# Evaluation of Tantalum Oxide-based Environmental Barrier Coatings

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**DOE/Energy Efficient Science Program under Cooperative Agreement DE-FC36-01CH11086-A000**

## Examination of Requirements for Environmental Barriers

- Thermal match with the substrate (AS800) (3.2 ppm/K)
- Corrosion resistance (water vapor- containing exhaust)
- Microstructural stability to high temperature (1300-1400C)
  - No phase changes
  - No ongoing chemical reactions with the substrate

Shows…..

→ $Ta_2O_5$ is a candidate coating



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Presented at EBC's for Microturbine and Industrial Gas Turbine Ceramics Workshop. November 18&19, 2003, Nashville, Tenn.

# DOE Program
# Set-up to Investigate performance of Plasma Sprayed $Ta_2O_5$

- Processing & Optimization of Tantalum Oxide-based Coatings
  - Optimize plasma spray conditions
- Compositional Tailoring of Tantalum Oxide Coatings
  - Stabilize low temp (β) phase
  - Limit Grain Growth
  - Match CTE
- Life Limiting Phenomena & Performance Testing
  - Thermal Cycling
  - Keiser Rig Testing
  - Residual Stress Evaluation
  - ~~Burner Rig Testing~~ → Testing awaits rig coming on-line

**The highlights of these efforts will be reviewed**



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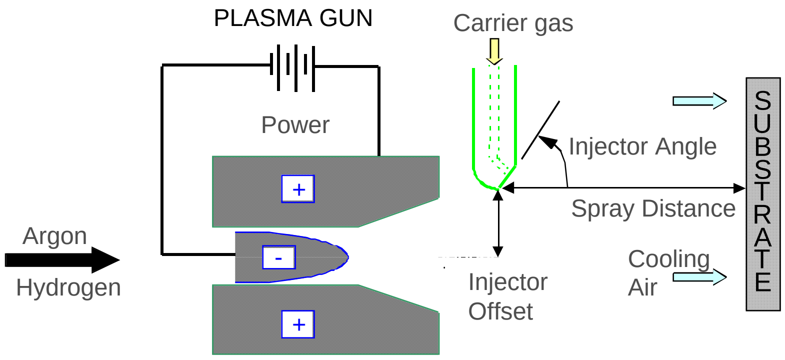
# Processing & Optimization of Tantalum Oxide based Coatings

- Optimize plasma spray conditions

Schematic of Small Particle Plama Spray (SPPS) apparatus




2 DOE's (7x2, 5x2+1x3),

Yield Optimized Conditions

| | |
|---|---|
| Robot scan rate (R) | 315 mm/min |
| Injector angle (A) | 0° |
| Injector offset (O) | 5 mm |
| Carrier gas flow (CF) | 3 slm |
| Power feeder disc speed (DS) | 0.4 rpm |
| Plasma gun power (P) | 40 kW |
| Total gas flow (TF) | 44 slm |
| % Hydrogen in plasma gas (%H) | 25% |

*Table 3. Optimized spraying conditions after second round of design experiments.*

# Optimized Plasma Spray Coatings

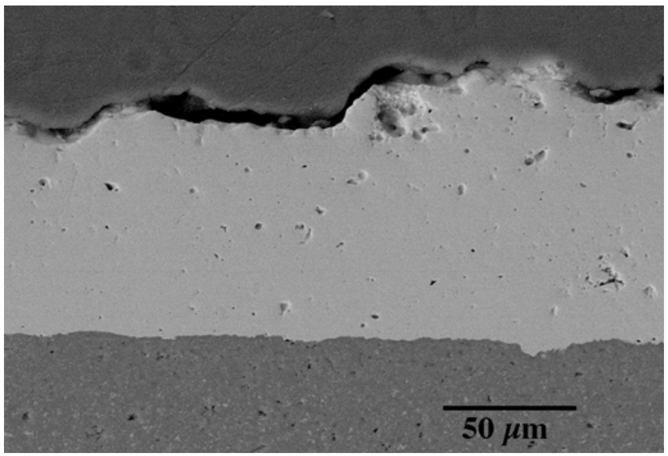



*Figure 2. Scanning electron micrograph of optimized $Ta_2O_5$ coating demonstrating low porosity and adequate thickness.*

