ODS Alloys in Coal-Fired Heat Exchangers – Prototypes and Testing

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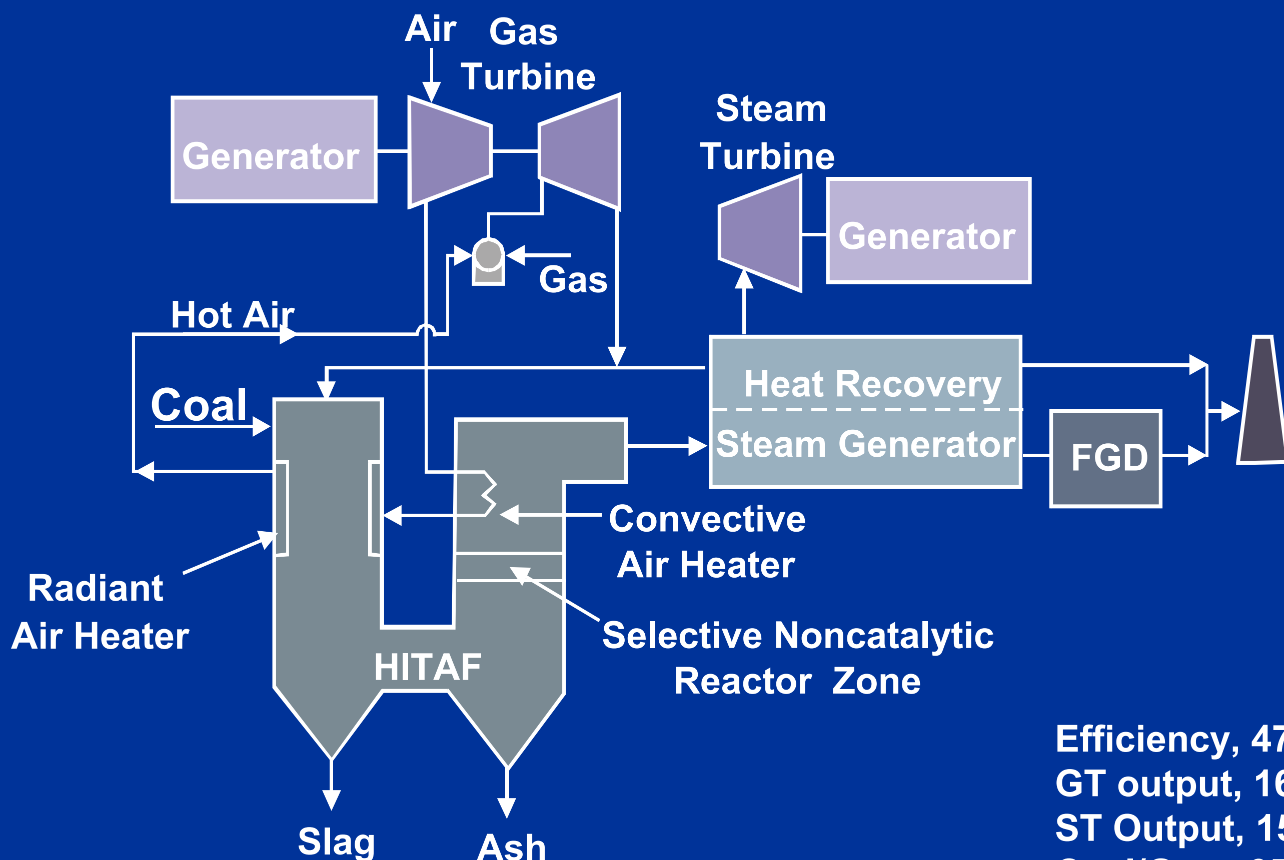
Indirectly Fired Combined Cycle (IFCC) Schematic

