Sublimation Protection Coatings for Thermoelectric Materials for Space Power Applications

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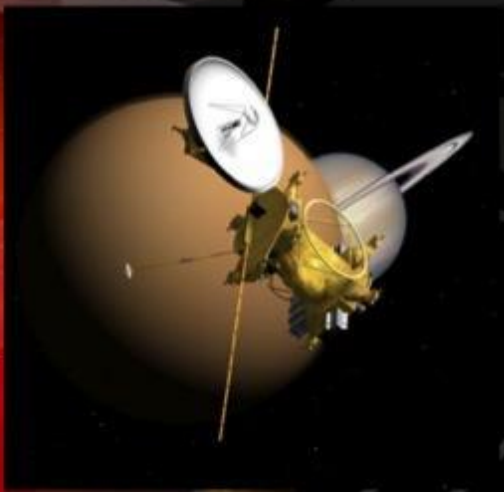
Radioisotope Power Systems

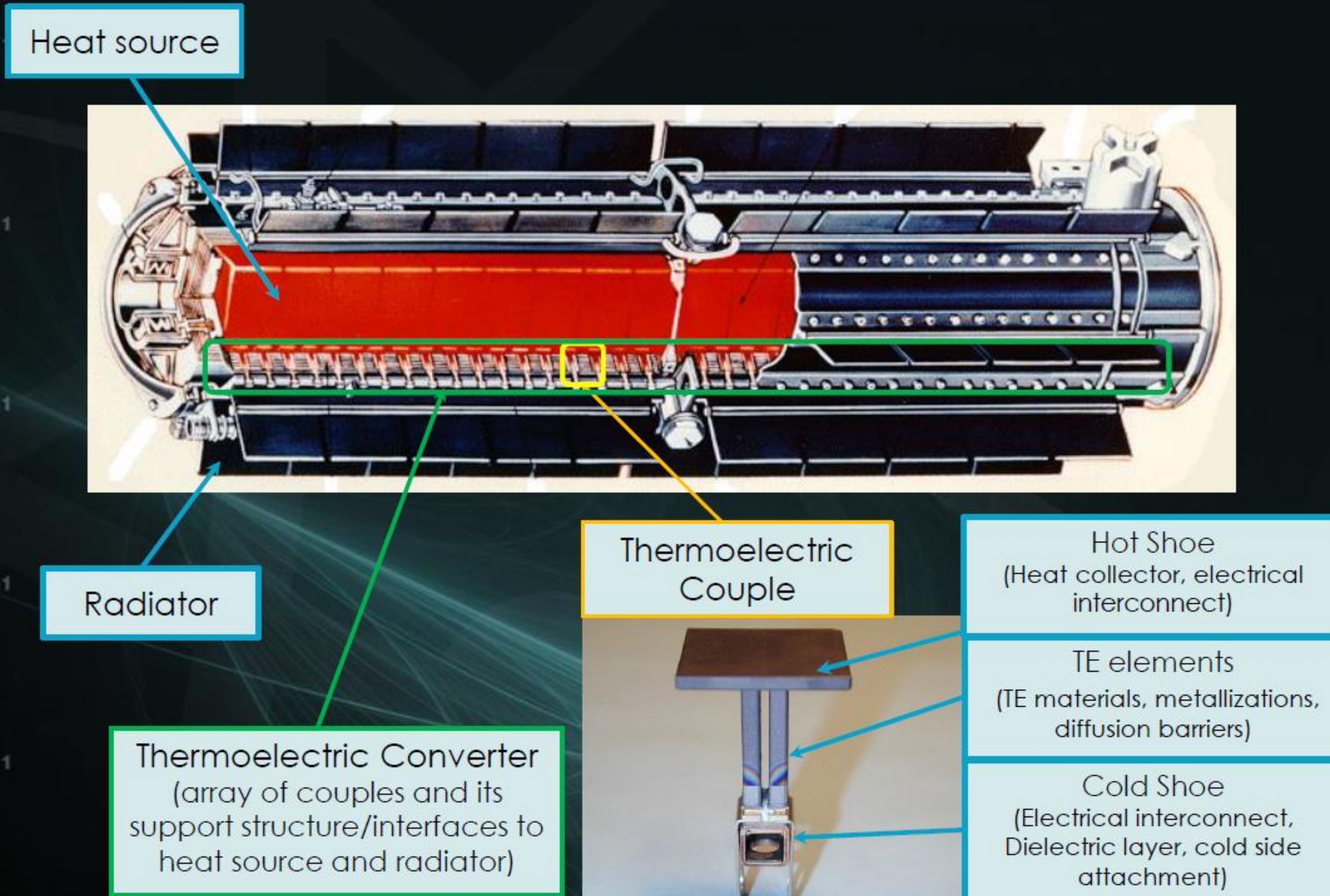


- Enable and enhance missions by providing electrical power to explore remote and challenging environments where solar power is unavailable
  - Spacecraft operation
  - Instrumentation
- Converts heat from a Radioisotope into electricity
  - Heat is the product of the natural decay process of the isotope

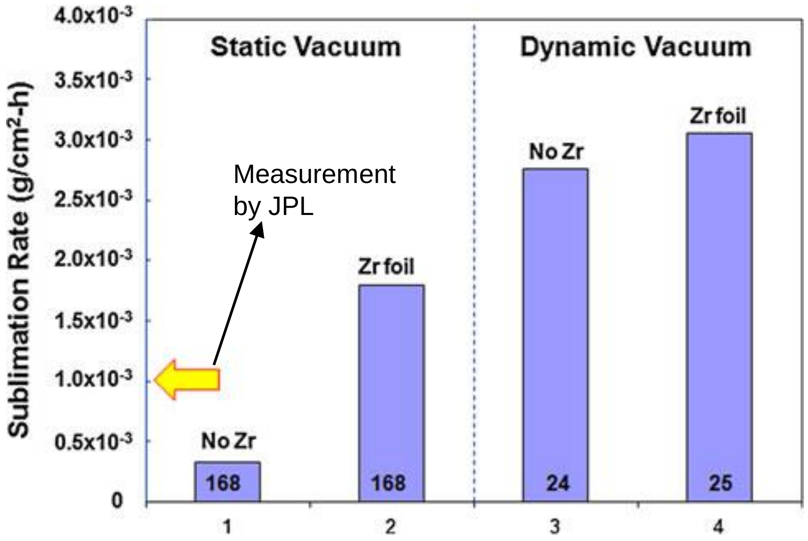
RTG (Radioisotope Thermoelectric Generator)

- An electrical generator that uses an array of thermocouples to convert the heat released by the decay of a radioactive material into electricity.
- Radioactive decay of the fuel produces heat. The temperature difference between the fuel and the heat sink allows the thermocouples to generate electricity.
- Si-Ge is current state-of-the-art thermoelectric material in current RTGs
- The compound $Yb_{14}MnSb_{11}$ is a thermoelectric material of interest to NASA as a candidate replacement for Si-Ge.
- $Yb_{14}MnSb_{11}$, however, suffers from a high sublimation rate at elevated temperatures (up to 1000^{o}C)
    - Requires a sublimation protection in order to survive the required RTG lifetime of 14 years.

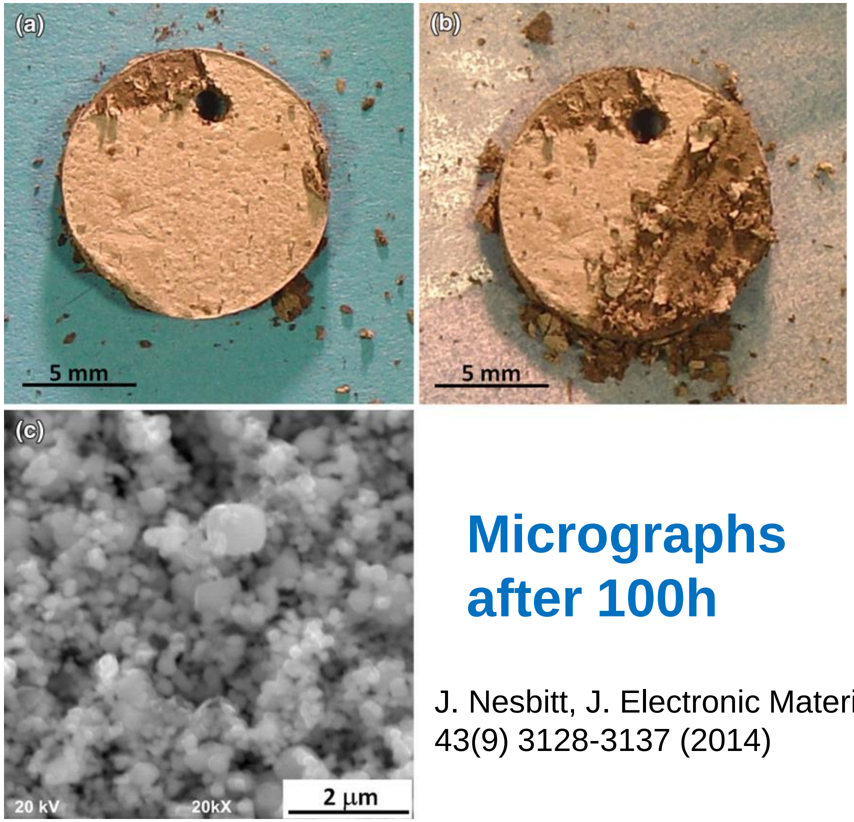
RTG: Thermoelectric Technology Nomenclature



