lower absorptivity of the solar spectrum (-)
 - Lower spectral emissivity in the BB emittance area (++)
- ⇒ To be confirmed with emissivity measurements at 1400 K

Oxidation in muffle furnace (6h at 1400 K)

Post-experimental SEM/EDS



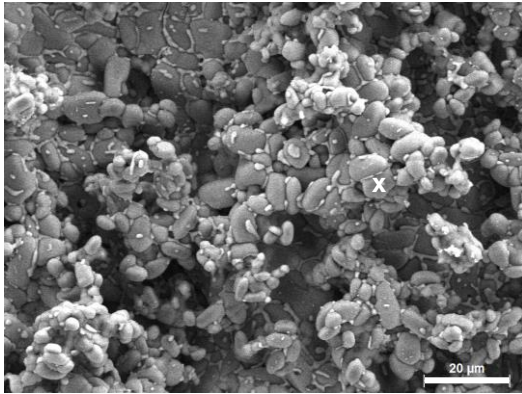
SEM image, oxidized sample



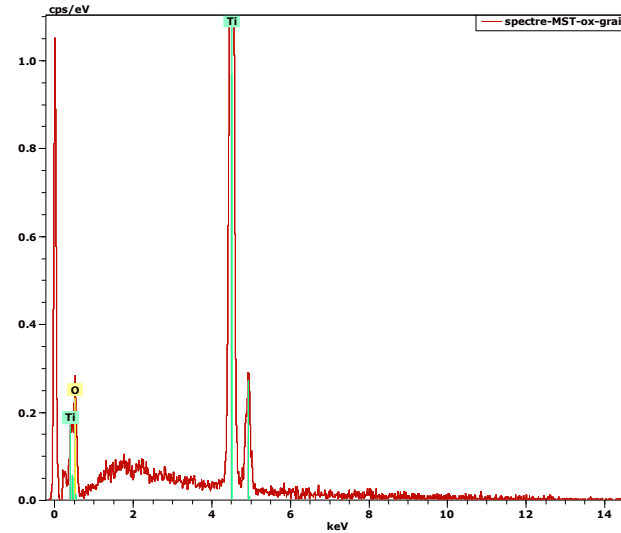
EDS spectrum from the scanned surface

- Revelation of grains during oxidation
- EDS on the scanned surface => oxidation with volatilization of MoO_3
- EDS on the grey grains => oxidized Ti phase
- EDS on the white phase => Mo-Ti-Si-O phases, with Cu enrichment

Oxidation in muffle furnace (6h at 1400 K) Post-experimental SEM/EDS



SEM image, oxidized sample

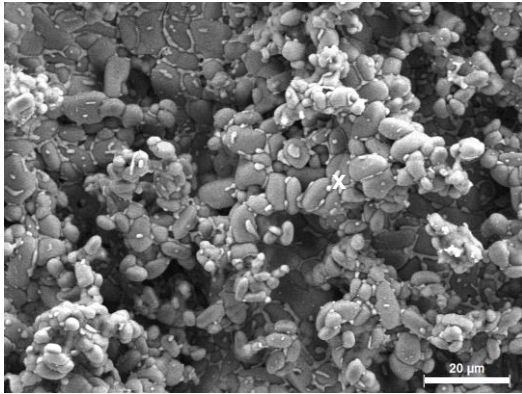


EDS spectrum from one grey grain

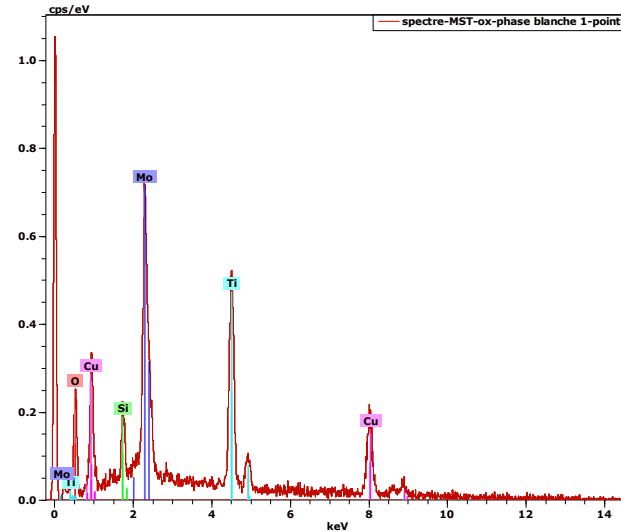
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Oxidation in muffle furnace (6h at 1400 K)