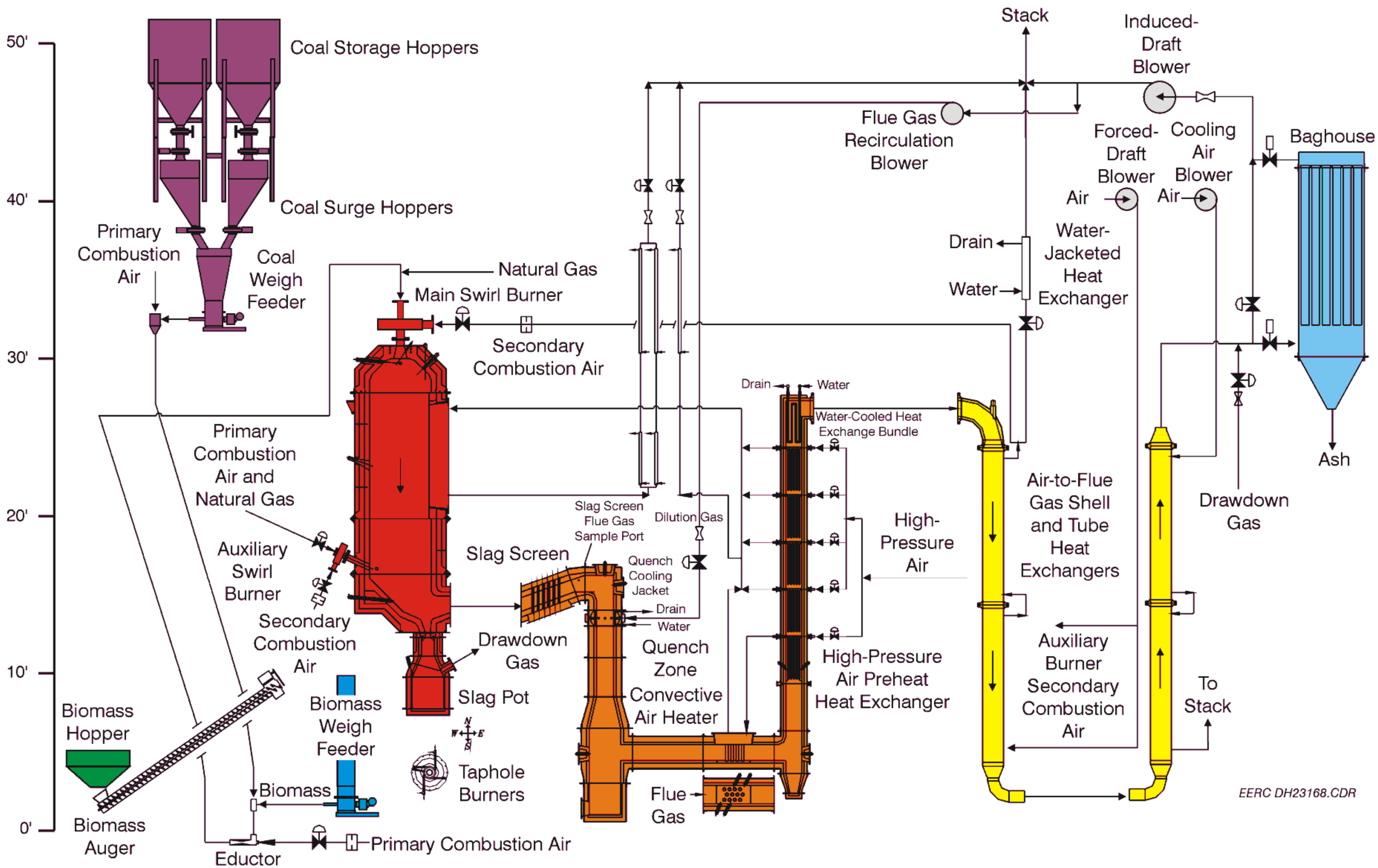


Efficiency, 47.3%
GT output, 161 MW
ST Output, 150 MW
Coal/Gas, 65%/35%

Advantages of IFCC

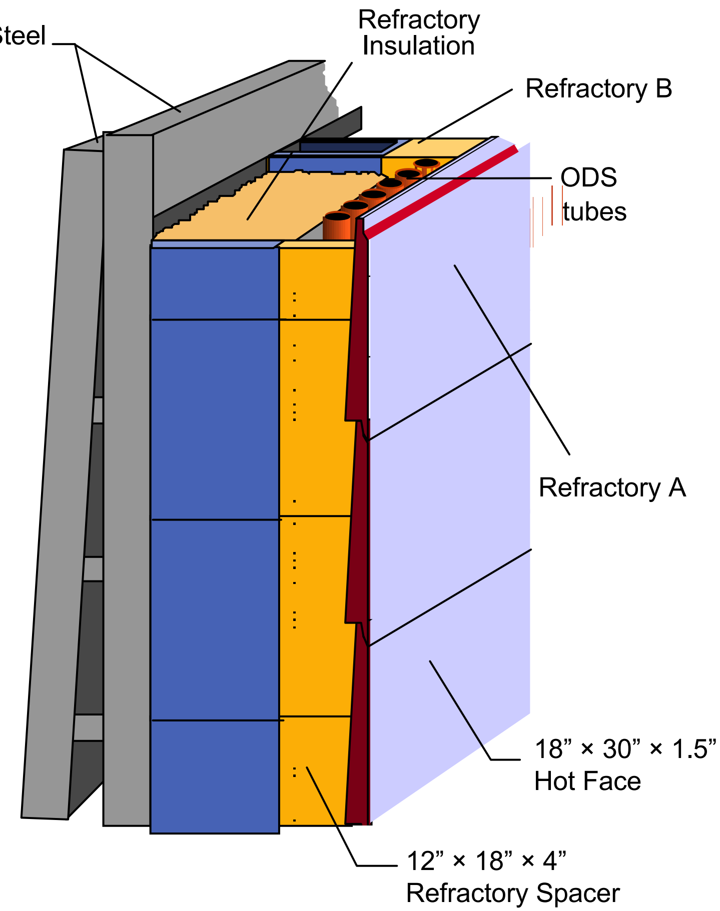
- Operations very similar to pulverized coal (pc)-fired boilers.
- Nearer-term technology.
- Higher efficiencies – 45% when firing coal, over 50% with natural gas (NG) supplement.
- Half the water usage of a typical steam-based plant because of the Brayton cycle.
- Slagging heat exchangers are self-cleaning:
  - Much lower loss of heat transfer because of fouling
  - Much less overconstruction

Air-Blown Slagging Furnace System (SFS) Configuration Modified for Biomass Biofiring

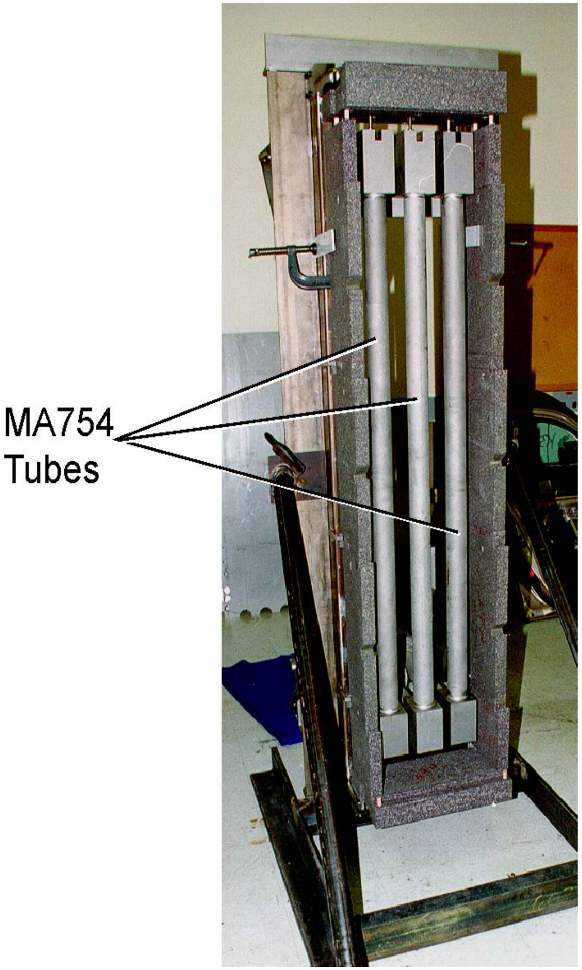


United Technologies Research Center (UTRC) "Tubes-in-a-Box" High-Temp. Heat Exchanger (HTHX)

- Made process air at 950°C and 150 psig for over 2000 hr.
- 1090°C and 100 psig maximum.
- Corrosion is a secondary issue – slag additives are very promising.
- Major issue – thermal shock of ceramic tiles.



Open View of Radiant Air Heater (RAH) Test Panel



Large RAH Panel Inside the Slagging Furnace

Scanning Electron Microscopy (SEM) Analyses of MA754 HTHX Joint

- Corrosion very low over 2000+ hours of exposure.
- Corrosion rate somewhat masked by residual processing contaminants.
- Residual braze compound may weaken the joint.

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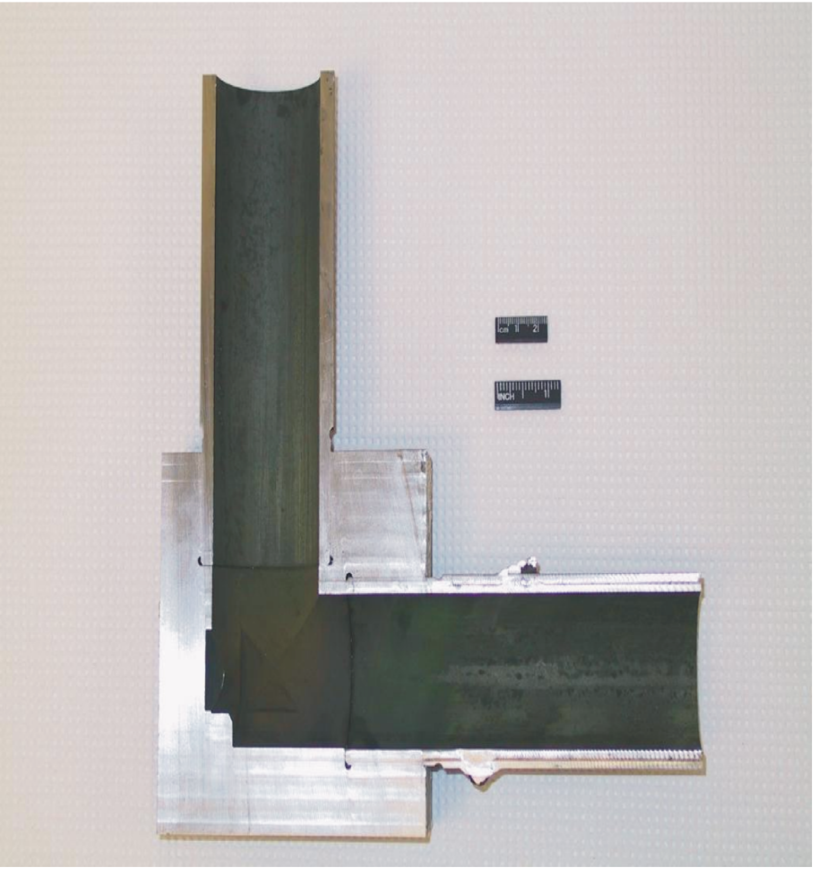

Summary of Tubes-in-a-Box Testing

- Heat transfer meets design criteria with Monofrax tiles.
- Standard process air 1750°F and 150 psig.
- 2000°F process air reached for short time at 100 psi.
- Slag layer less than 1 mm thick on panels.
- Thermal shock is biggest problem for ceramic panels.
- Corrosion of panels is secondary issue:
  - Additives may substantially reduce corrosion.
  - Prevent dripping to prevent channeling of slag.