Sublimation of $Yb_{14}MnSb_{11}$
(1000^oC, 4 - 6 x 10^{-6} Torr)



J. Nesbitt et al, J. Electronic Materials, 41(6) 1267-1273 (2012)

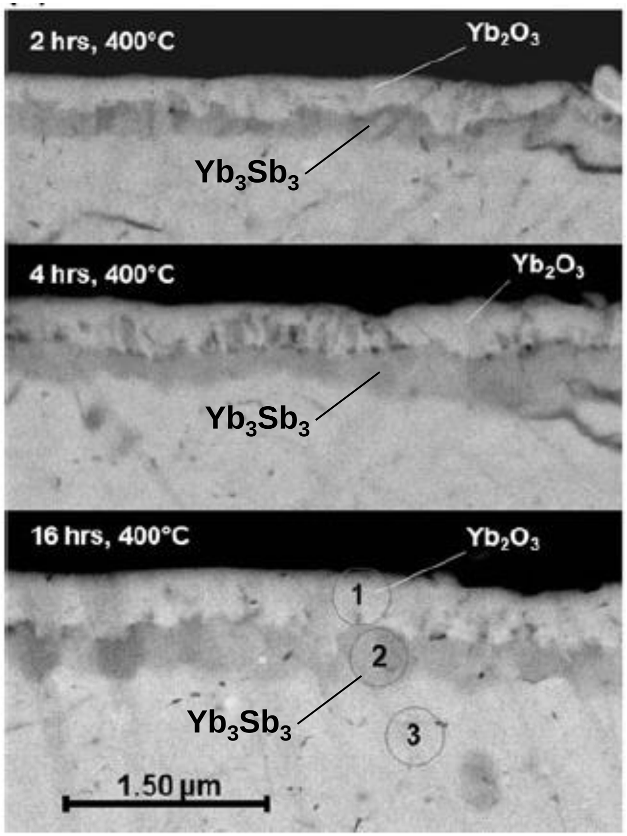


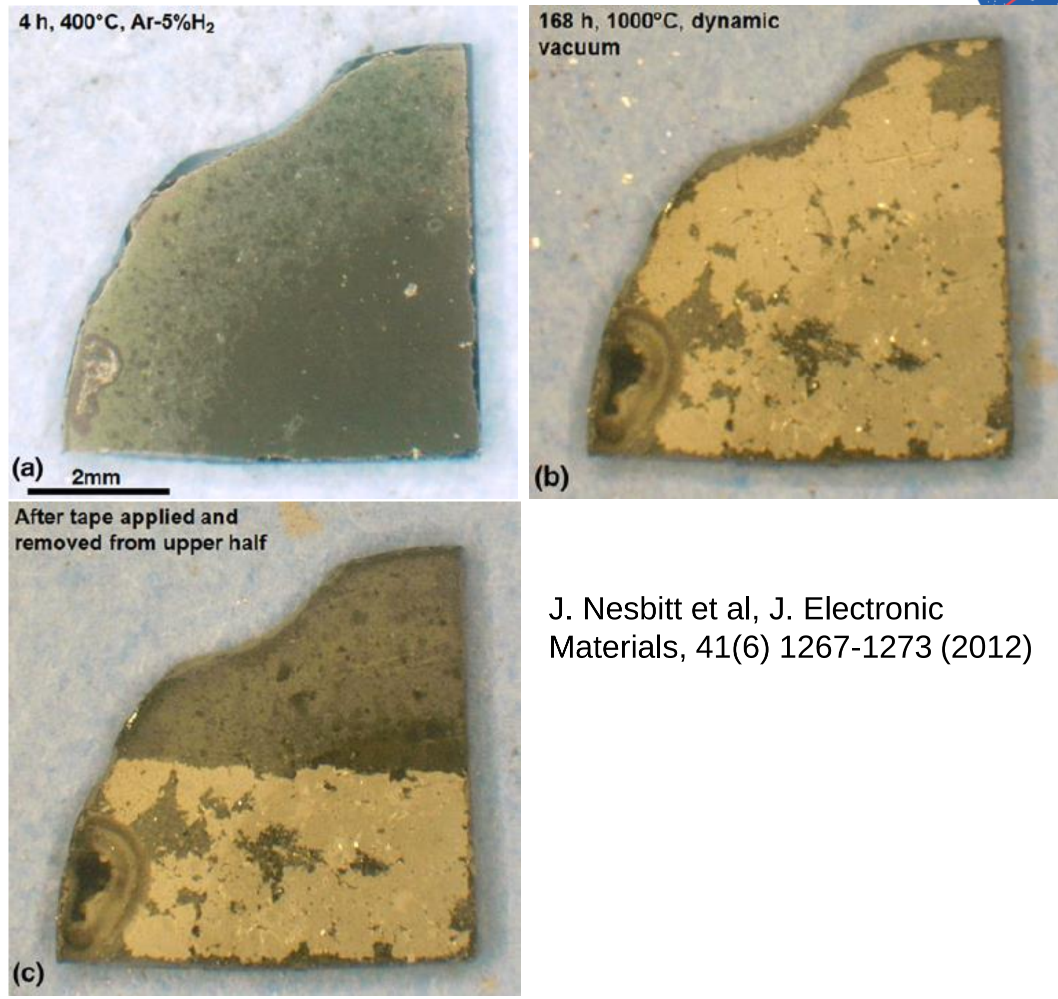
Micrographs after 100h

J. Nesbitt, J. Electronic Materials, 43(9) 3128-3137 (2014)

- Sublimation rates: 0.3 x 10^{-3} g/cm^2 - 3 x 10^{-3} g/cm^2
  - Three orders of magnitude higher than the target rates (1 x 10^{-6} g/cm^2)
- White, powdery oxide on the surface, which was identified by XRD as Yb_2O_3

Pre-oxidation
(400ºC, Ar-5% H_2)

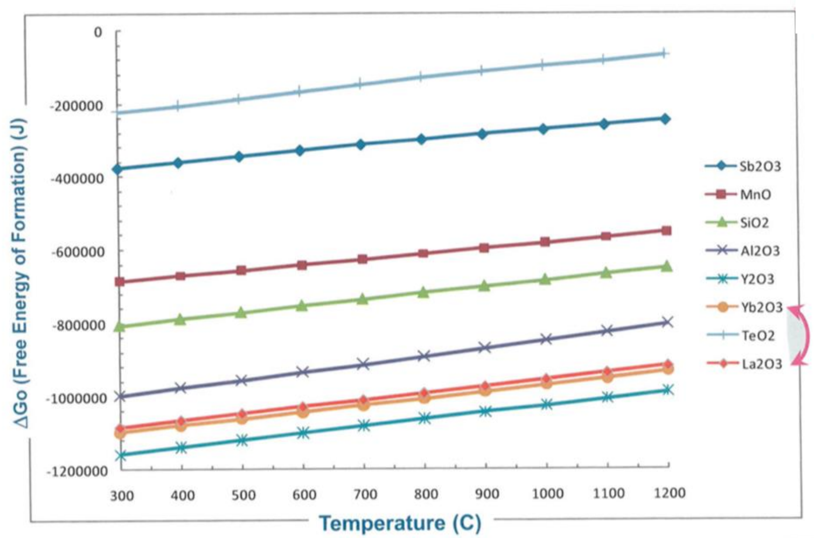


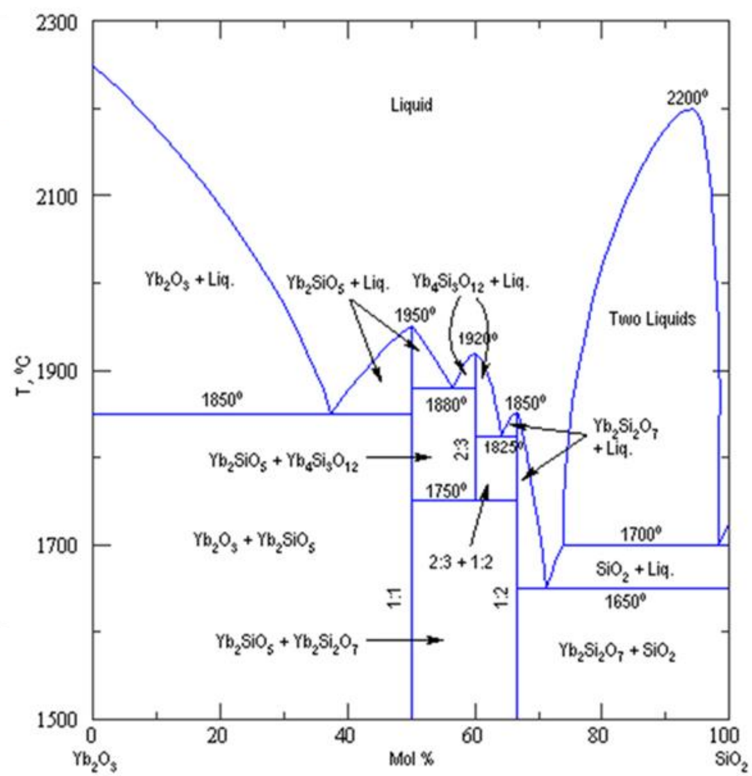


J. Nesbitt et al, J. Electronic Materials, 41(6) 1267-1273 (2012)

- In Ar-5% H_2, there was sufficient oxygen present in the furnace system to form thin, transparent, adherent scale
- After 168h at 1000ºC in vacuum, the scale became opaque, friable, and detached
  - Not effective as sublimation barriers

