Feasibility Assessment of Self-Grading Metallic Bond Coat Alloys to Protect Si-Based Ceramics

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Goal: Oxygen and/or H_2O Barrier Coating for Si-Based Ceramics

- Prevent substrate oxidation or at least block H_2O

- Few (any?) oxides with stability in water vapor, low ion transport, and thermal expansion compatibility with Si_3N_4/SiC
  - -Single-layer homogeneous coating unlikely to succeed
  - -Multi-layer graded coating gives best chance (e.g. BSAS-Mullite/Si coatings)

- Not clear what to use/how to achieve stable graded layer (at least to me!)

Al_2O_3 Shows Promise for Stability in H_2O at Temperatures up to ~1200-1300°C

But:

•Al_2O_3 Thermal Expansion (~ 9) >> Si_3N_4 (~ 3): yields tensile stress on cooling/**cracks!**

-want protective oxide to have a **equal/lower** thermal expansion to get compressive stress/resist cracking

•Al penetration into substrate ceramic may be problematic for mechanical properties

How to deal with these incompatibilities?

Approach: Metallic Alloy Coatings to Form Al_2O_3 on Si-Based Ceramics

Two Exploratory Concepts

- Thin Alloy Coating as Precursor to Oxide: **H_2O Barrier**
  - -pretreatment to convert **all** metal to oxide
  - -Substrate compatibility by self-grading during conversion to oxide, effectively a surface alloying

- Alloy Bond Coat Approach: **Oxygen and H_2O Barrier**
  - - Al-rich metallic reservoir to maintain/heal Al_2O_3
  - -coating alloy design for compatibility with substrate

Talk Highlights Series of Small Exploratory Experiments Designed to Assess Potential of Alloy-Based Protection Concepts

•**Alloy Precursor**: 1-3 micron sputtered layers of a range of Al_2O_3-forming alloys on Si_3N_4/SiC

-NiAl+Hf, NiCrAlY, $Cr_2Al(Y)$, FeCrAlY, TiCrAl

-Oxidized 1 - 1000 h, 1000-1200°C (isothermal and cyclically)

•**Alloy Bond Coat**: TiCrAl coating (Ti-51Al-12Cr at.%)

-10-25 micron sputtered

-75 micron low pressure plasma sprayed

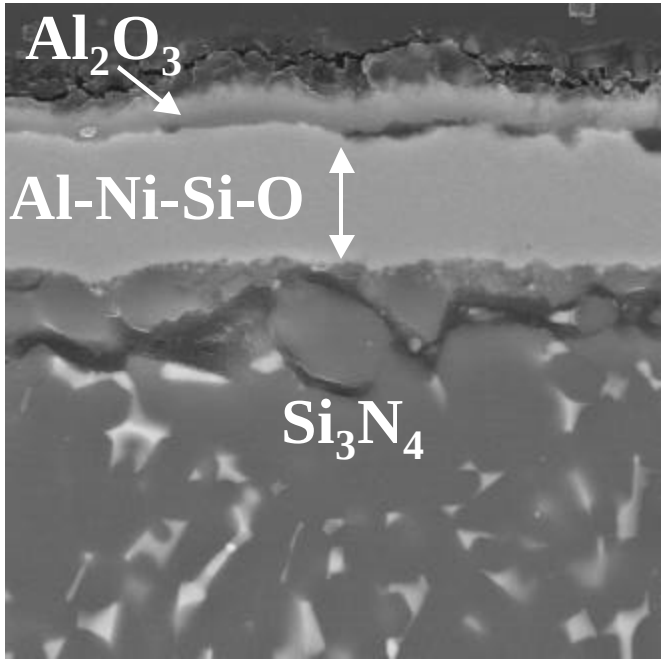
-Si_3N_4 (SN 282)