Bolted MA956 HTHX Tube

- Bolts machined from MA956.
- Mica/Inconel gaskets.
- 500 hours of service with five cycles has caused no leaks.

MA956 Tube Installed in the HTHX

Concerns with Bare-Tube Testing

- Uneven heat flux may cause warping.
- Insufficient heat-transfer rates to the pressurized air may cause excessive surface temperatures.
- Slag deposits may corrode.
- Slag deposits may insulate.

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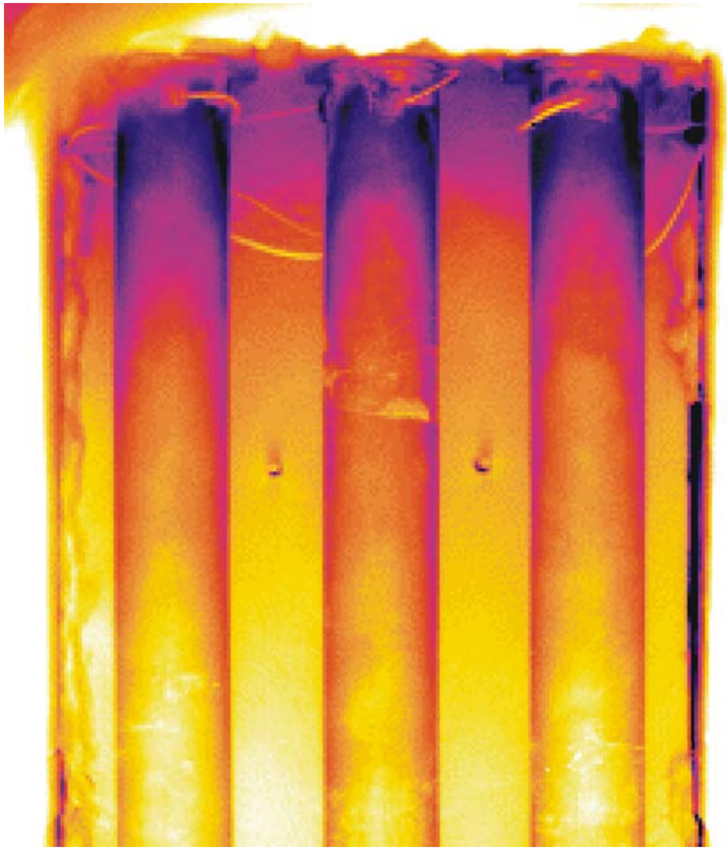
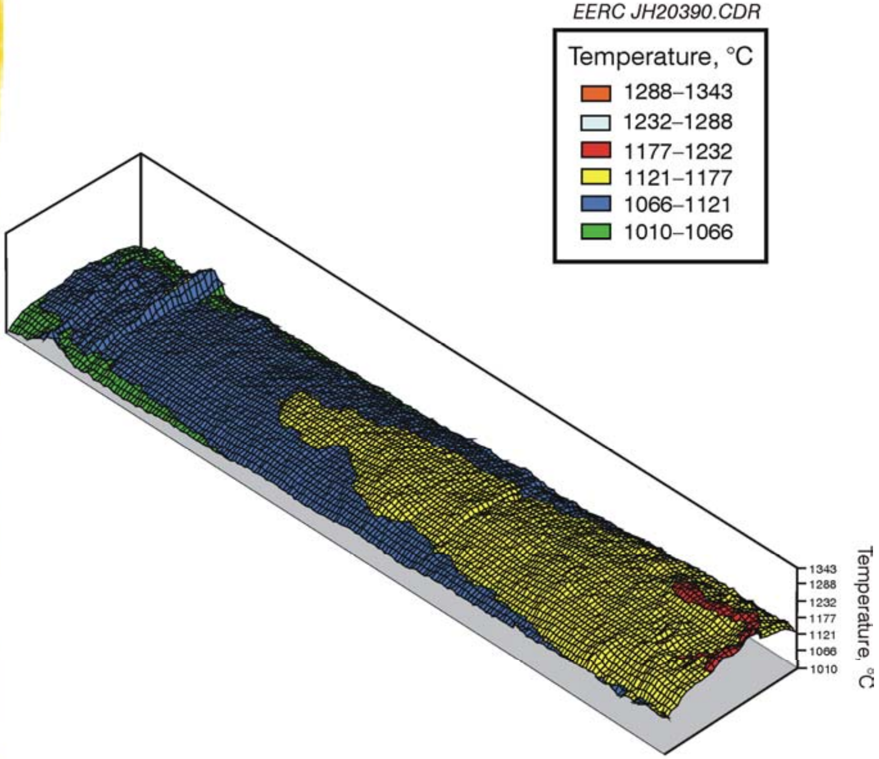
Infrared Image and Temperature Distribution of the Upper Portion of the Middle Tube in the HTHX While Firing on Natural Gas



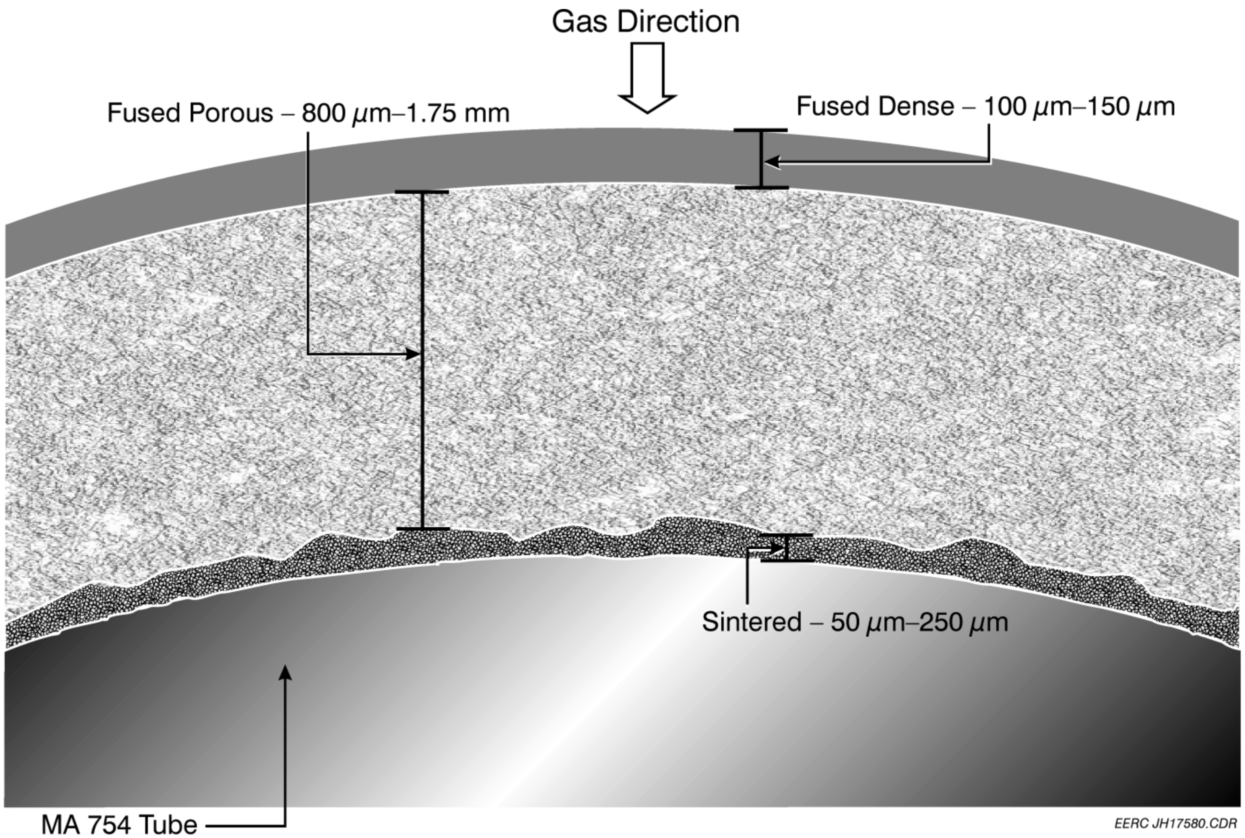


HTHX Tubes After August 2001 Test

- Slag layer self-cleaning.
- 3 mm thick maximum.
- Reduces heat flow by 15% as compared to 50% for sintered ash.