Rare Earth Oxide and Rare Earth Silicates are Thermodynamically Compatible with $Yb_{14}MnSb_{11}$

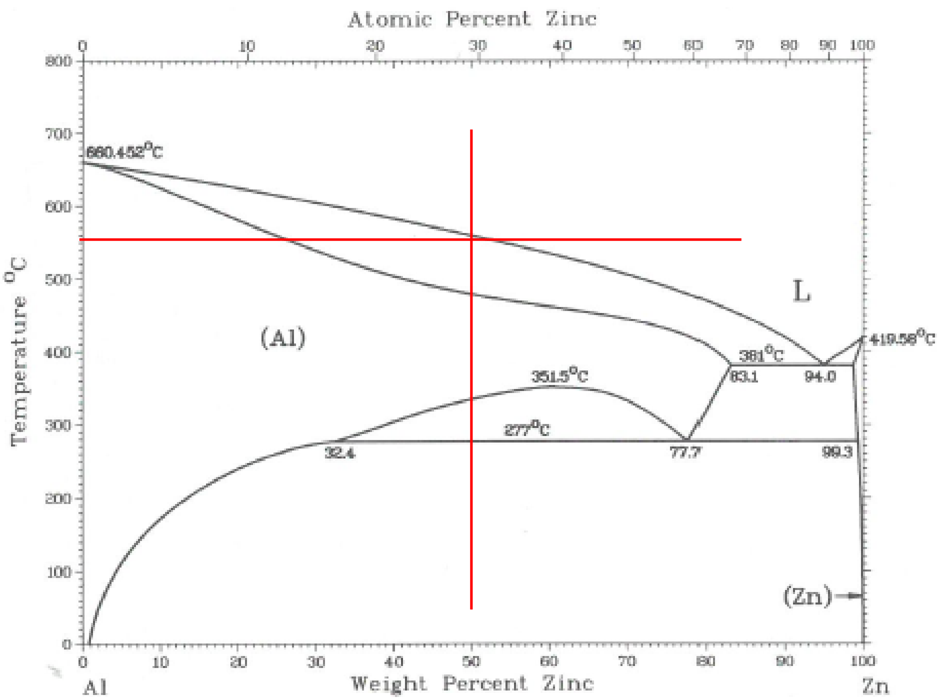


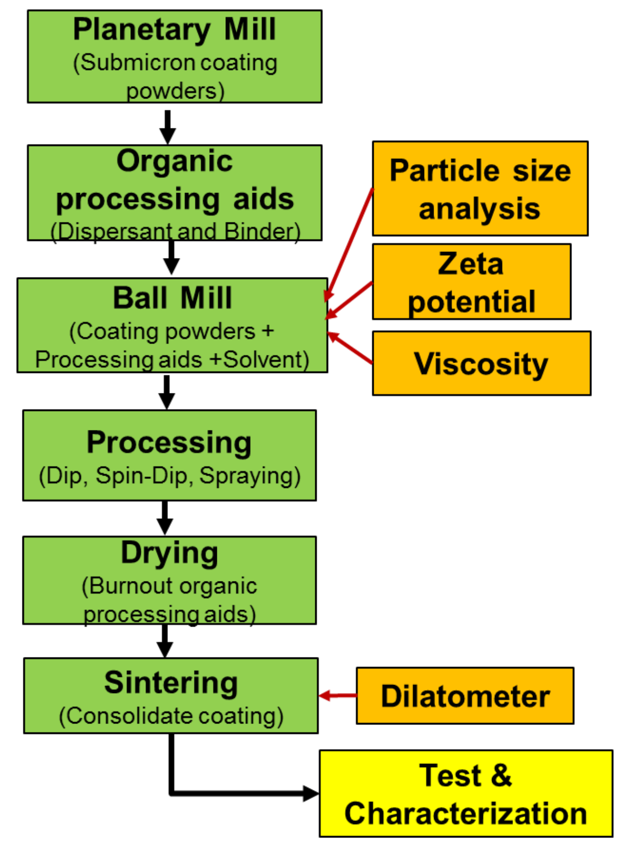


- Most oxides are reduced by Yb_2O_3 because of its very low free energy of formation
- Yb_2SiO_5 is thermodynamically stable in contact with Yb_2O_3
- Other rare earth oxides should be stable in contact with Yb_2O_3 as long as they do not form a solid solution

Objective

- Develop a sublimation protection coating for $Yb_{14}MnSb_{11}$ via slurry process
  - Derived from our experience with slurry-based EBCs (environmental barrier coatings)
  - Candidate coating material: Y_2O_3, Yb_2SiO_5, 7YSZ (ZrO_2 + 7wt% Y_2O_3)
  - Sintering temperature < 1000ºC
    - Sintering aids: Al , Al + Zn (50 wt% + 50 wt%)
    - Sintering: 2-3 hr @ <1000ºC, vacuum
  - Durability Test: 100 hr @ 1000ºC, vacuum

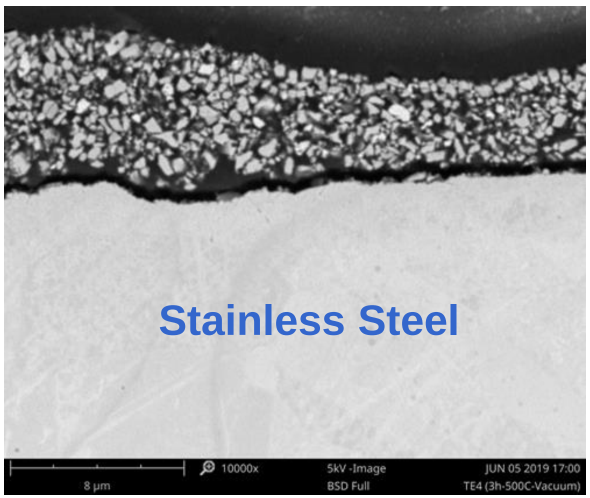




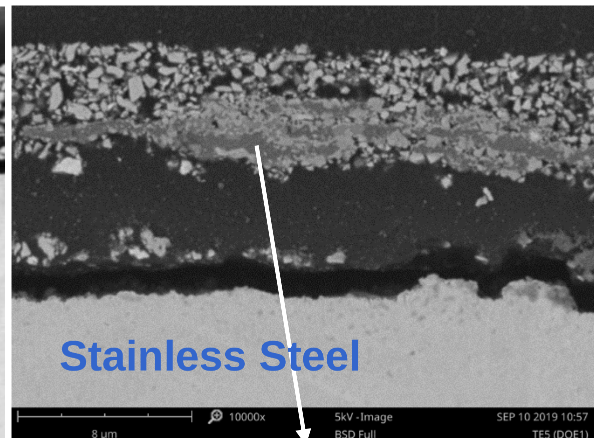
Y_2SiO_5 + Al Slurry Coating on Stainless Steel

Sintered at 700°C for 3 hr in vacuum (10^{-6} ~ 10^{-7} Torr)

Y_2SiO_5 + 2 wt% Al

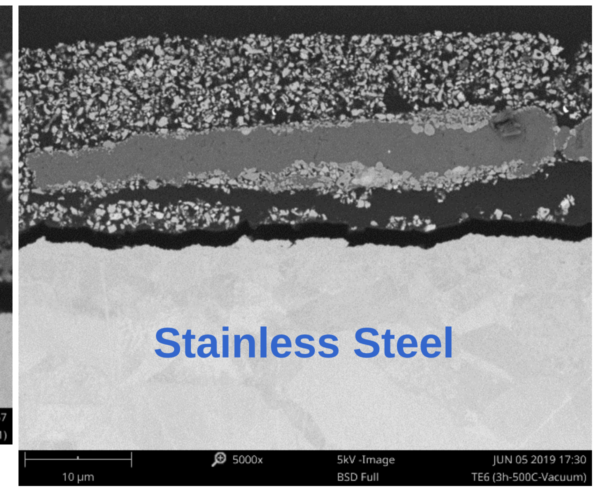


Y_2SiO_5 + 5 wt% Al



	Al	Fe	Cr	O	Si
Wt%	29.4	36.0	26.6	7.0	1

Y_2SiO_5 +10 wt% Al

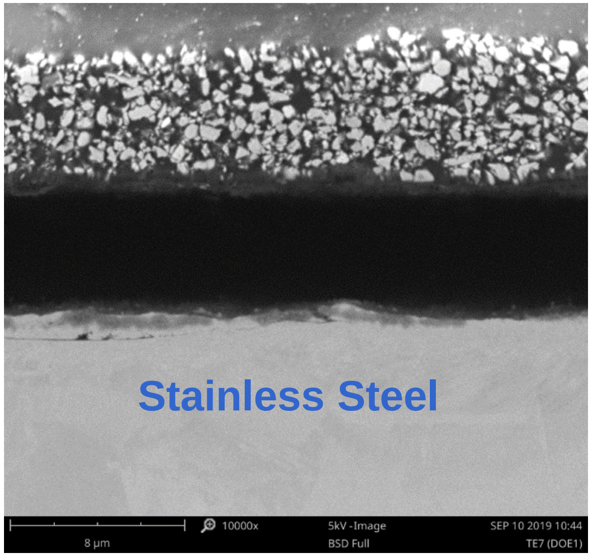


- Excess Al (Al = 5 wt% & 10 wt%) leads to coating debonding and spallation
- No excess Al visible with 2 wt% Al, however coating is not well bonded