-Cyclically oxidized

Duplex Graded Scales Formed by Conversion of Alloy Precursor to Oxide

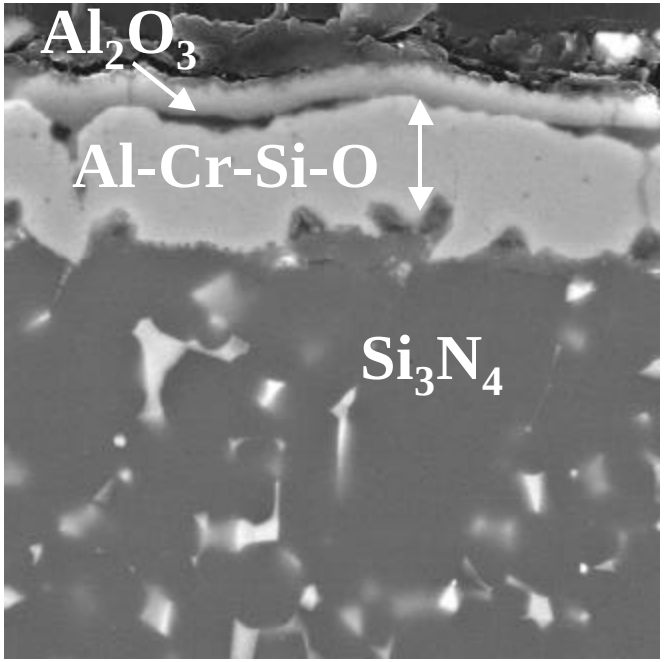
SEM Cross-Sections of Alloy Coatings on SN 282 After Oxidation Pretreatment (1150-1250°C, 30 min – 1 h)

NiAl+Hf



2 μm

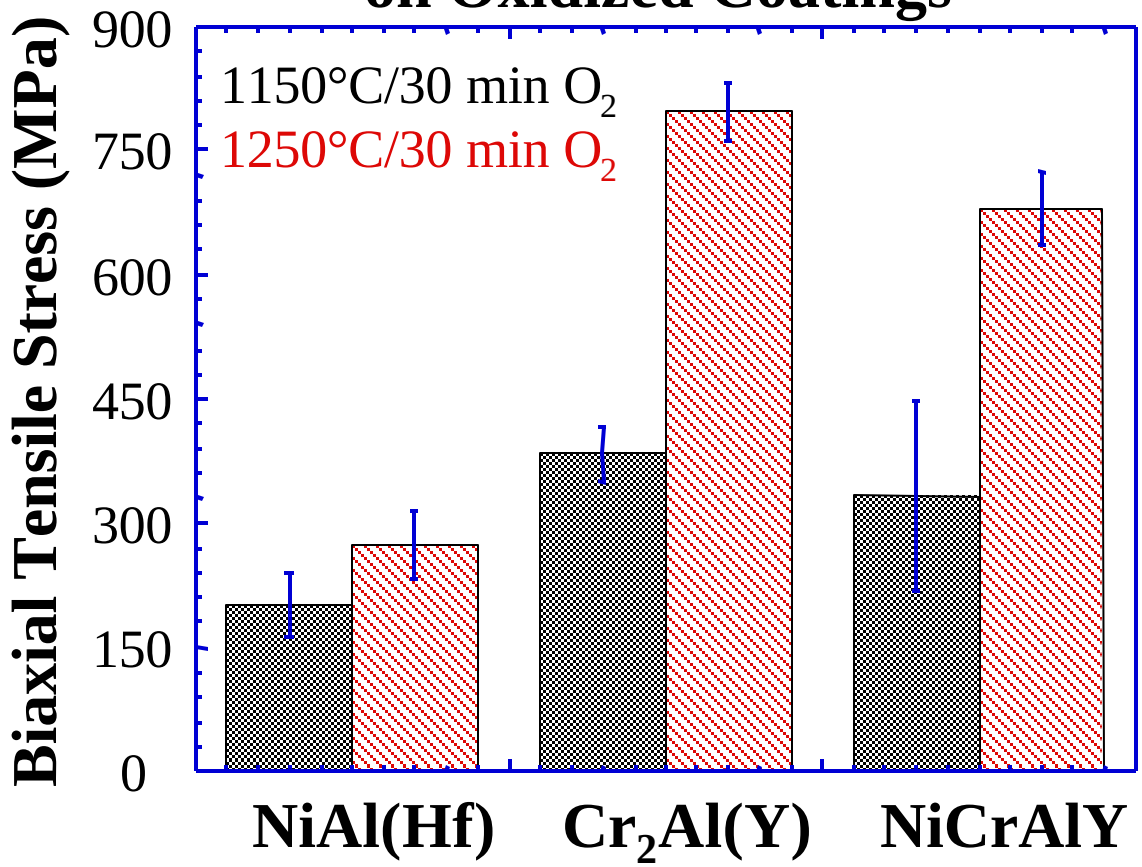
Cr_2Al+Y



- Continuous Al_2O_3 overlying mixed oxides with coating base metal (Ni, Cr in above) and Si from substrate Si_3N_4