MA754 Direct Exposure

- Surface cooled to 2000°F
- 1.5-mm-thick detached slag layer developed on surface
- No nickel or chrome in the detached slag layer
- 20-μm-thick attached slag layer
- 10 μm chromia
- Corrosion layer under attached slag



Summary of Bare-Tube HTHX Testing

- Heat removal rates are increased by a factor of 4 to 6 by removing the ceramic panels.
- This change will lower the cost of the heat exchanger by a factor of 10 over the tubes-in-a-box design.
- Initial ash deposit is thin and sintered, which protects the tube from rapid corrosion with a minimum of insulation.
- A flowing slag layer is created within a few millimeters of the surface, minimizing insulating value and becoming self-cleaning.

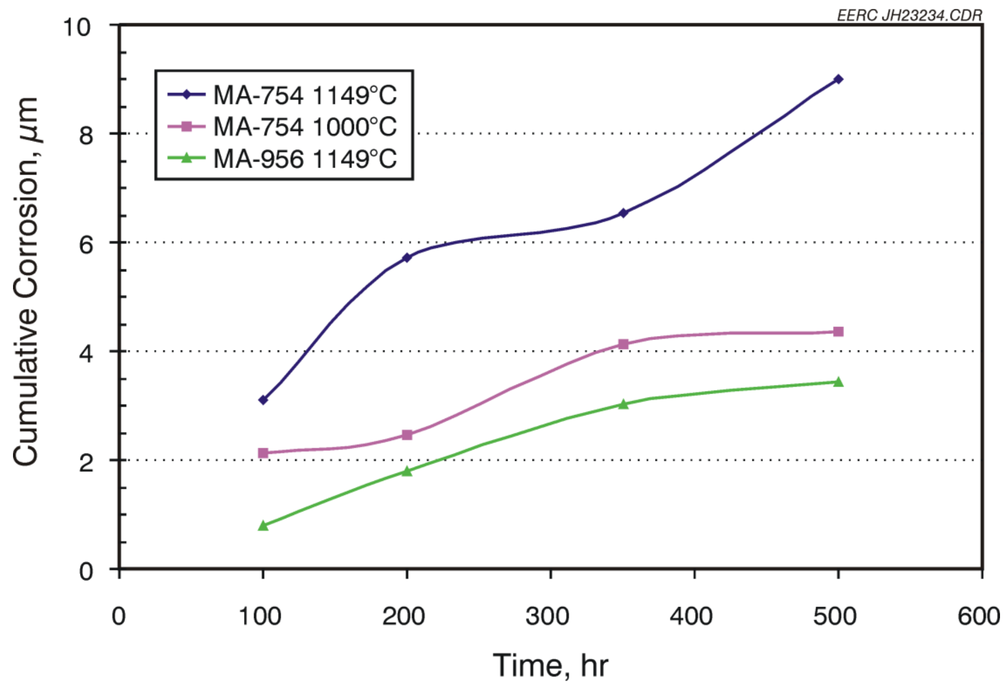
Bare-Tube Testing Summary (continued)

- Both MA754 and MA956 have very low corrosion rates.
- MA754 chromia layer partially separates on cycling.
- MA956 alumina layer remains attached on cycling.
- Most likely industries interested in first trying the technology are fossil energy-intensive industries, not the power sector.

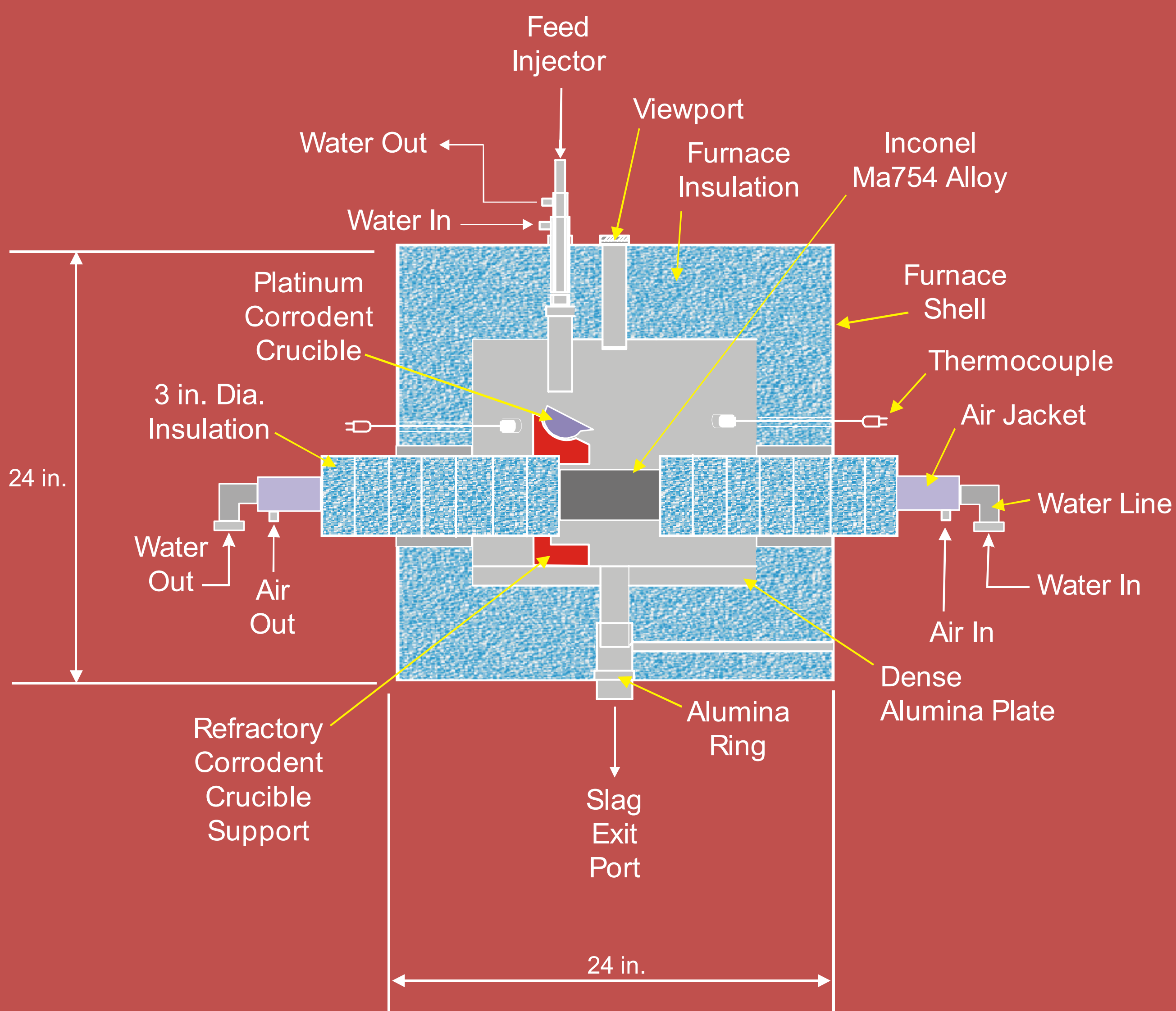
- Later testing in an aluminum melter showed severe corrosion of MA956 due to halogens, less corrosion of MA754.