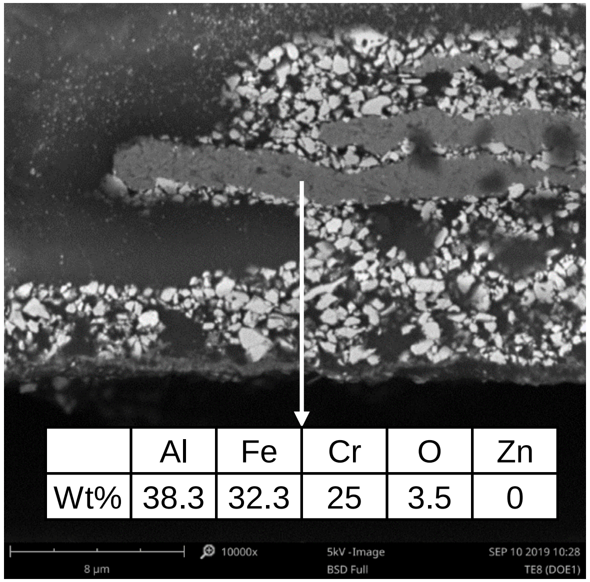
Y_2SiO_5 + (Al + Zn) Slurry Coating on Stainless Steel

Sintered at 500°C for 3 hr in vacuum (10^{-6} ~ 10^{-7} Torr)

Y_2SiO_5 + 2 wt% Al + 2 wt% Zn

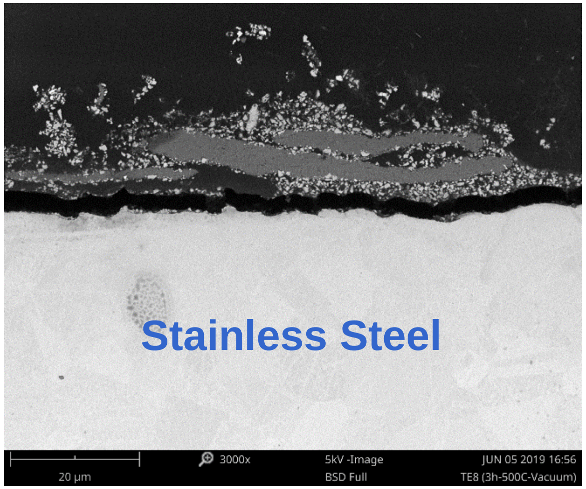


Y_2SiO_5 + 5 wt% Al + 5 wt% Zn



	Al	Fe	Cr	O	Zn
Wt%	38.3	32.3	25	3.5	0

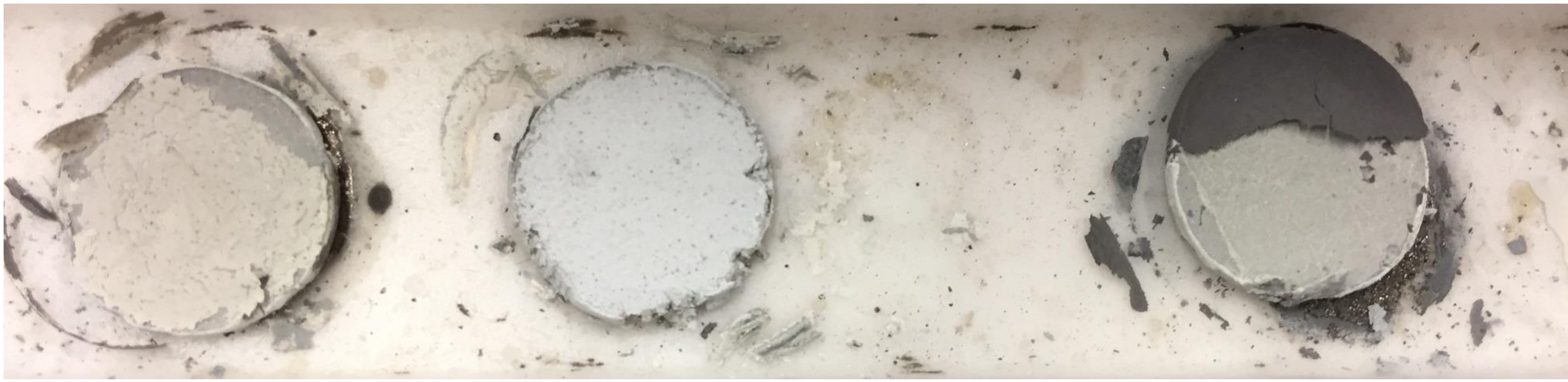
Y_2SiO_5 + 5 wt% Al + 5 wt% Zn



- Excess Al + Zn (Al + Zn = 5 + 5 wt% & 10 + 10 wt%) leads to coating debonding and spallation
- No excess Al visible with 2 wt% + 2 wt% Zn, however coating is completely debonded

Slurry Coatings on $Yb_{14}MnSb_{11}$
(Sintering Aid = 2 wt% Al + 2 wt% Zn)

Y_2O_3 | **Yb_2SiO_5** | **ZrO_2 + 7 w% Y_2O_3**



Sintering in vacuum (10^{-6} ~ 10^{-7} Torr)

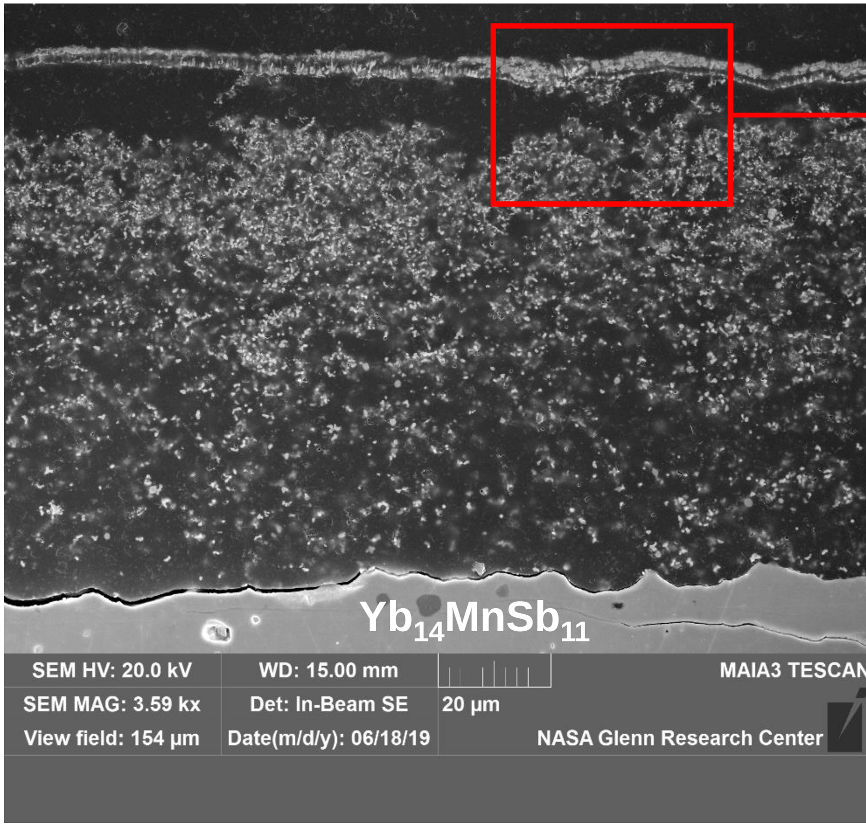
- Ramp to 500°C (4°C/min)
- Dwell at 500°C for 3 hr
- Cool down to RT (5°C/min)

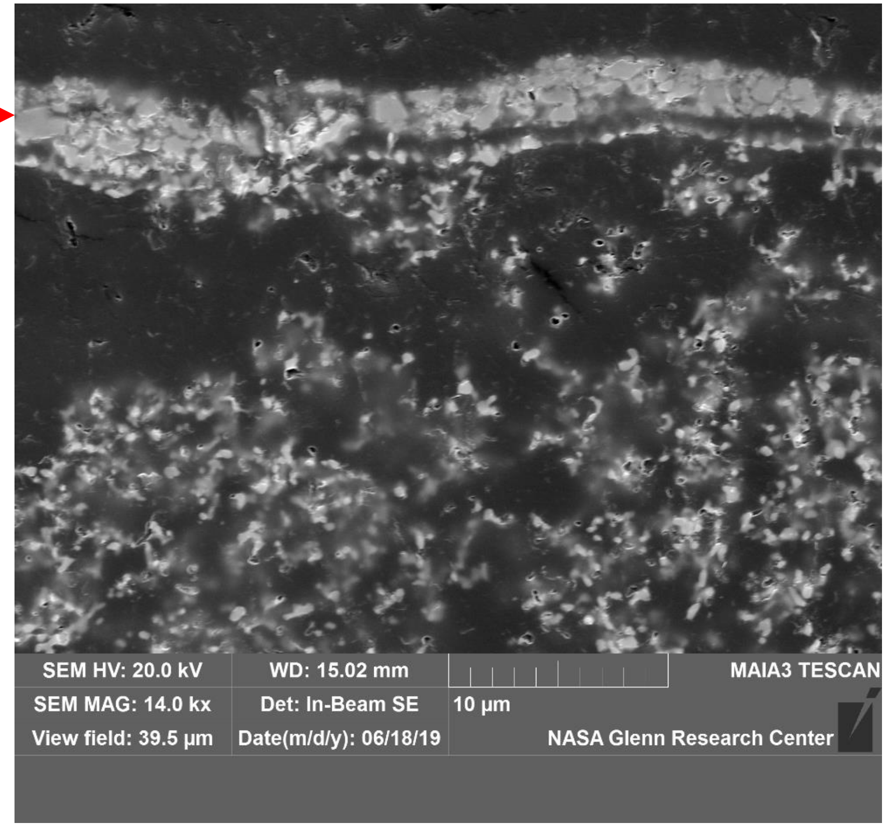
Oxidation in vacuum (10^{-6} ~ 10^{-7} Torr)