But: Residual Tensile Stress in the Al_2O_3 Formed from All Precursor Alloys

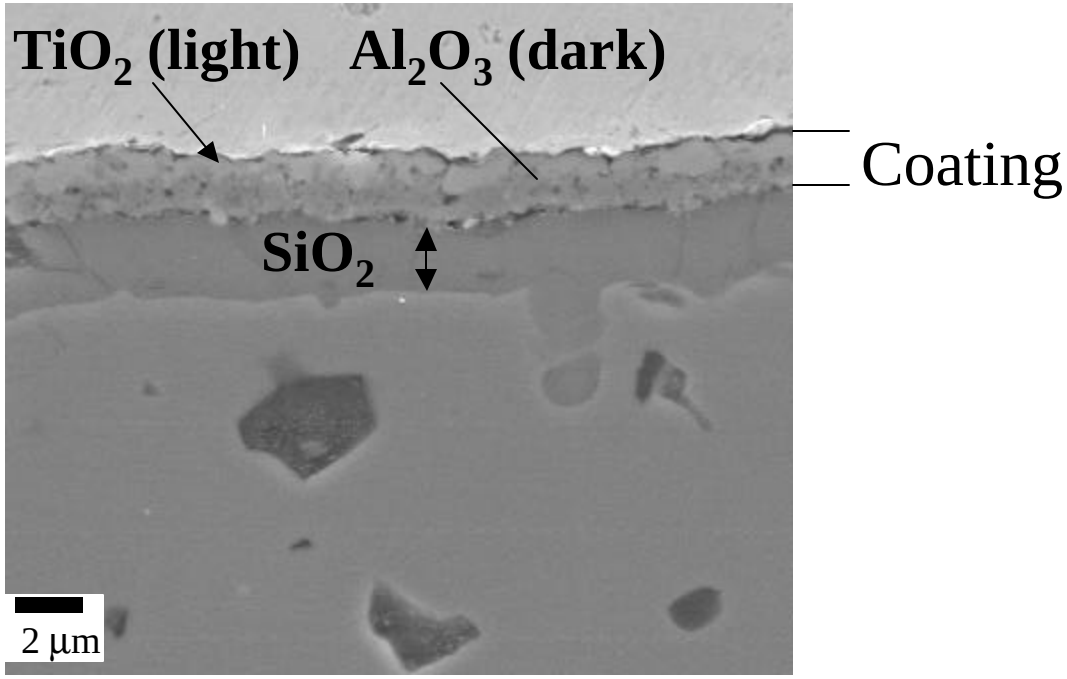
Typical Room-Temperature PSLS Stress Measurements on Oxidized Coatings



•All but NiAl and TiCrAl (not shown) showed severe cracking, spalling during cycling