Static Corrosion of MA754 and MA956 with Illinois No. 6 Ash

- Corrosion rates of both oxide dispersion-strengthened (ODS) alloys are commercially acceptable with Illinois No. 6 ash.
- MA754 corrosion rate of 160 µm/year at 1149°C.
- MA956 corrosion rate of 60 µm/year.

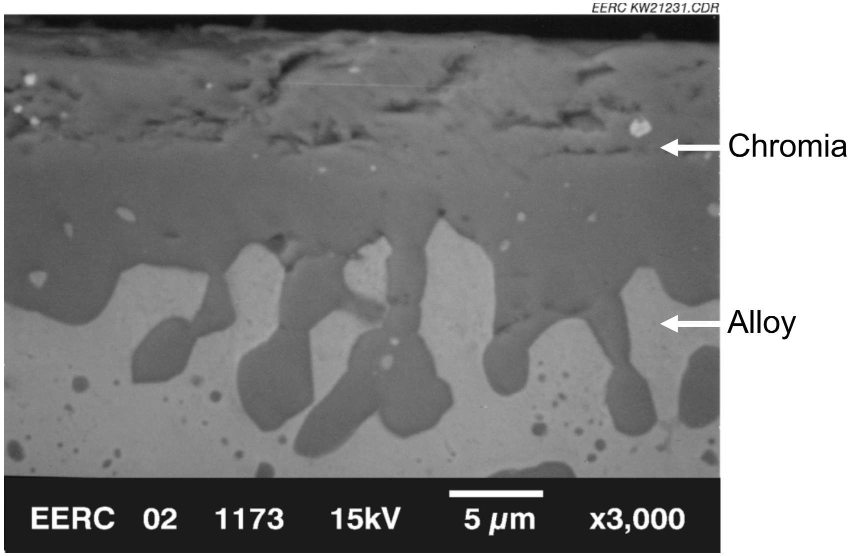


Flowing Slag Corrosion Testing of Air-Cooled Pipes

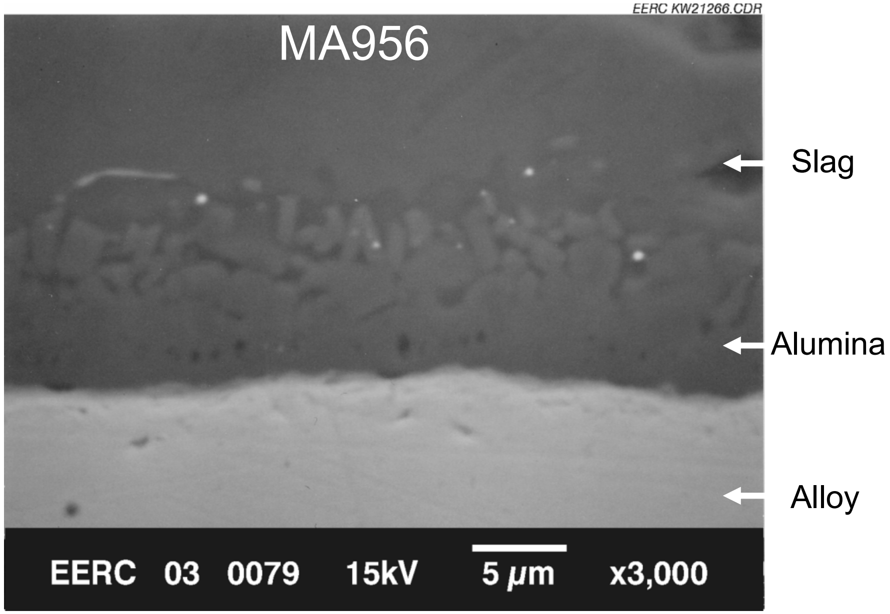


Alloy Scales After 100-hour Exposures Illinois No. 6 Slag – 1200°C

MA754

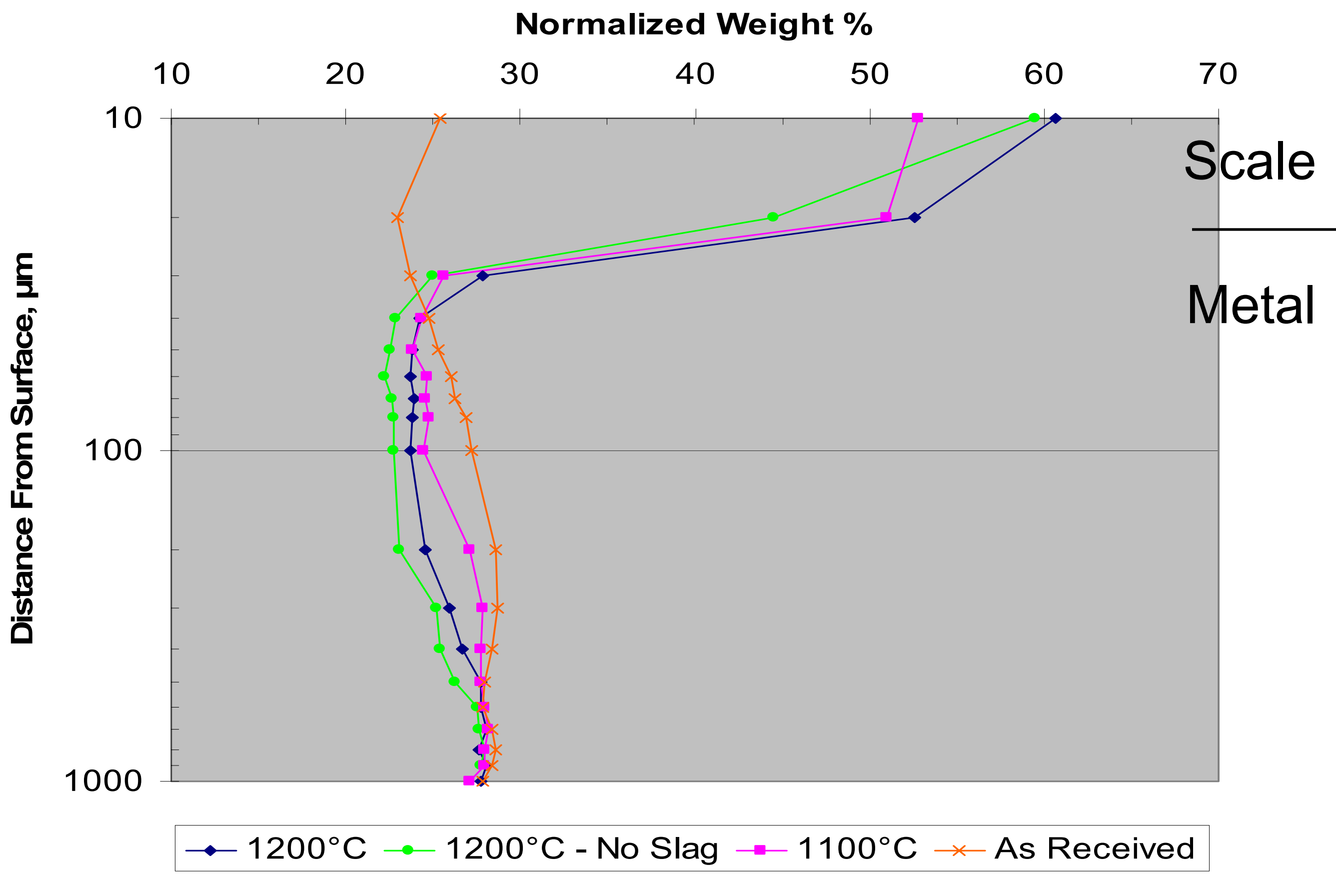


MA956



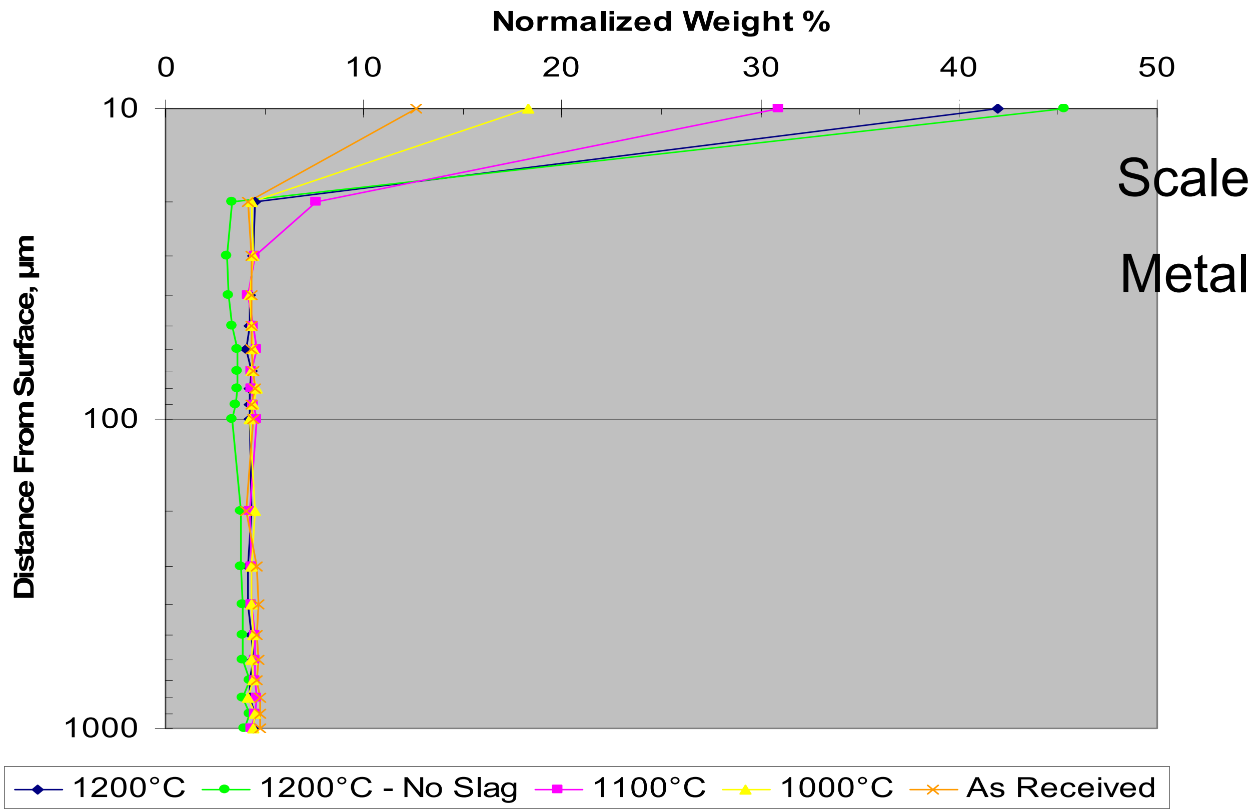
MA754 Chromium Content