- Ramp to 1000°C (4°C/min)
- Dwell at 1000°C for 100 hr
- Cool down to RT (5°C/min)

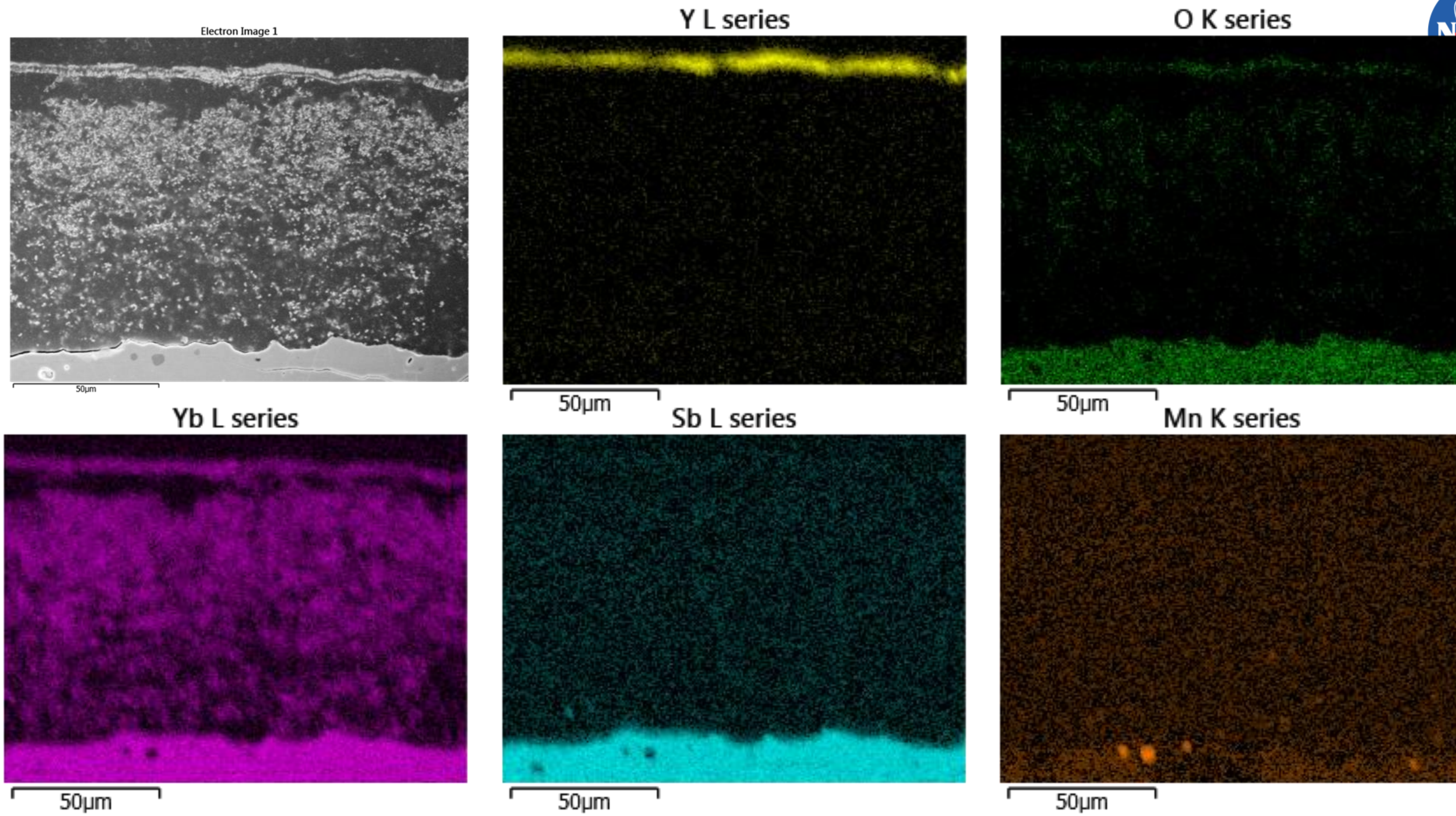
- Y_2O_3 was powdery: Crumbled on handling (darker gray edges are spalled areas)
- Yb_2SiO_5 looked best: Edges damaged by tweezers, indicating the coating is friable
- 7YSZ spalled: Black is remaining coating and gray is exposed substrate after spall

Y_2O_3 + 2 wt% Al + 2 wt% Zn





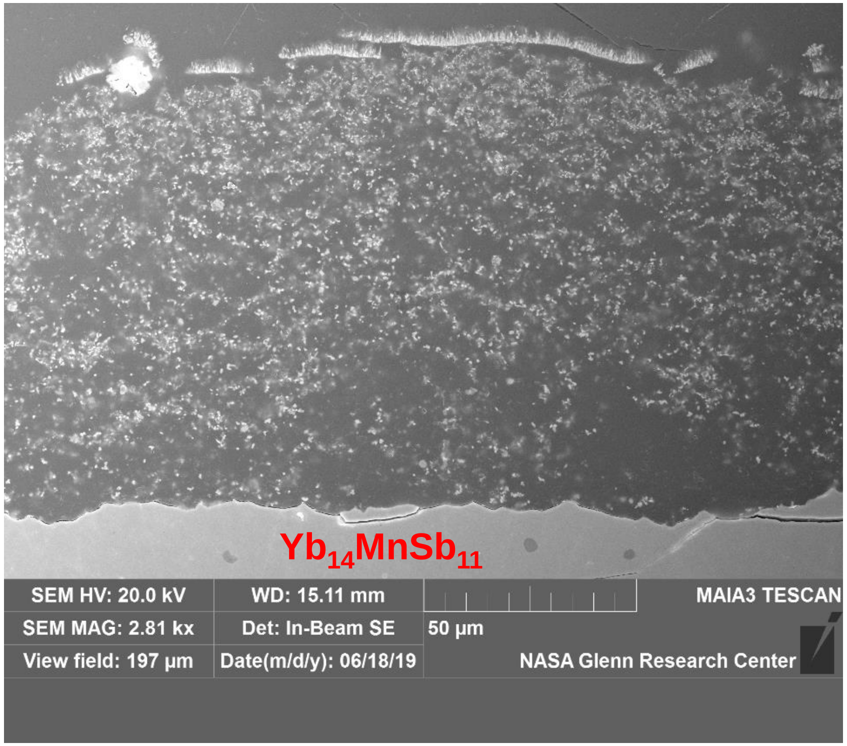
- An outer layer separated from the substrate by cloud of particles



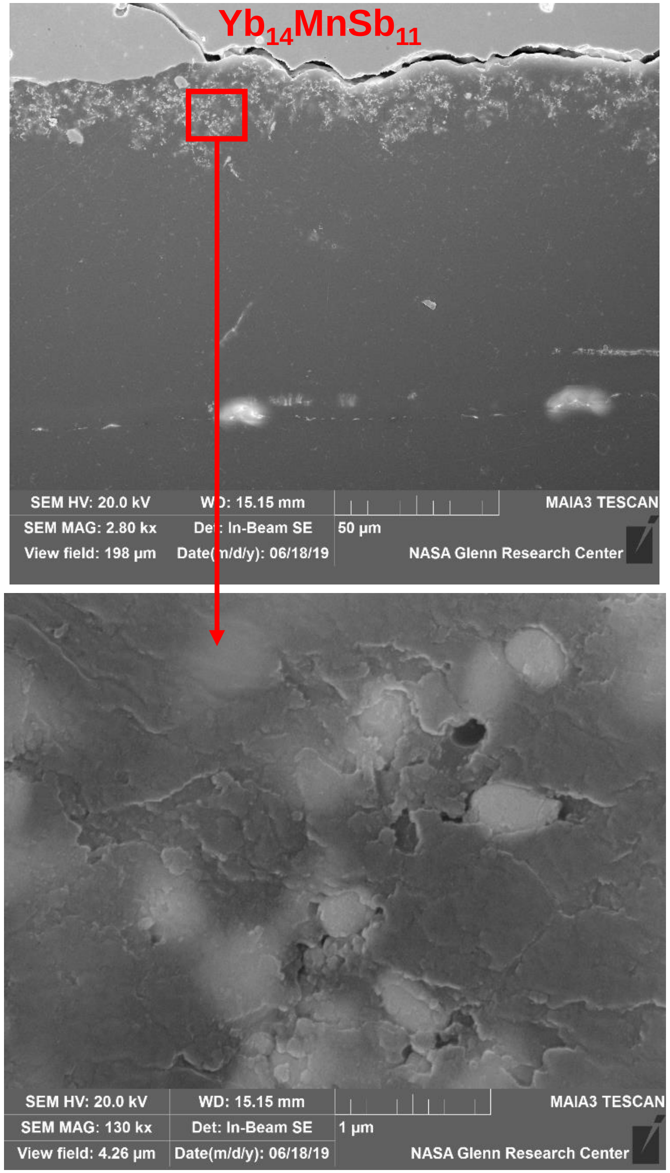
- The outer layer appears to be a Y_2O_3 + Yb_2O_3 solid solution
  - No Al and Zn detected in the coating by EDS – presumably dissolved in the substrate
- Cloud of particles is Yb_2O_3 due to the oxidation of substrate
  - Yb_2O_3 is thermodynamically more stable than Sb_2O_3 and MnO