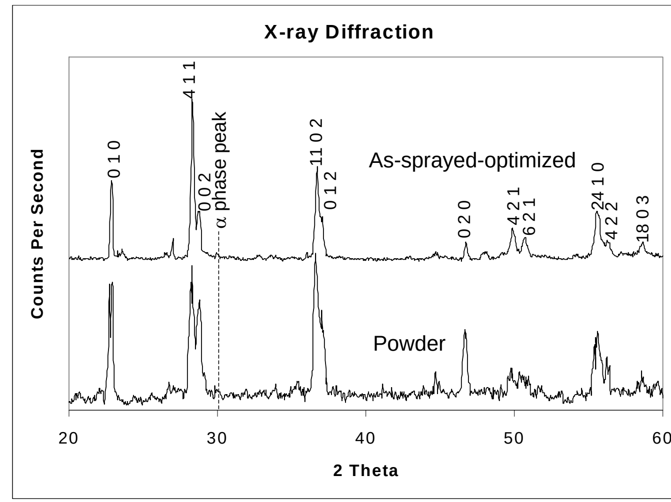



*Figure 5: X-ray diffraction pattern of tantalum oxide powder and optimized, as-sprayed coating with β phase peaks labeled showing the location of the absent primary α phase peak.*

Optimized coatings show good adherence and very little α- $Ta_2O_5$.



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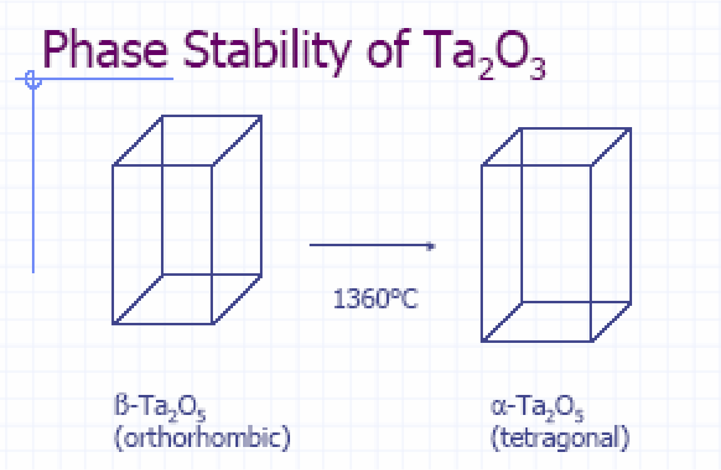
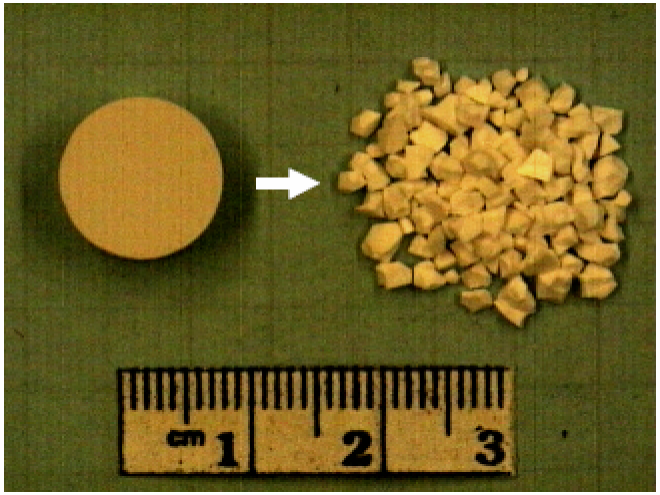
# Compositional Tailoring of Tantalum Oxide Coatings




$\Delta V$= 6-8%

**Pure Ta2O5 compact before and after firing at 1400ºC**



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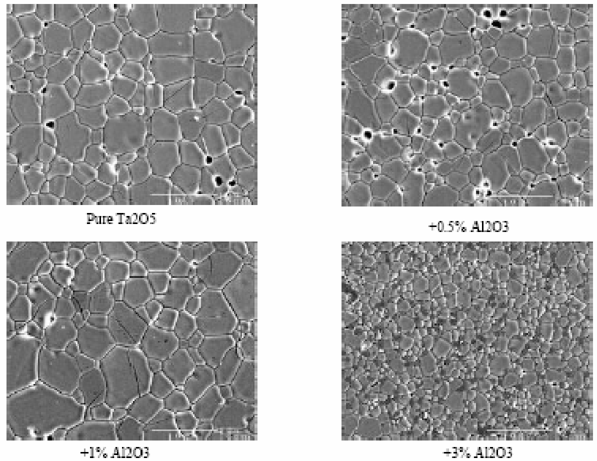
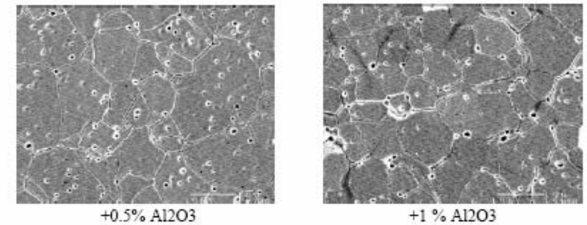
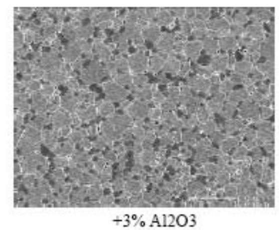
# $Al_2O_3$ Stabilizes β-phase to Higher Temperatures