Oxides Formed From TiCrAl and NiAl Precursor Coatings Showed Good Adherence

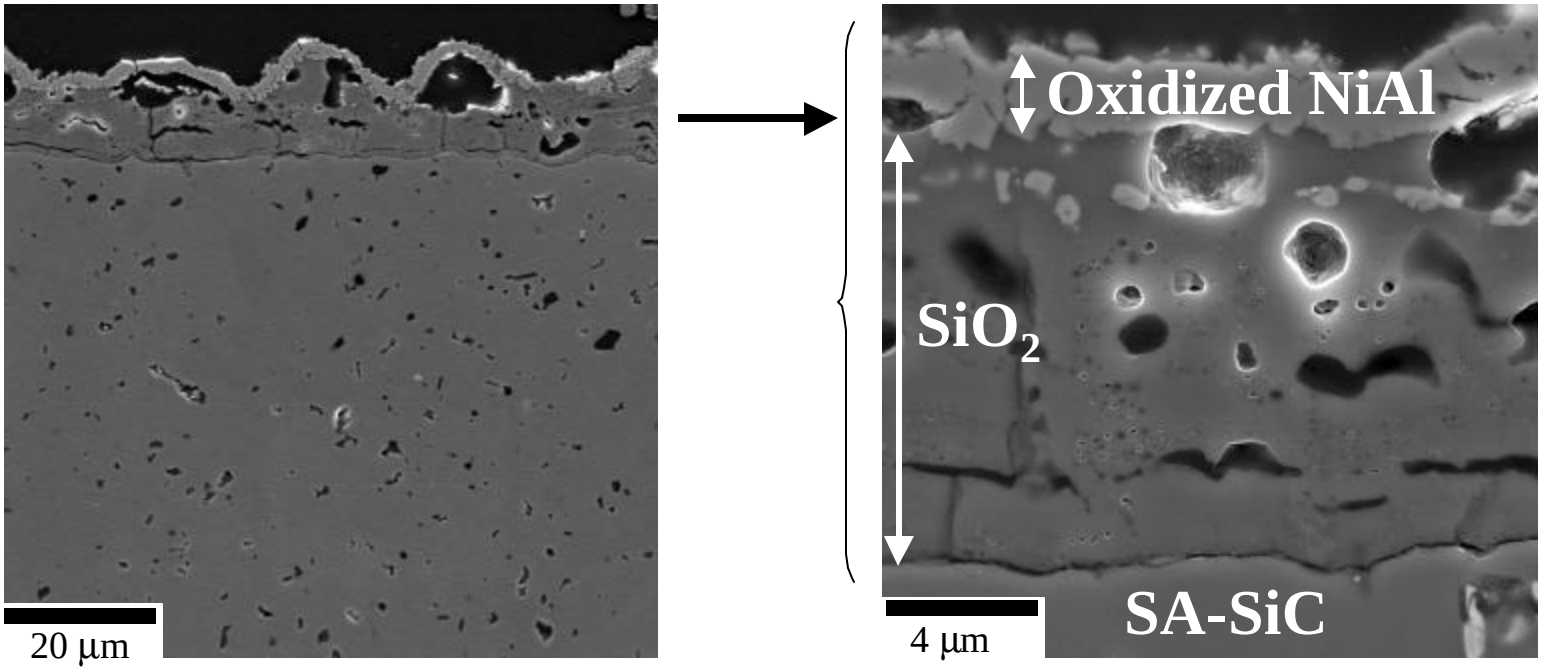
SEM Cross-Section of TiCrAl on SA-SiC
10-100 h Cycles (1000 h total), 1100°C, Air



- No spallation of coating observed- adherent in “dry” air cycling (some cracking observed)
- Substrate SiO_2 growth (coating not an oxygen barrier)

Oxide Formed from Metal Precursor Not an Effective H_2O Barrier

SEM Cross-sections: 1200°C, 500 h, 100% H_2O



- Some local oxide coating surface cracking despite good adherence in dry air: H_2O penetration and rapid SiO_2 formation/coating failure

Need to Have Some Mechanism for Healing of Protective Oxide Layer

- **Bond coat approach would allow for healing**

- **Complications w/ alloy bond coats on Si-based ceramics**

  -Compatibility: Conventional Ni- and Fe- base bond coats may form low melting point silicides (Ni-Si, Fe-Si)

  -Al interaction/loss with substrate (major TBC issue)

  -CTE mismatch: Alloys (15-20), Al_2O_3 (8)

  -Al_2O_3 growth rate limitations-too fast at temperatures of interest

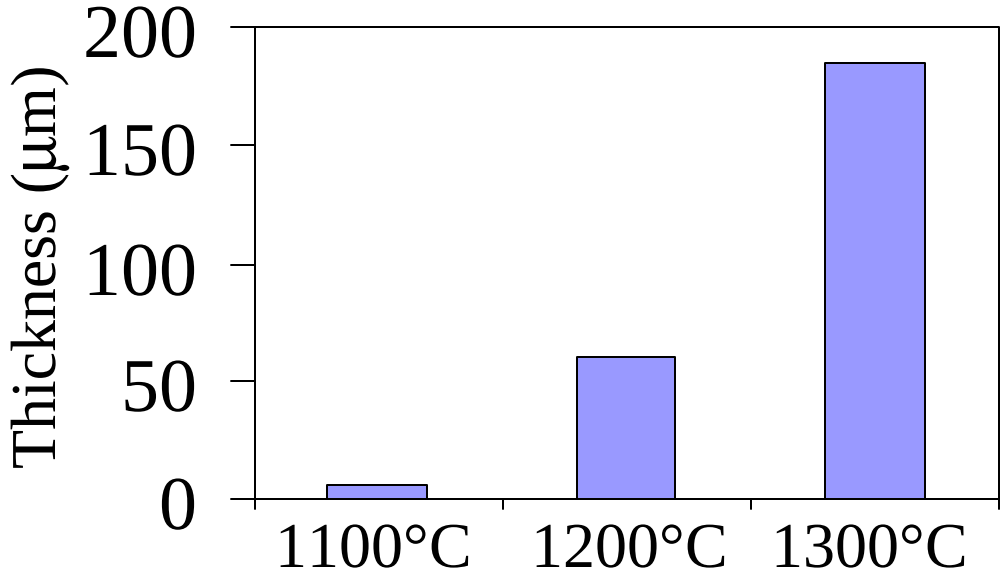
TiCrAl Family of Bond Coats May Solve Compatibility Issues