Yb_2SiO_5 + 2 wt% Al + 2 wt% Zn

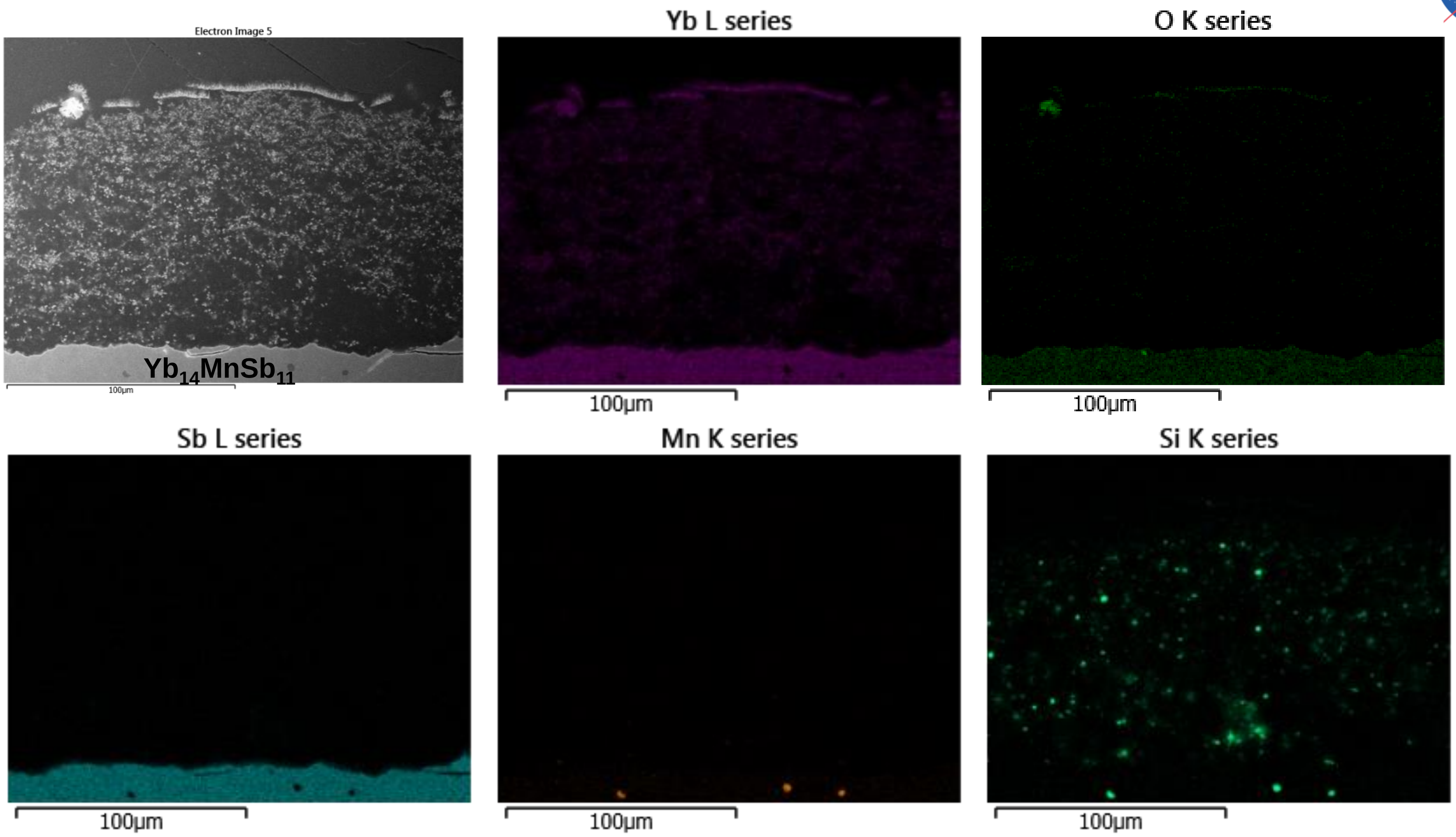
Coated Side



Uncoated Side



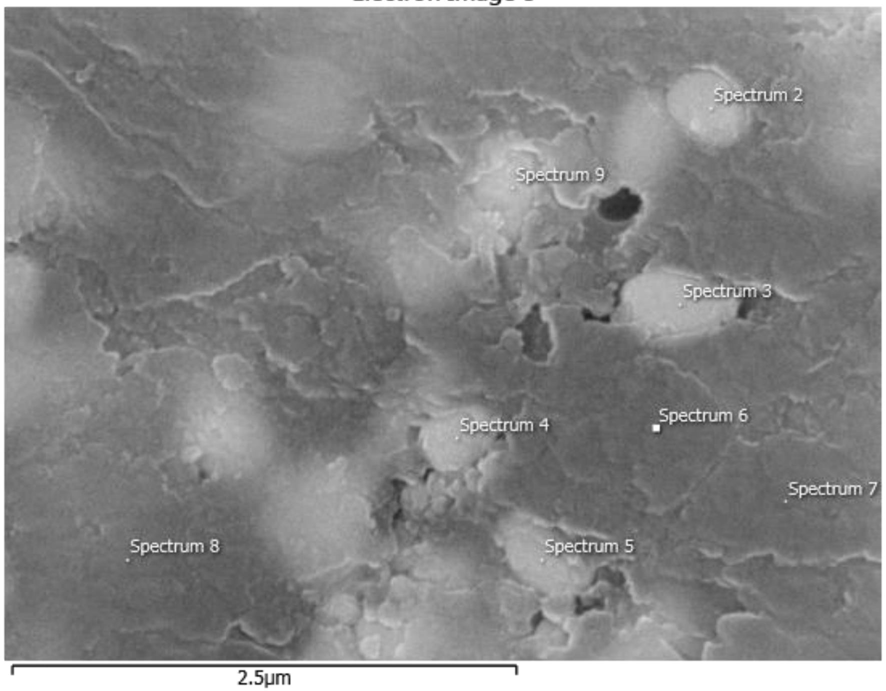
- Similar microstructure to Y_2O_3 coating
- Uncoated side has cloud of particles only



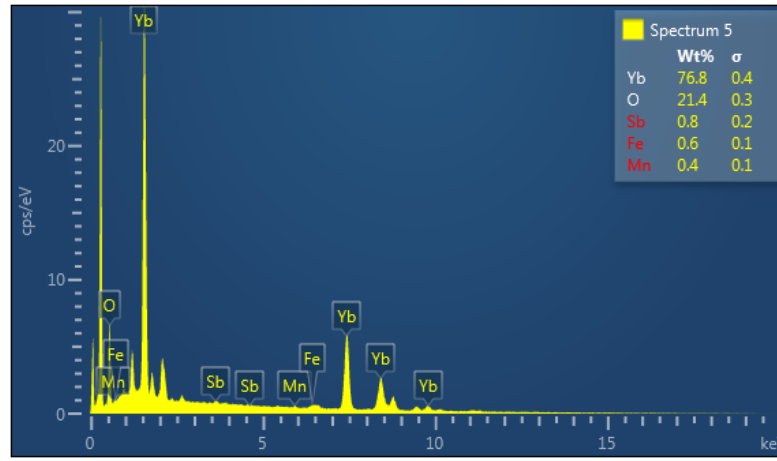
- No Si in the outer layer, but Si in the cloud of particles
  - Need further investigation to understand this
- No Al and Zn detected in the coating by EDS – presumably dissolved in the substrate