1350C/50H

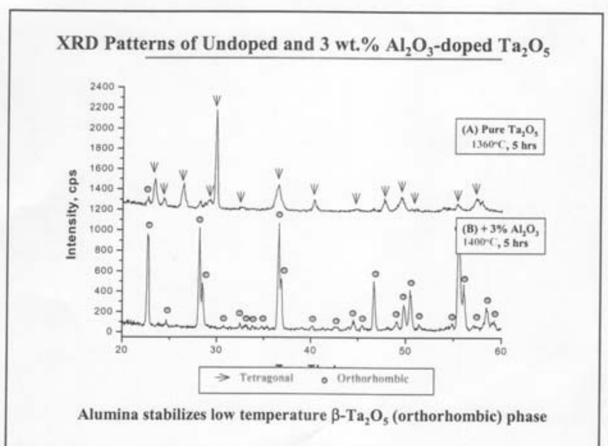



**Dopant Effect**

**Microstructures of $Ta_2O_5$ Doped with $Al_2O_3$ fired @ 1450°C for 5 hrs**

1450C/5H

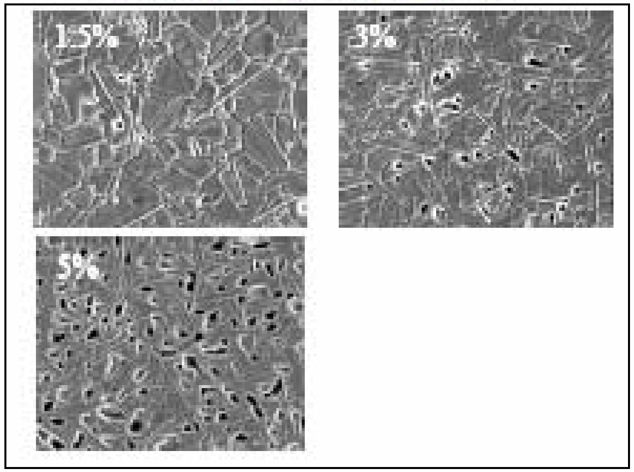


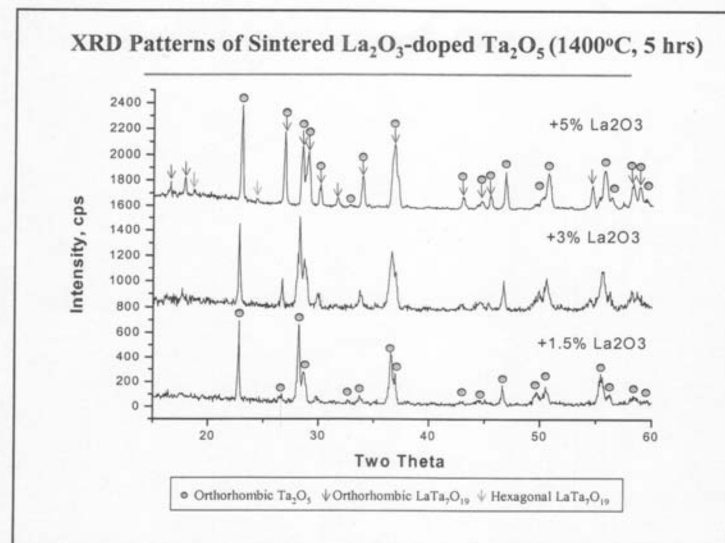

Alumina stabilizes low temperature β-$Ta_2O_5$ (orthorhombic) phase

- 3w% needed to suppress partial transformation @1300C.
- While Al in solid solution enhances grain growth, $AlTaO_4$ pinning retards it.

# $La_2O_3$ Gives Acicular Microstructure while also Stabilizing β-phase to Higher Temperatures

Effect of $La_2O_3$ (1340°C, 10 hrs)




• 1-2w% $La_2O_3$ seen as a good compromise between β-stabilization, reinforcement, and lowered density.