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SEM image, oxidized sample

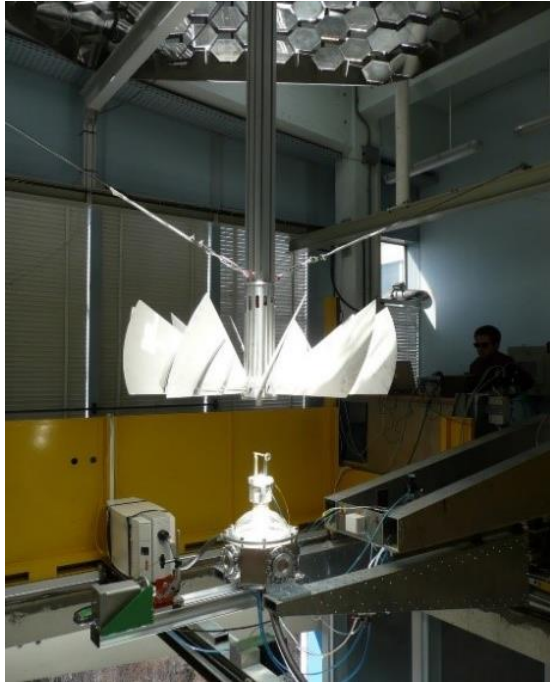


EDS spectrum from the white phases

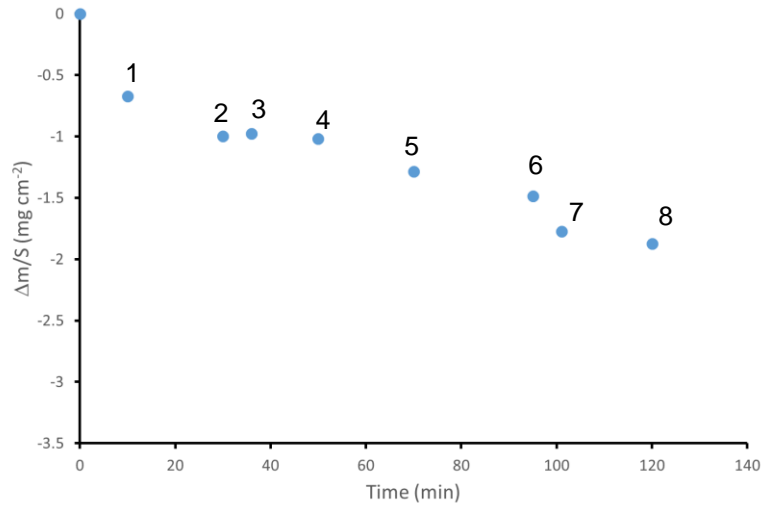
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Oxidation in solar furnace (REHPTS), 2h at 1400 K

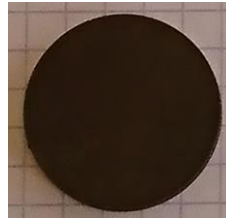
Pictures and mass change



REHPTS set-up
(REacteur Hautes Pression et
Température Solaire)



Evolution of the mass variation with time



$t = 0$ min.
(as-received)
 $m = 8.8869$ g



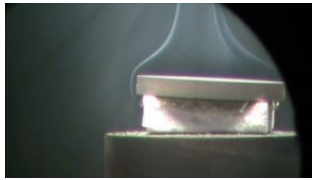
$t = 30$ min.
(after cycle 2)
 $m = 8.8820$ g



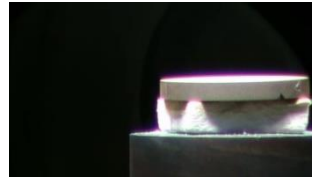
$t = 120$ min.
(after cycle 8)
 $m = 8.8777$ g

Oxidation in solar furnace (REHPTS), 2h at 1400 K

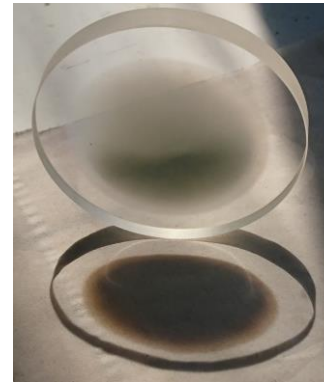
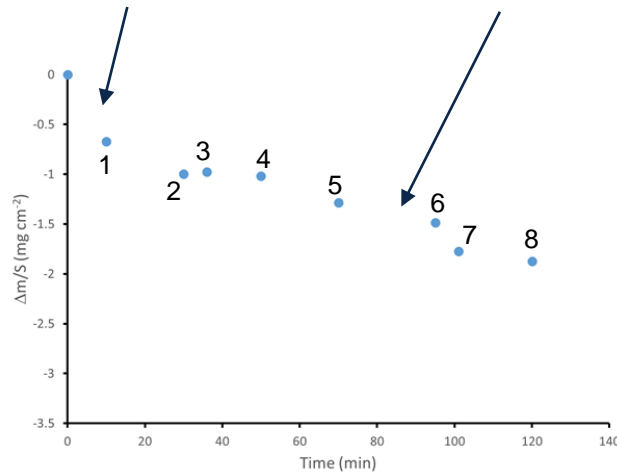
Video captions – Condensation



Video caption at $t = 2$ min.



Video caption at $t = 80$ min.



CaF_2 window at $t = 10$ min.
(cycle 1)



CaF_2 window at $t = 120$ min.
(cycle 8)

- Smoke production during the first oxidation cycle, condensation on the upper window (MoO_3)
 - Production decreasing with the oxidation time, with a less important condensation after 2h (protective oxide layer ?)
- ⇒ On-going characterizations (XRD, Raman, XPS, SEM/EDS) to analyze the structure of the oxide layer after 2 and 120 min. oxidation time

Conclusions - perspective



Conclusions - perspectives

The oxidations of the Mo-20Si-52.8Ti alloys at 1400 K in air have shown:

- Significant mass loss with production of smoke (MoO_3 volatilization and condensation ?)
- Surface oxidation with different phase formation (Ti-O, and complex Mo-Si-Ti-O phase identified with SEM/EDS)
- Diminution of the spectral emissivity that may affect solar absorptivity (-) and thermal radiative losses (++) for solar concentrated applications

Future works:

- Complementary analyses (XRD, Raman, XPS, cross-section SEM/EDS...) on MST samples at different oxidation time to confirm the oxidation mechanisms
- Comparison with other equimolar alloys: Ta-Mo-Cr-Al and Ta-Mo-Cr-Ti-Al





Thank you for your attention!

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SEM imaging and EDS analyses achieved by Y. Gorand, UPVD.

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