Particles on the Uncoated Side

Electron Image 8



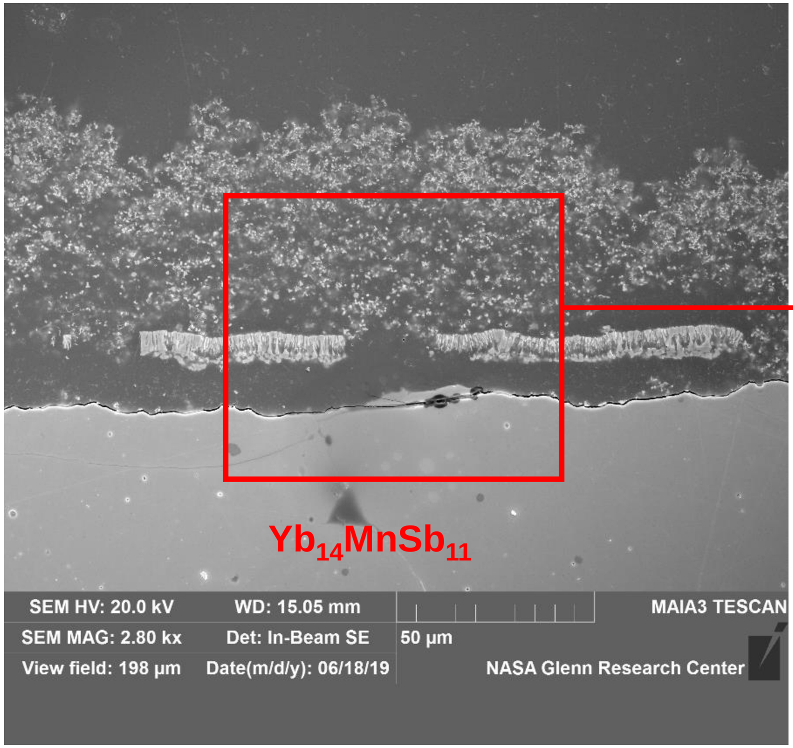
Spectrum 2, 3, 4, 5, 9

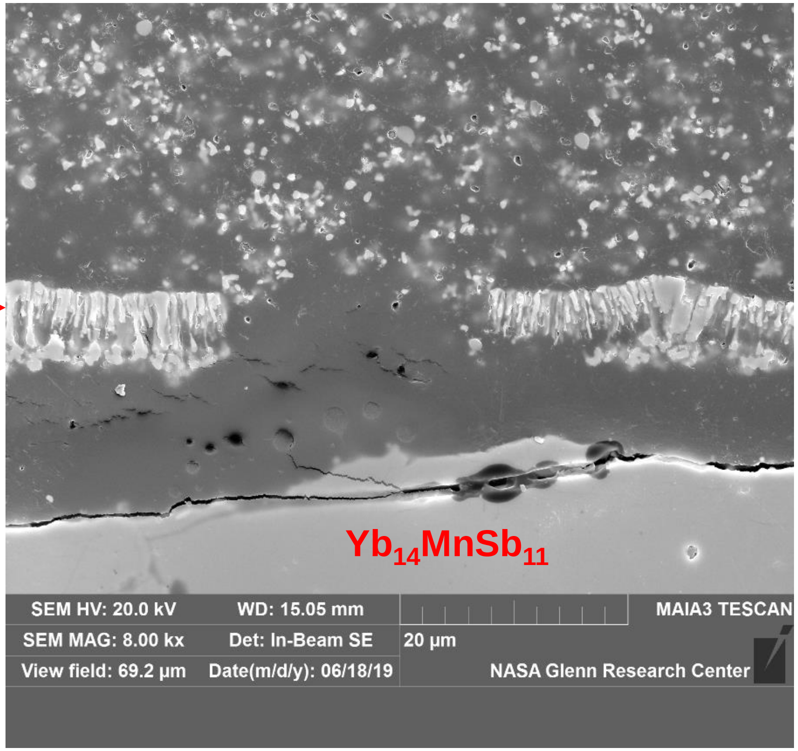


Yb_2O_3 = 87.8 wt% Y + 12.2 wt% O

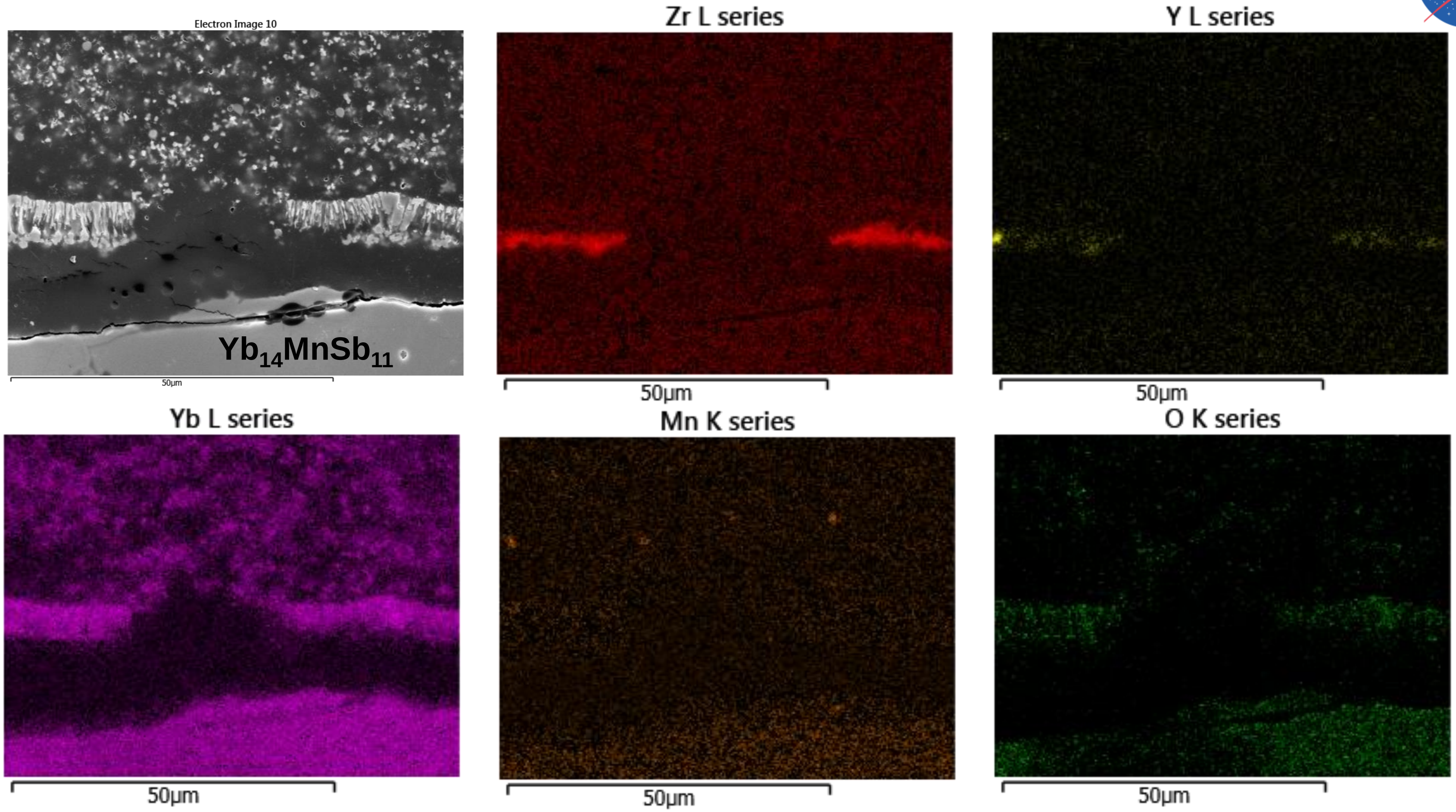
- Particles are likely Yb_2O_3

YSZ (ZrO_2 + 7 w% Y_2O_3) + 2 wt% Al + 2 wt% Zn





- YSZ coating is buried in the cloud of particles



- Yb_2O_3 layer grew on YSZ layer
- Cloud particles is Yb_2O_3

Yb_2SiO_5 + 2 wt% Al

Sintering in vacuum (10^{-6} ~ 10^{-7} Torr)

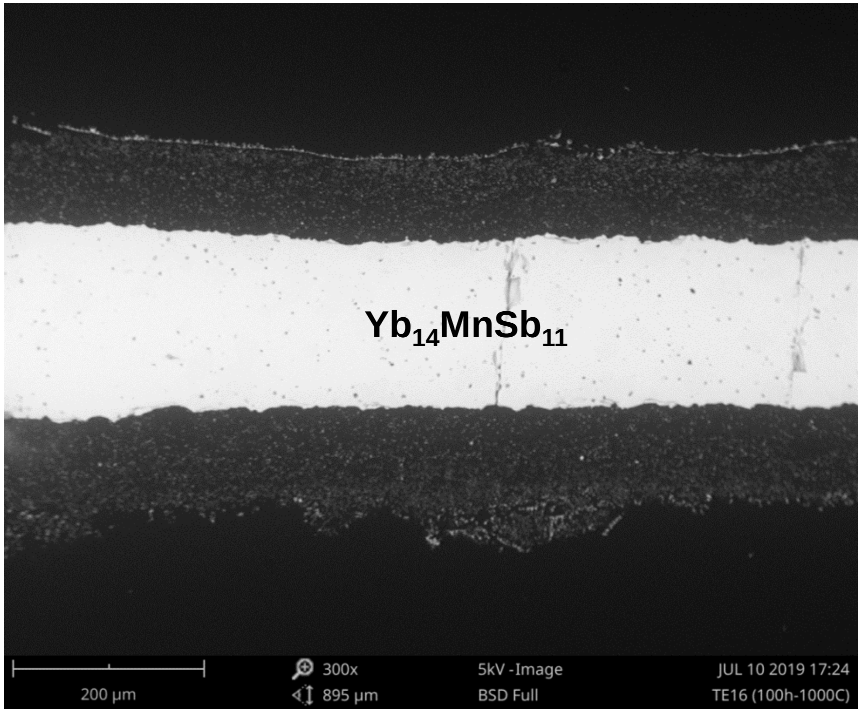
- Ramp to 700°C (4°C/min)
- Dwell at 700°C for 3 hr
- Cool down to RT (5°C/min)