# $Al_2O_3$ / $La_2O_3$ Co-doping Gives Dense, Stable Microstructures without Microcracking at 1450C

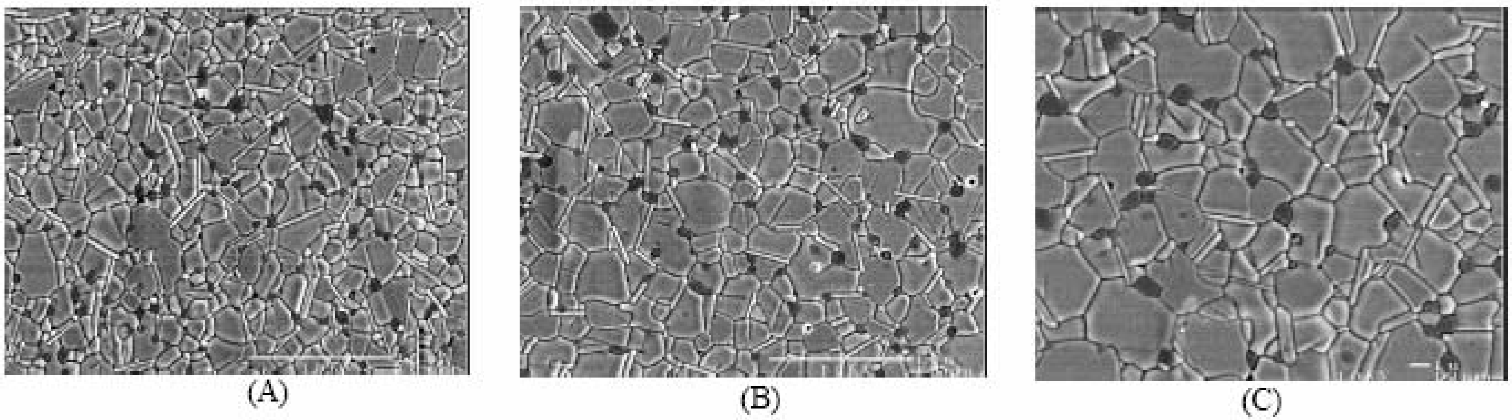



Figure 5. Microstructures of $Ta_2O_5$ doped with 2% $\gamma$-$Al_2O_3$ and 1% $La_2O_3$ fired at (A) 1350°C, (B) 1400°C and (C) 1450°C for 5 hours.



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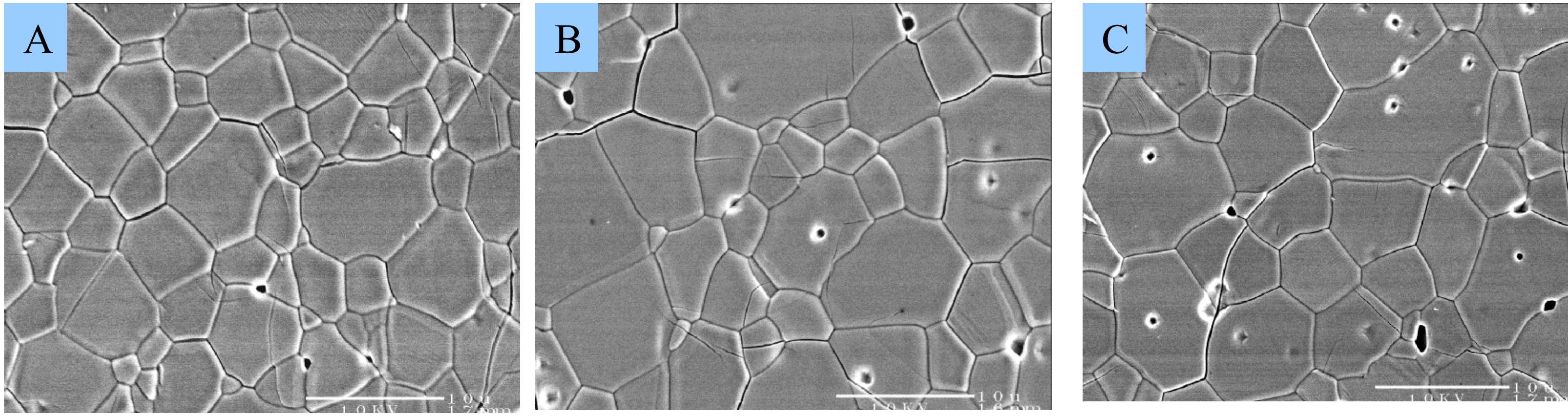
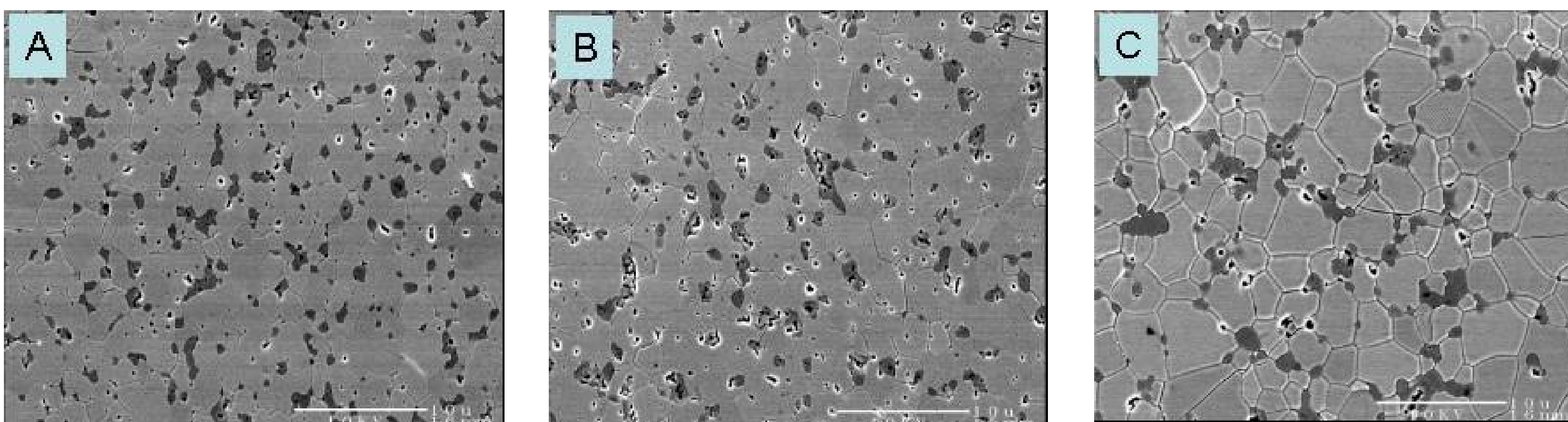
# $Nb_2O_5$-Dopant Work has Begun