- Ti-51Al-12Cr at.%: Developed for γ titanium aluminides
- Eutectics in Ti-Si system > ~ 1300°C
- High affinity of Ti for Nitrogen may lead to self-graded coating, prevent Al loss to substrate
- Relatively low CTE for a Metal (~15)
- Thin TiCrAl precursor coatings showed good compatibility and adherence to Si_3N_4/SiC in exploratory experiments

Upper-Use Temperature for Al_2O_3 on Order of 1100°C for 40,000 h Lifetime

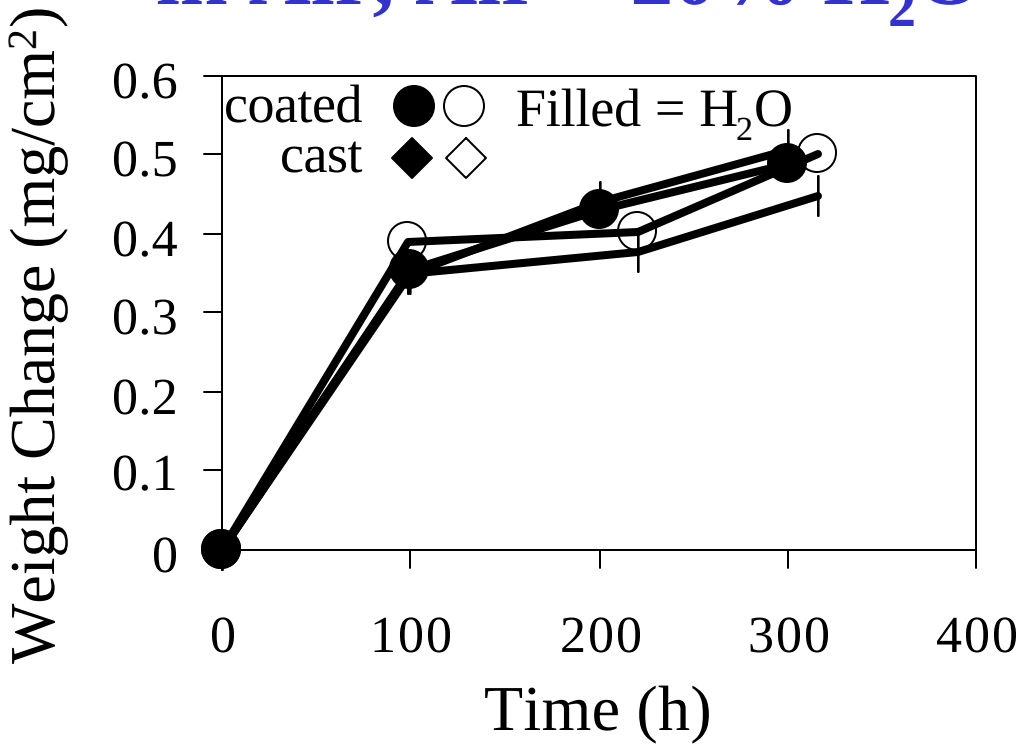
(Initial Driver for Interest in SiO_2 Formers)

Al_2O_3 Growth (mm) in 40,000 h



- Simple parabolic extrapolation from oxidation of optimized Hf- doped NiAl (Pint): spallation, Al depletion <u>not</u> considered
- TBC/EBC: Ceramic topcoat over TiCrAl/cooling to push service above 1100°C

TiCrAl Coated SN 282 Same as Cast TiCrAl in 3-100 h Cycle Screening at 1000°C in Air, Air + 20% H_2O