Flowing Illinois No. 6 Slag – 100 hours

- Chromium depletion excessive for MA754 at 1100°C or above.
- Slag layer lost on cooling, shortening life.
- Slag reduces chromium loss during a single cycle.



MA956 Aluminum Content
Flowing Illinois No. 6 Slag – 100 hours

- Oxygen penetration and aluminum depletion minimal at up to 1200°C under flowing slag.
- Slag layer retained on temperature cycling.
- Slag may reduce aluminum depletion.



Alumina Layer on MA956 Before Corrosion Testing

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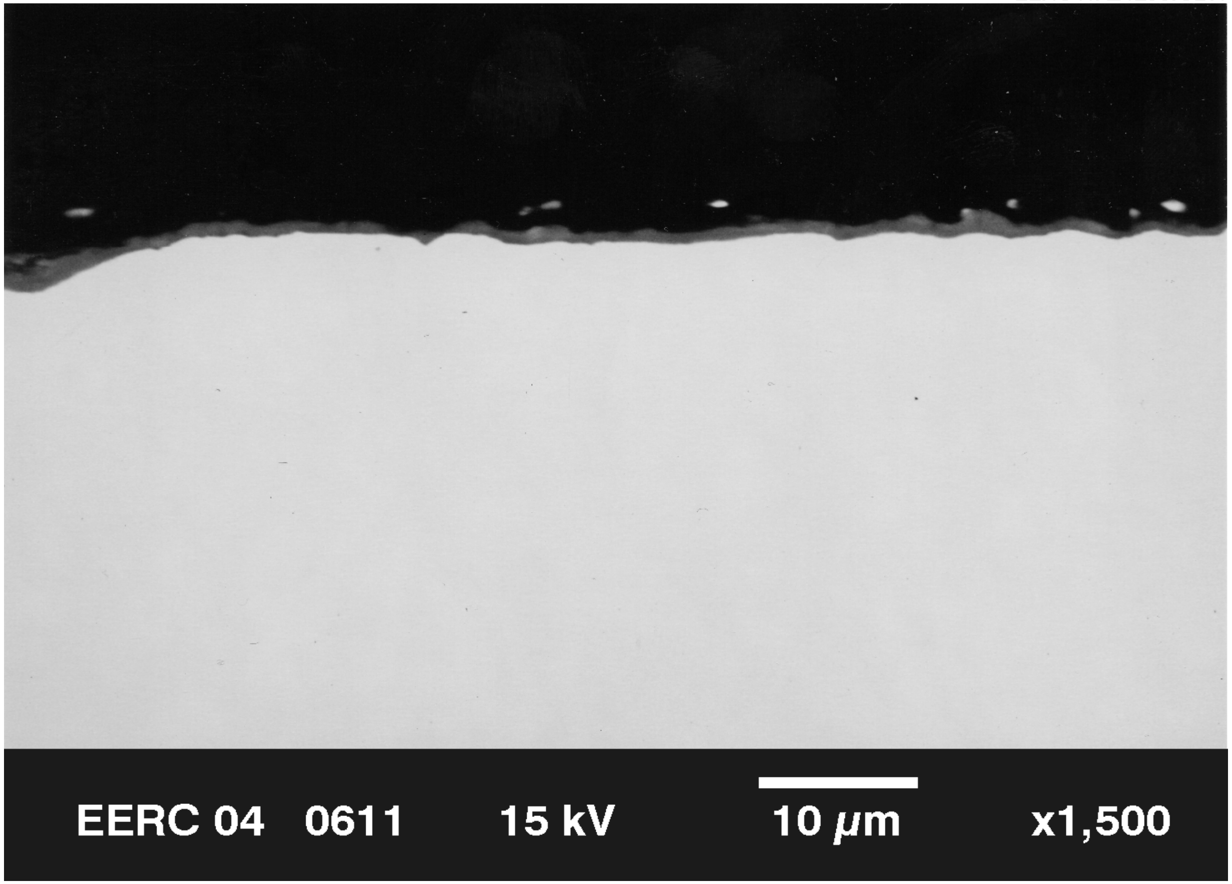