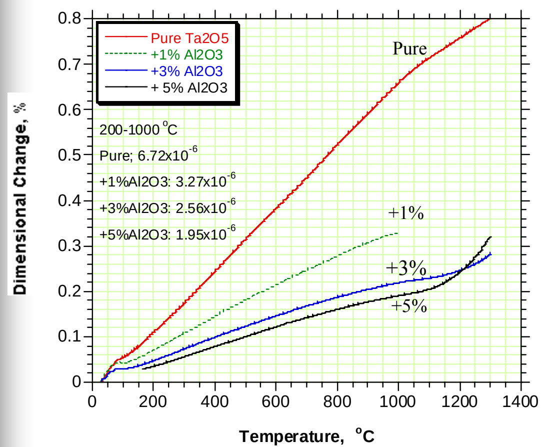

Microstructures of (a) 1, (b) 3 and (c) 5% $Nb_2O_5$ doped $Ta_2O_5$ fired at 1380°C for 5 hrs.

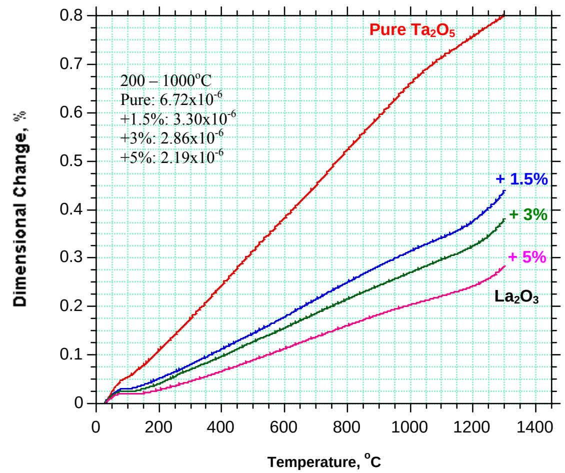
Note: Microcracking is common in all samples indicating partial β-to-α phase transformation

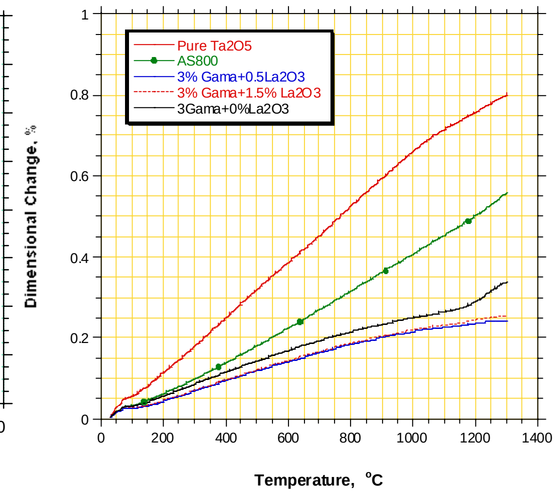


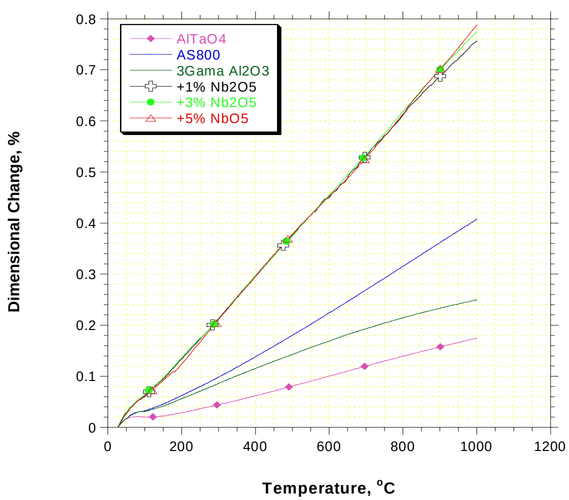

Microstructures of $Ta_2O_5$ doped with 3% $Al_2O_3$ and various amount of $Nb_2O_5$: (A) 1%; (B) 3%; (C) 5%.
Samples were fired at 1380°C for 5 hrs.