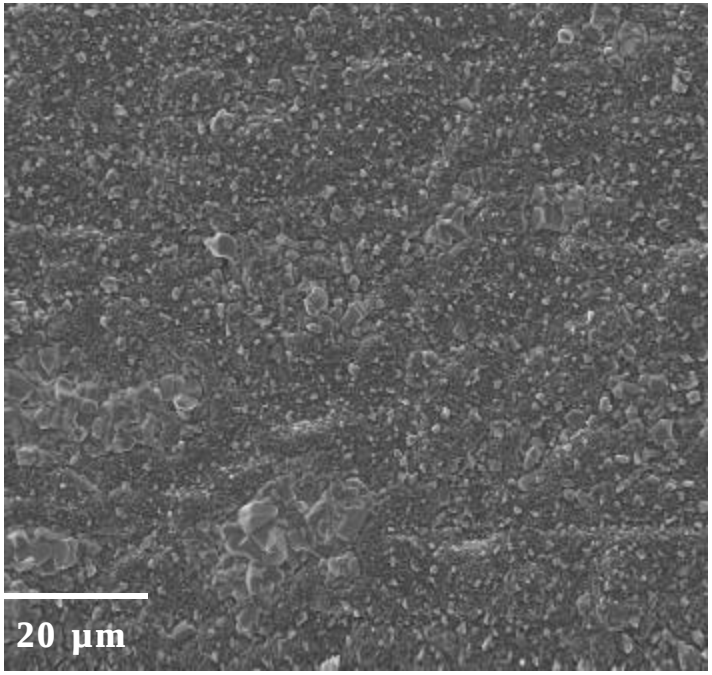


- Phase transformation complication with TiCrAl at ~ 1100°C
  - -good chance to eliminate with alloying
  - -initial screening at 1000°C
- 1-face sputtered coated TiCrAl (10 μm): No spallation

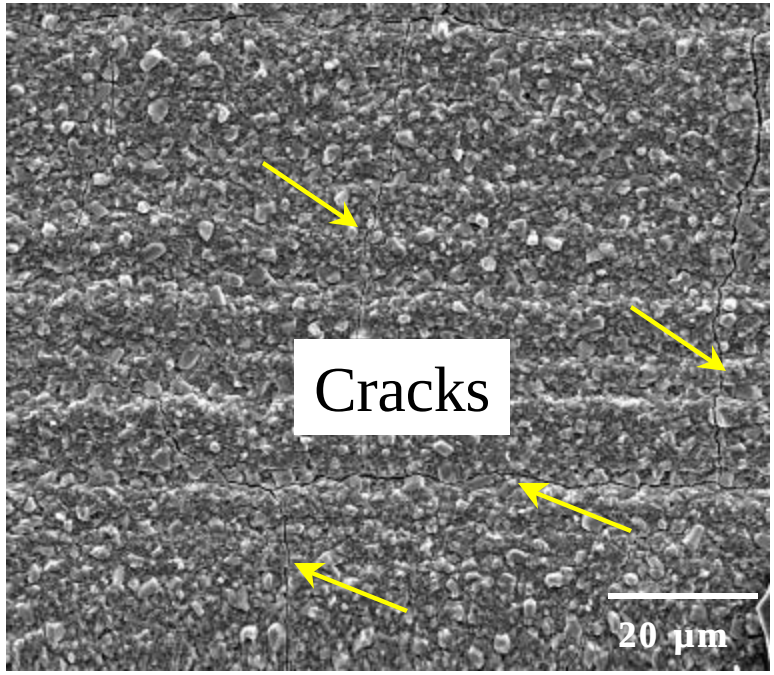
Compressive Stress/Surface Cracks in TiCrAl on Si_3N_4 after 1000°C, 3-100 Cycles

SEM Surfaces After 1000°C Cyclic Exposure
(No differences between Air, Air + 20% H_2O)