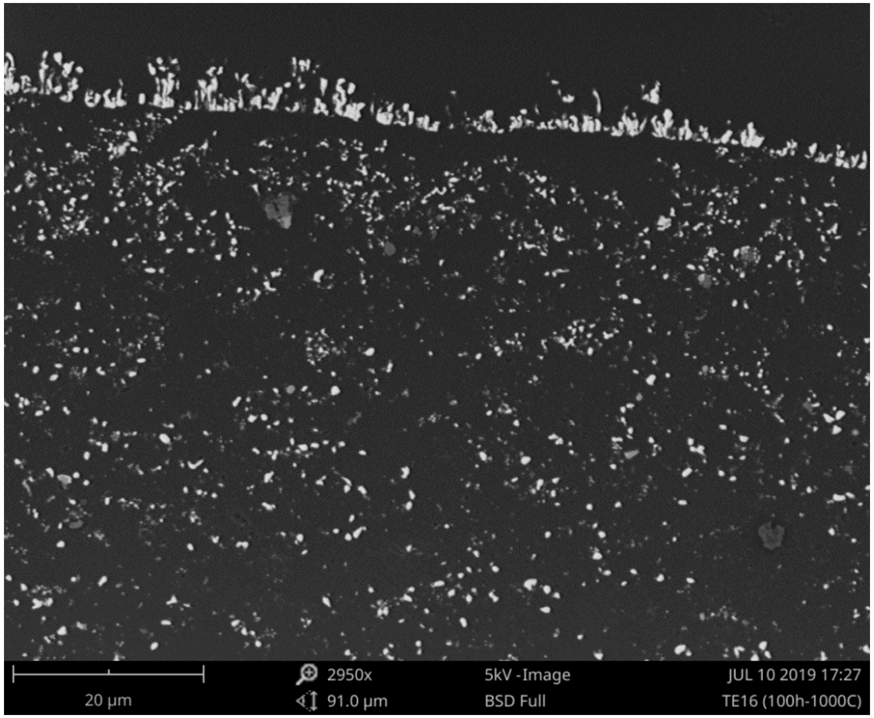
Oxidation in vacuum (10^{-6} ~ 10^{-7} Torr)

- Ramp to 1000°C (4°C/min)
- Dwell at 1000°C for 100 hr
- Cool down to RT (5°C/min)

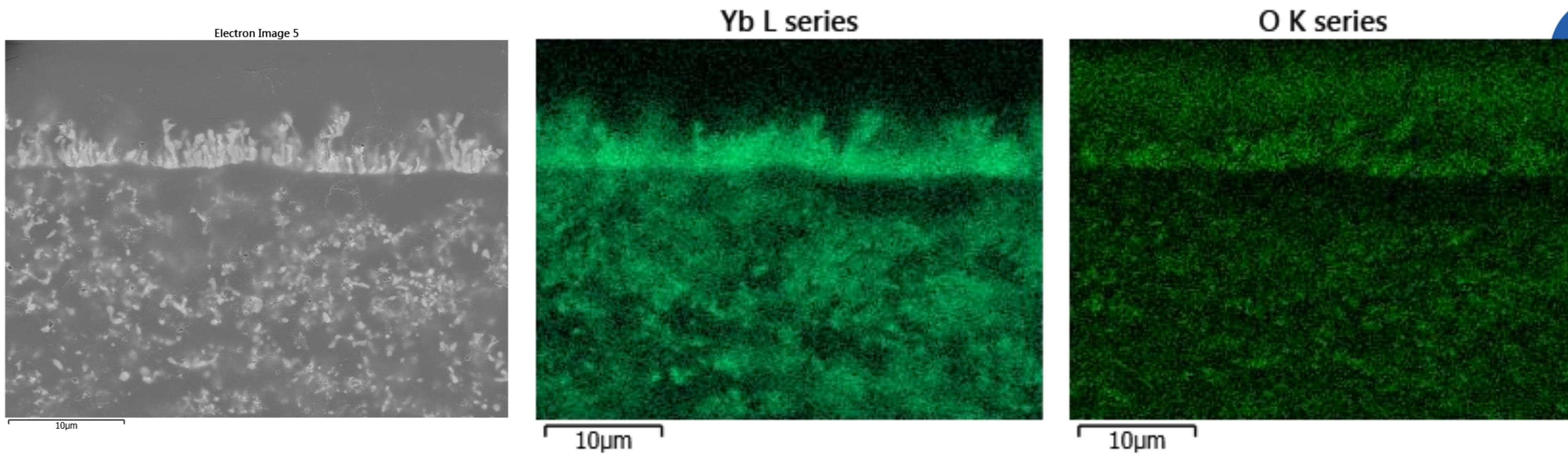
- Coating stayed on after 100h / 1000°C exposure, however, it was friable

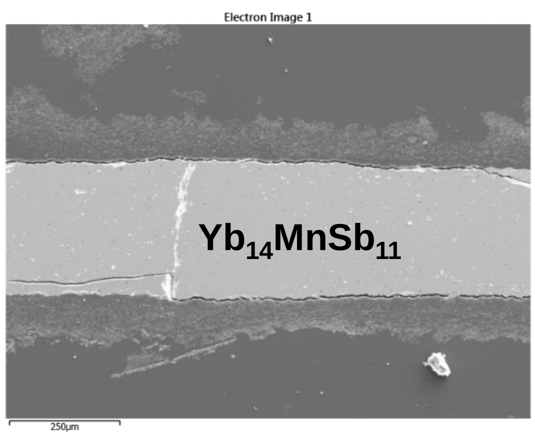
Yb_2SiO_5 + 2 wt% Al after Oxidation

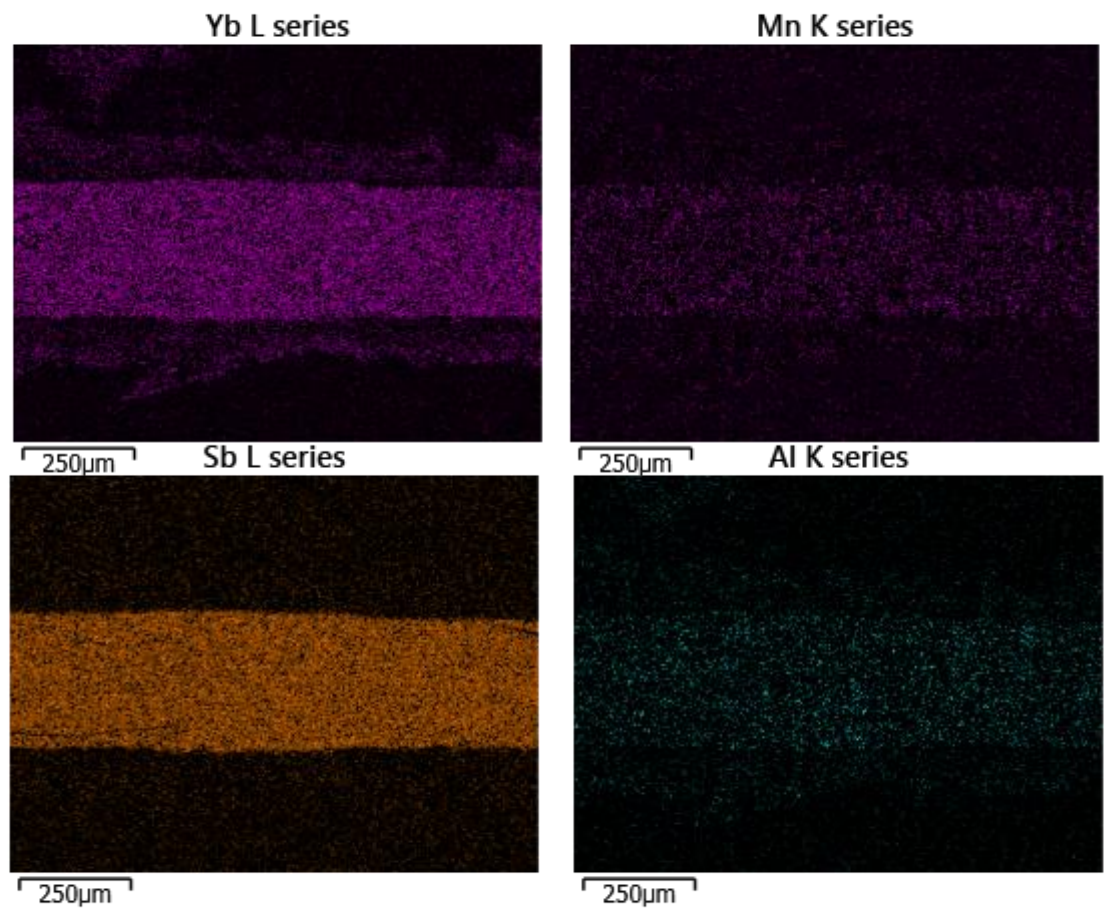




- Similar microstructure to Yb_2SiO_5 coating with Al + Zn sintering aid







- No Al in the coating detected by EDS
- Al presumably dissolved in the substrate

Conclusion

- $Yb_{14}MnSb_{11}$ requires sublimation protection coating to be useful as a thermoelectric material for next gen Radioisotope Thermoelectric Generator (RTG)
- Rare oxides, rare earth silicate, and ZrO_2 + 7 Y_2O_3 (YSZ) are promising coating candidates because they are chemically compatible with the substrate
  - Yb_2O_3 is very stable, due to its very low free energy of formation, however, is friable, causing the coating to debond
  - Debonded coating was weak and friable, presumably because Al and Al + Zn are not effective sintering aids as they dissolve into the substrate
- Alternative sintering aids that do not react with the substrate required
- Even with a better sintering aid, debonding may be unavoidable due to the weak and friable nature of Yb_2O_3 oxide
  - Alternative strategy is to develop a coating with strong cohesive strength that can be physically harnessed to the substrate to mitigate sublimation

Acknowledgements

- Wayne Jennings (NASA Glenn) – SEM analysis