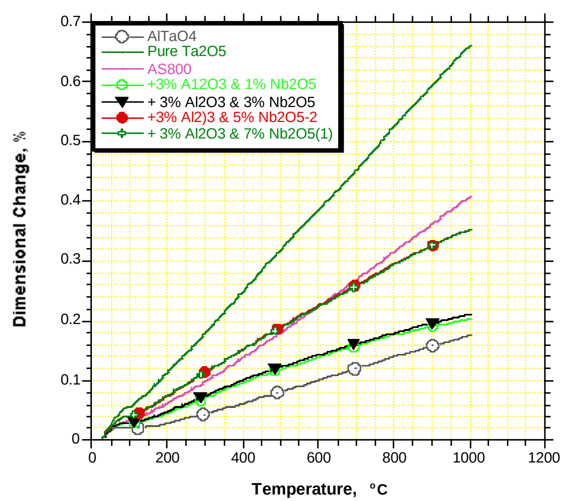
# Alloy Additions Change the Thermal Expansion



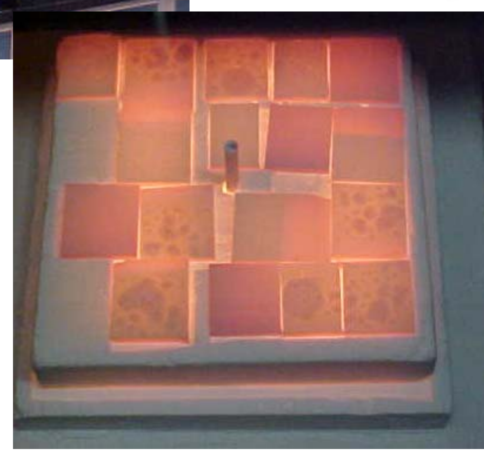



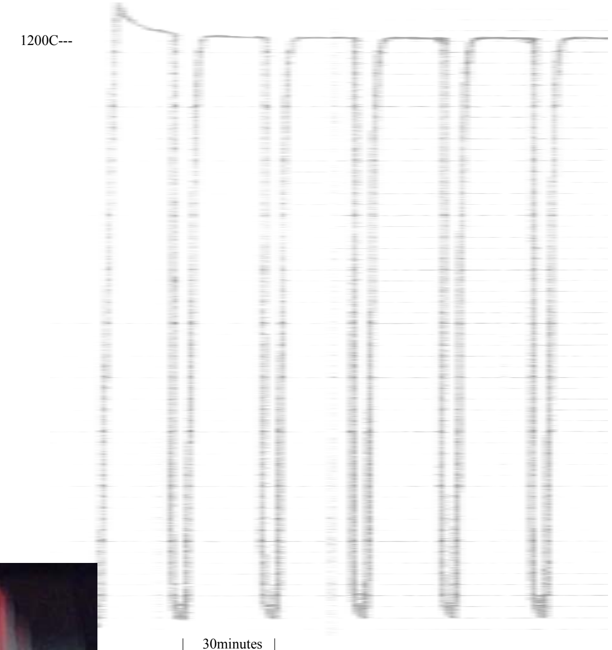



# Life Limiting Phenomena: Thermal Cycling




Thermal cycling of SPPS'd coatings show certain coatings to be robust (and some not).

# Life Limiting Phenomena: Thermal Cycling

<u>Summary of results:</u>

- Approximately 4000 cycles logged on 30 coated & uncoated samples from limited # of thermal spray trials:
~2000 cycles at 1200C. ~2000 cycles at 1315C

- Spallation on the following samples:

Pure $Ta_2O_5$

$Ta_2O_5$+ 2w%$Al_2O_3$,

$Ta_2O_5$+ 3w%$Al_2O_3$,

$Ta_2O_5$+5w%$Al_2O_3$ samples

- No Spallation seen on any of the following samples:

$Ta_2O_5$+ 1.5w%$Al_2O_3$

$Ta_2O_5$+ 1.5w%$Al_2O_3$ + 1.5w%$La_2O_3$

$Ta_2O_5$+ 3w%$Al_2O_3$ + 3w%$La_2O_3$

## Life Limiting Phenomena: Keiser Rig Testing

Studies conducted to date indicate:

Pure-$Ta_2O_5$ is not an effective barrier for oxygen or water vapor transport @ 1200 or 1315C.