MA956 Tube with Oxide Layer Above Slag Drip Point After 1050°C Coal/Hog Fuel Test

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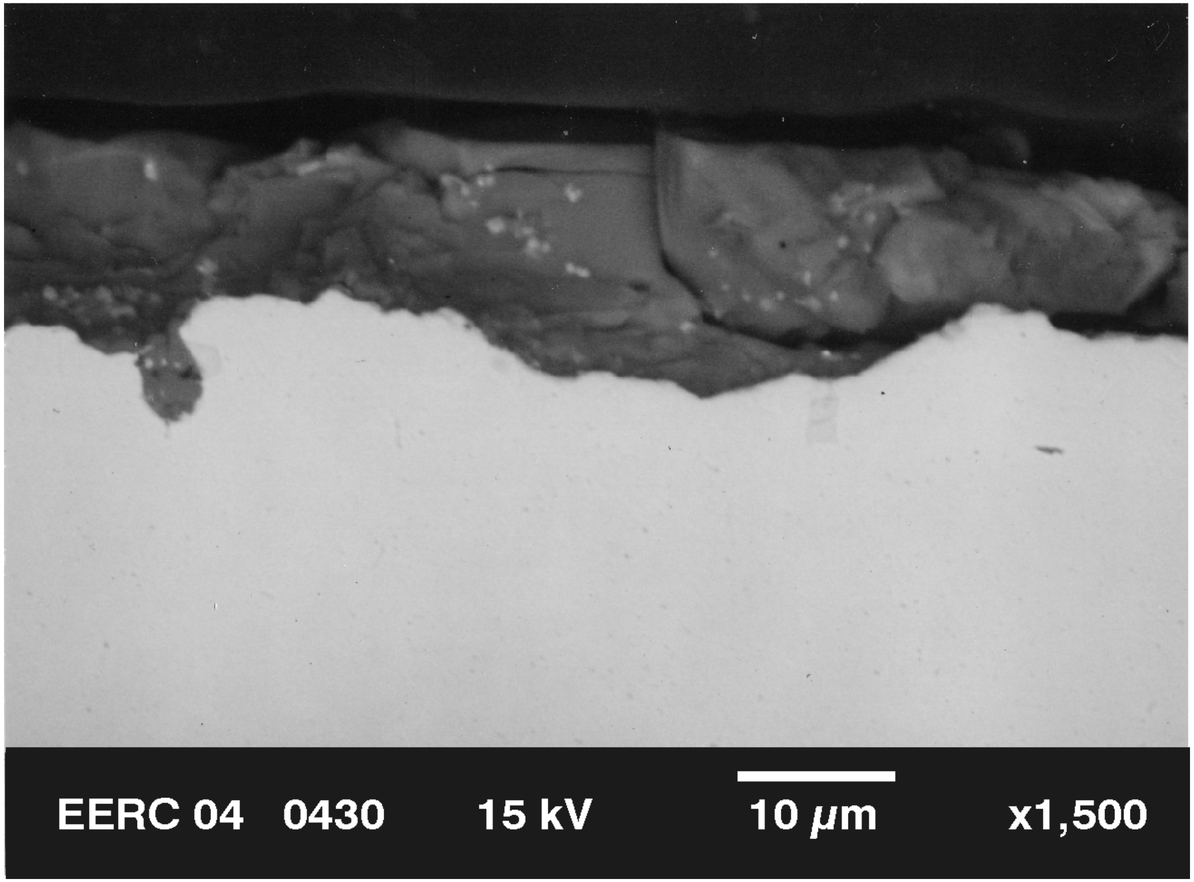

MA956 Tube with Attached Slag Layer

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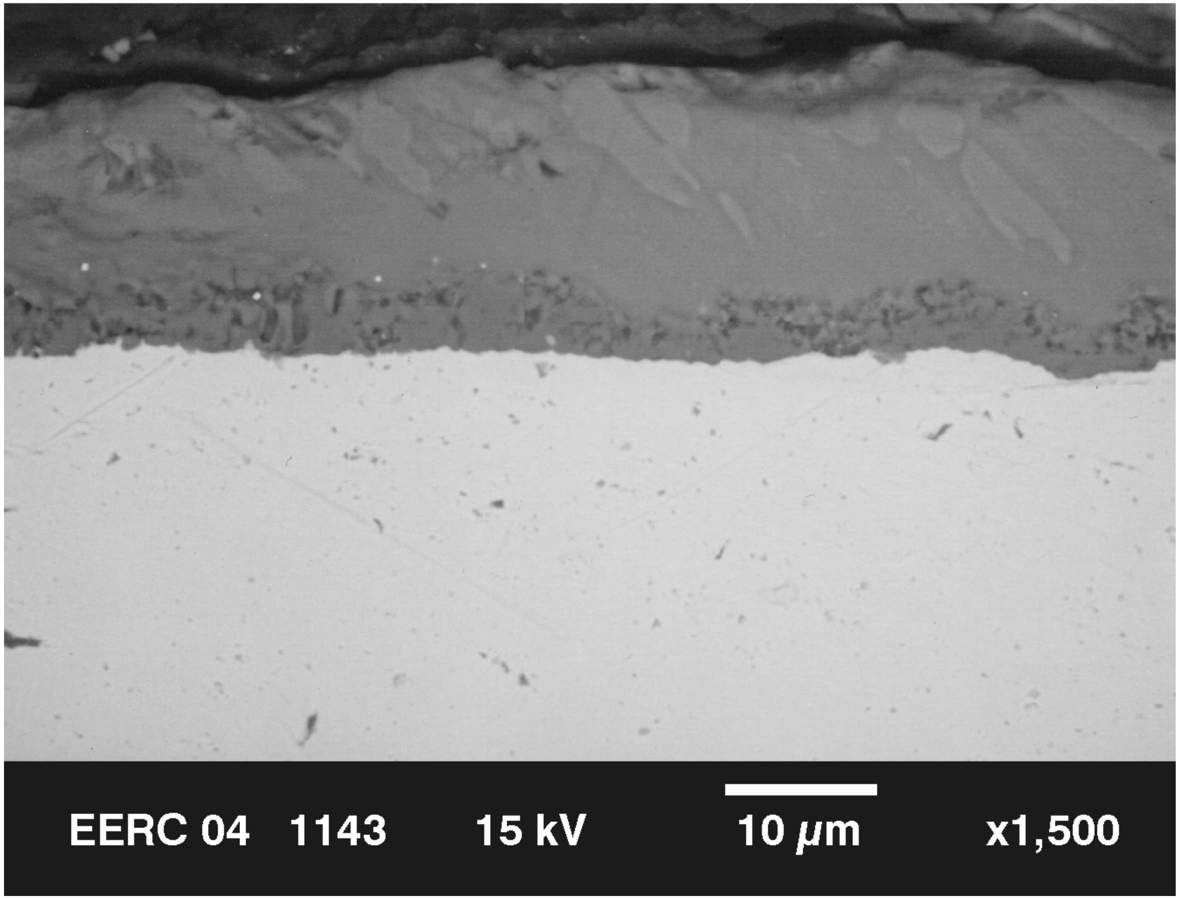

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Conclusions on 100-hour Flowing Coal–Biomass Slag Corrosion of MA956

- No surface recession measurable for any test.
- Slag layer remains attached after temperature cycling for all slags except coal–switchgrass at 1150°C.
- Some alumina dissolved into attached slag but not spalled slag.
- Attached slag layer protects alumina scale upon cycling.
- Slag layer reduces thickness of alumina scale.
- No measurable aluminum depletion from alloy.