Cast TiCrAl: -2.9 GPa Biaxial Stress



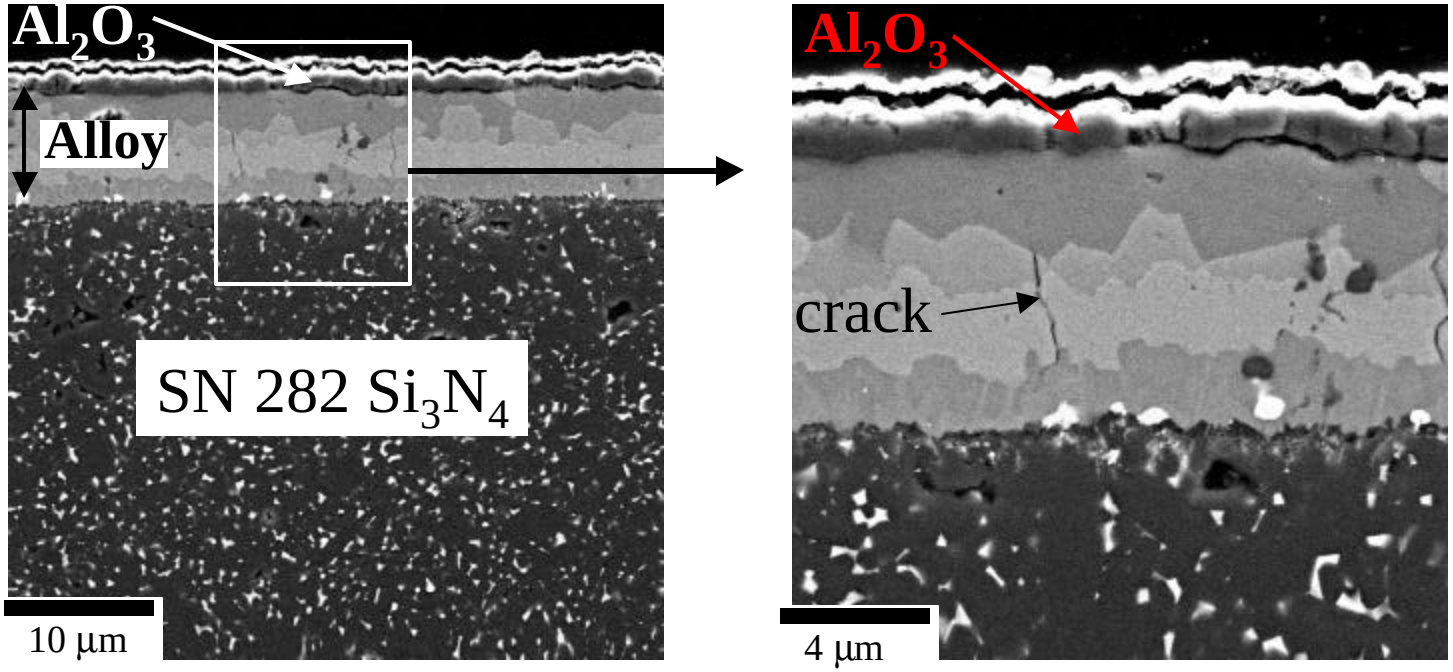
TiCrAl-Coated SN 282 -330 MPa Biaxial Stress