Initial SPPS Pure-$Ta_2O_5$ is not thermally stable at 1200C or 1315C. Changes in microstructure with exposure time were seen.

**Results indicate that stand-alone SPPS pure $Ta_2O_5$ will have limited value as a EBC for $Si_3N_4$.**

# Life Limiting Phenomena & Performance Testing

- Residual Stress Evaluation

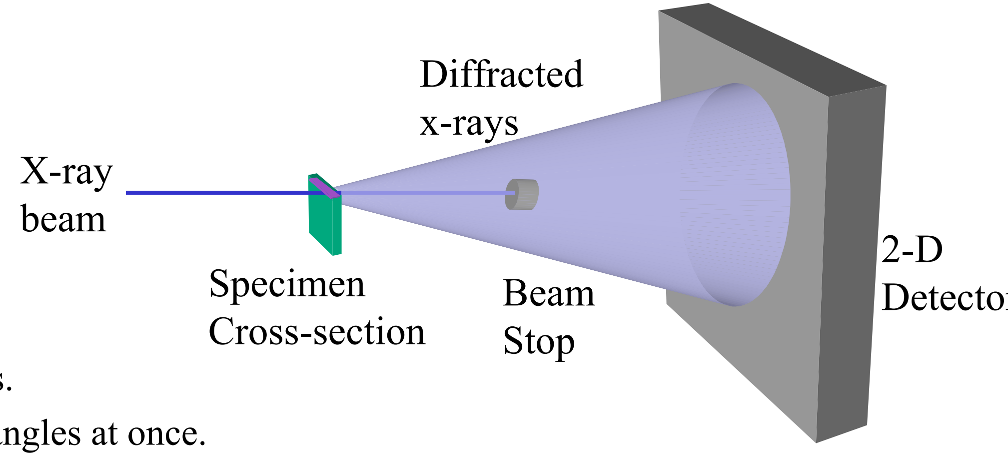
X-ray techniques used to assess the changes in the coating residual stress stated before and after thermal cycling.

- Residual stresses present due to:
  - CTE mismatch between substrate and coating
  - Temperature differences between plasma stream and substrate
- Residual stress alters D-spacings,

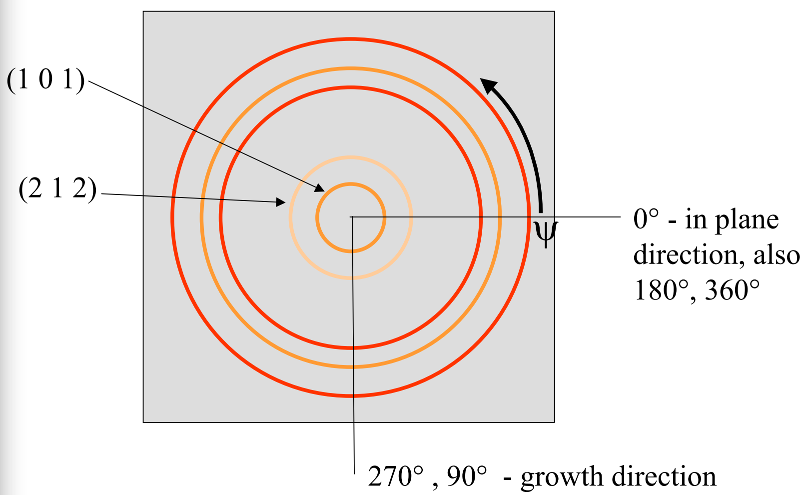
  (and the Debye-Scherrer pattern ring shape)

**Determine the D-Spacings from the ring pattern shape & determine the stress state assuming Hooke's law.**

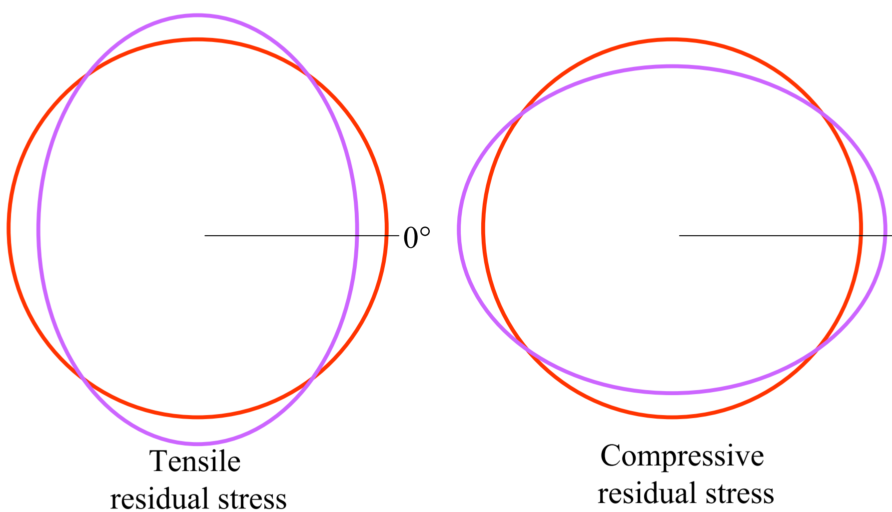
# EXPERIMENTAL PROCEDURE - APS




- Specimens sectioned to 0.5-2 mm thick.
- Transmission experiment with 80 keV x-rays.
- 2-D detector - allows for collection of all ψ angles at once.
- Each specimen was probed through the thickness of the coating and into the substrate.




Shift of rings from circles to ellipses indicates lattice strain



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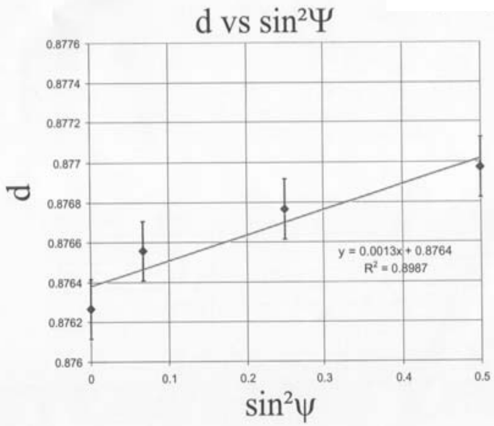
For Biaxial Stress State:

$$\frac{d_{\phi\Psi} - d_O}{d_O} = \frac{1+\nu}{E}\sigma_\phi \sin^2\Psi - \frac{\nu}{E}(\sigma_{11} + \sigma_{22})$$




Solving for σ gives Residual stress

Stress State seen to change as a function of Exposure conditions.

| Composition | Preheat | Heat Treat | Stress (MPa) | +/- Error |
|---|---|---|---|---|
| Pure | 900 | As-Sprayed | 187.22 | 16.38 |
| Pure | 900 | 139 Cycles | -258.11 | 32.31 |
| Pure | 900 | 489 Cycles | -121.1 | 28.79 |
| Pure | 900 | 986 Cycles | -245.61 | 34.09 |
| Pure | 900 | 1074 Cycles | -22.83 | 33.2 |
| Pure | 450 | 139 Cycles | -208.3 | 28.4 |
| Pure | 450 | 489 Cycles | -240.79 | 31.73 |
| Pure | 900 | 72 Hours Static | 71.58 | 18.92 |
| Pure | 900 | 168 Hours Static | -152.96 | 18.92 |
| 2% Al2O3 | 900 | As-Sprayed | 251.57 | 13.96 |
| 2% Al2O3 | 900 | 145 Cycles | 372.14 | 22.35 |
| 2% Al2O3 | 900 | 489 Cycles | -156.49 | 127.83 |
| 2% Al2O3 | 900 | 72 Hours Static | 349.3 | 22.65 |
| 2% Al2O3 | 900 | 168 Hours Static | -171.32 | 46.12 |
| 3% Al2O3 | 900 | As-Sprayed | 227.75 | 10.26 |
| 3% Al2O3 | 450 | As-Sprayed | -18.4 | 13.17 |
| 3% Al2O3 | 900 | 72 Hours Static | 351.97 | 39.51 |
| 3% Al2O3 | 900 | 168 Hours Static | 190.01 | 15.69 |

Table II: Residual stresses in various tantalum oxide based EBCs. Heat treatments were at 1200°C in air with cycles of 25 minutes at temperature and 5 minutes fan cooling.

# Summary of Current Program Findings

• Methods to successfully plasma spray $Ta_2O_5$ and $Ta_2O_5$-based alloys were developed. SPPS gives dense, adherent coatings.

• $Ta_2O_5$alloy compositions that stabilize β-$Ta_2O_5$ up to 1450C, limit grain growth, and match the CTE of Silicon-based ceramics were developed.

• SPPS coatings are capable of extended thermal cycling to 1200C and 1315C on AS800.

• Residual Stress Changes are seen to occur as a function of exposure time for SPPS'd $Ta_2O_5$-based coatings. Additional work is ongoing to understand and explain these observations.

• Keiser Rig testing has shown that stand-alone SPPS Pure-$Ta_2O_5$ coatings undergo changes during exposure and allow substrate changes to occur. The evaluation of the performance of Ta2O5-based alloys showed similar results under a separate DOE program. Therefore, it seems likely that use of Ta2O5 and Ta2O5-based alloys for EBCs will only be as part of a multi-layer coating system.



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