- No spallation was observed- the coating remained adherent

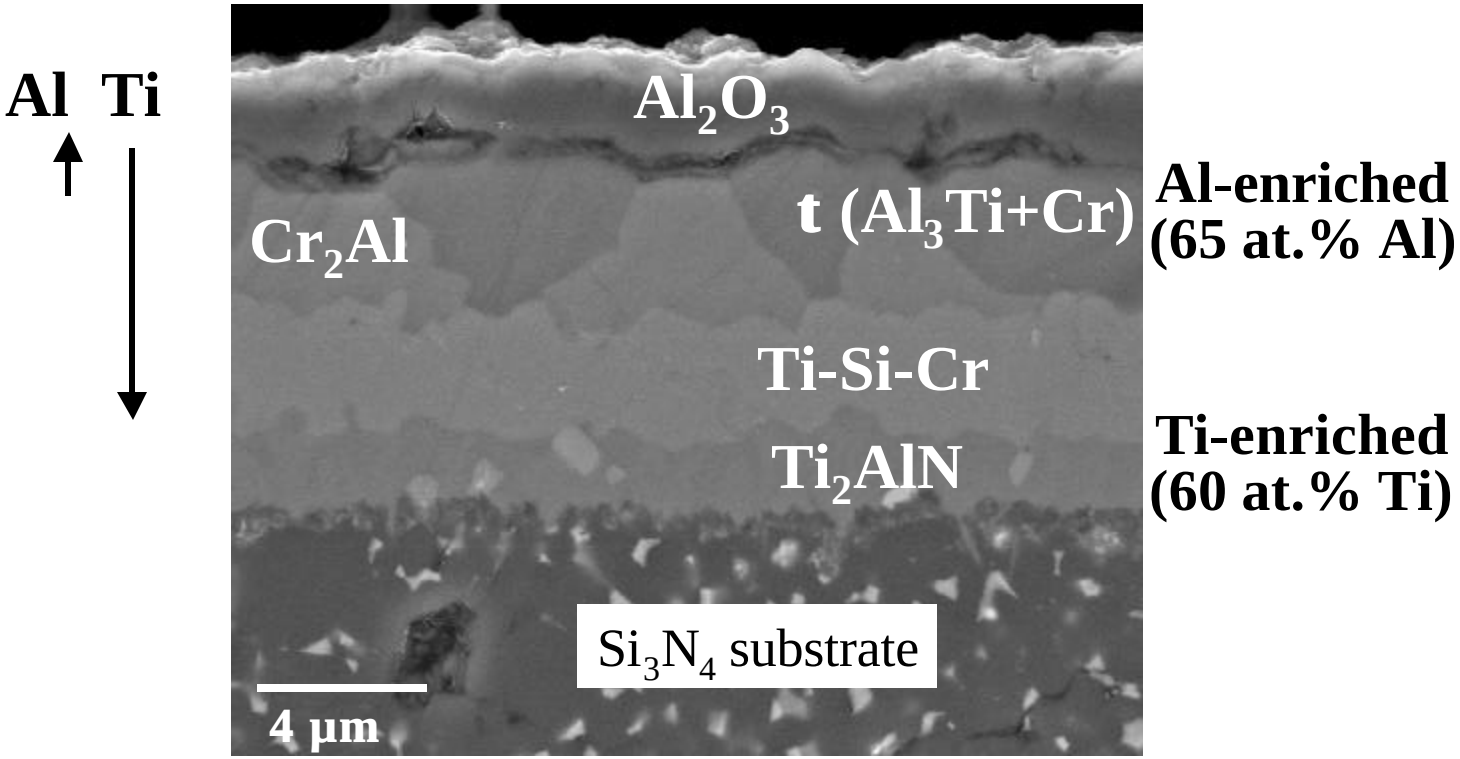
No Through Thickness Cracks or SiO_2 Formation From Substrate Si_3N_4 Observed (Preliminary Analysis)

SEM Cross-Sections after 1000°C Cyclic Exposures



- Al_2O_3 surface cracks healed or not entirely through thickness
- Blunting of cracks within alloy layer

Rapid Back Diffusion/Reaction of Ti with Si_3N_4 Results in Al-Enrichment Under Al_2O_3



- Al enrichment allows local healing of cracks in Al_2O_3
- No evidence of significant Al penetration into Si_3N_4

Movement of Al/Ti in TiCrAl on Si_3N_4 Very Interesting and Unusual Result!

•For Al_2O_3-forming bond coat alloys on TBC's usually see Al-depletion under Al_2O_3 and Al loss to superalloy substrate (life-limiting factor)

-Speculation: Solve Al loss problem in superalloy/TBC systems by similar phenomena to Al-enrichment effect in TiCrAl/Si_3N_4 system???

•Repeated surface cracking/rehealing of TiCrAl-formed Al_2O_3 on Si_3N_4 may lead to high Al consumption rates

- problem for frequent thermal cycle applications (jets)
- may be tolerable in land based turbine

•Formation of Cr_2Al a concern (low melting point)

-TiCrAl examined not yet optimized for Si_3N_4

Conclusions

- Thin metallic precursor coatings can be used to form dense, adherent oxide layer(s) on Si-based ceramics
  - -useful approach to explore interaction issues
  - -not effective as volatility barrier

- Al_2O_3-forming bond coats to protect Si-based ceramics may be viable at ~ 1100°C (higher with TBC/cooling)
  - -longer term/more aggressive exposures needed to more fully validate proof of principle

Future work

•1000 h+ exposures in water vapor environments at 1100°C for TiCrAl on SN 282

•Thicker plasma sprayed TiCrAl coatings on SN 282 (visual inspection suggests 75 micron coating adherent/high quality (collaboration with NASA Glenn)

- Role of coating thickness on cracking/adherence?

•Interest from industry for 1100°C applications or for use of TBC/EBC with cooling for higher temperature applications?

•Incorporation of alloy concepts explored to other EBC approaches and efforts?