Transient Liquid-Phase (TLP) Bonding

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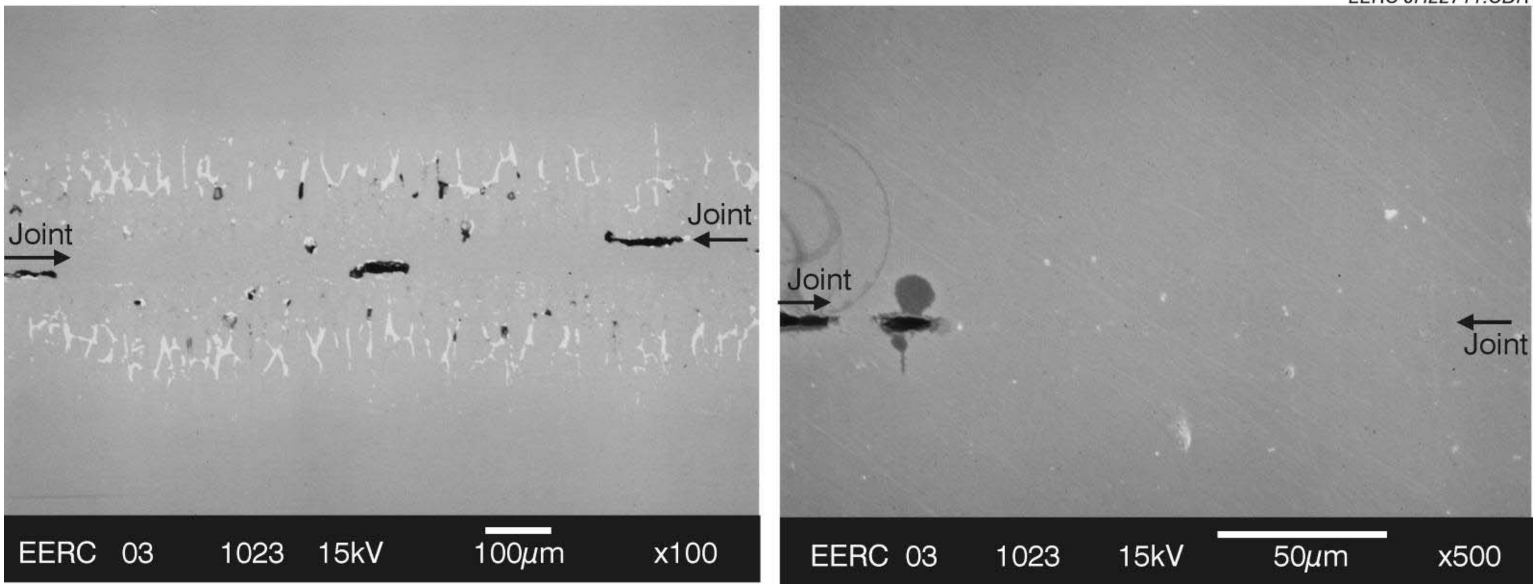
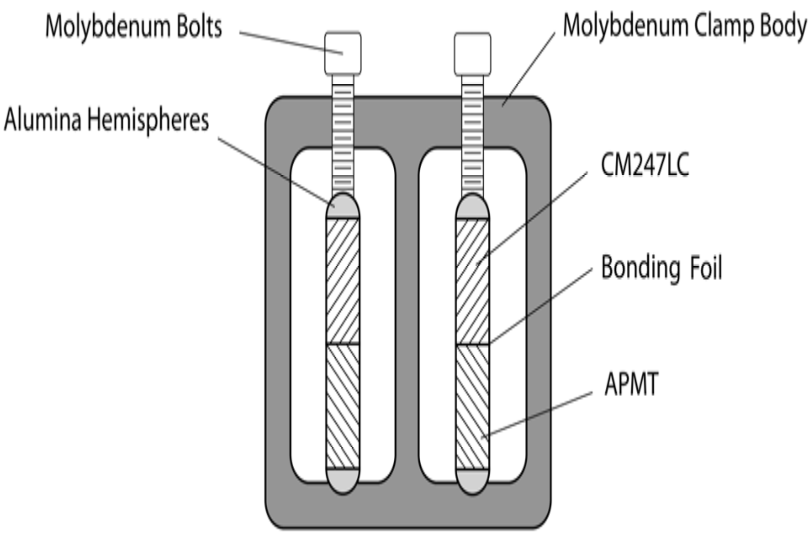


- Welding of advanced alloys is not possible because critical structures are destroyed.
- TLP bonding uses a reactive braze that diffuses away from the joint.
- Bonding alloys need to have lower melting points, be soluble, and not form intermetallics.

Articulated Clamping System

- Initial tests done with rods polished flat.
- Clamp made from low CTE metal (Mo).
- Ceramic hemispheres used to articulate the pieces, which is necessary because of the thinness of the foils.
- Later joints done with thin sandwiches of APM and APMT and with complex curves.



Clamping System for Joining APMT to CM247LC

TLP Bonding MA956–MA956

- Joints typically have 80% of alloy ultimate tensile strength at room temperature - no recrystallization treatments.
- Strengths not tested at high temperatures
- Breaks are intergranular.

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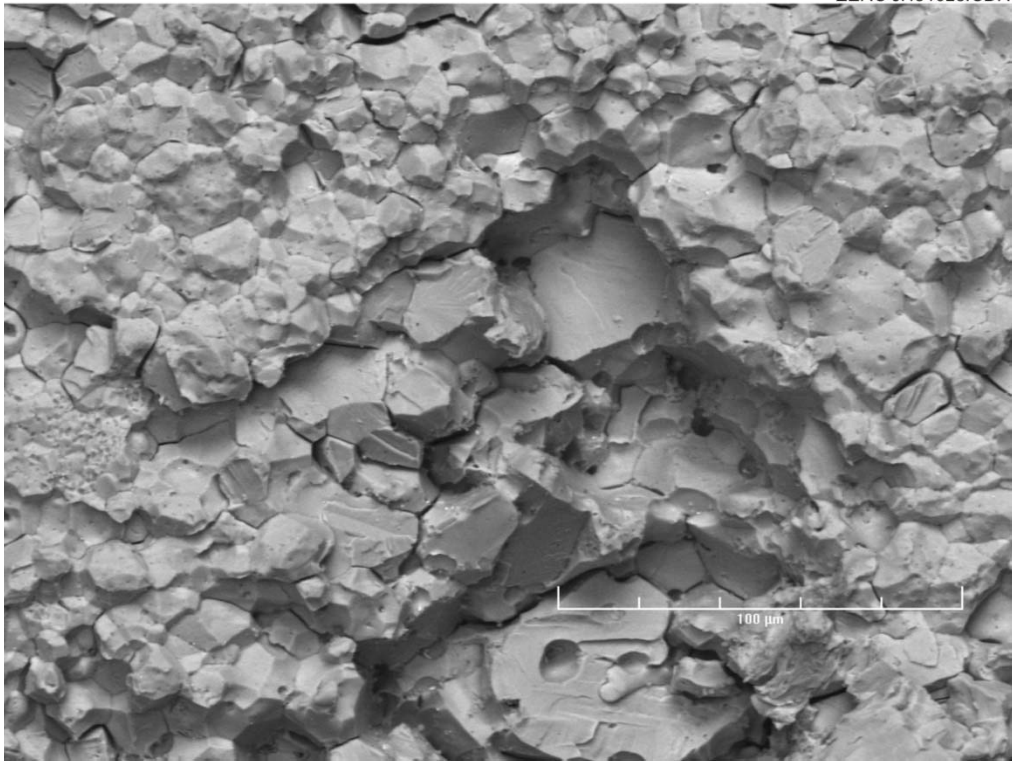
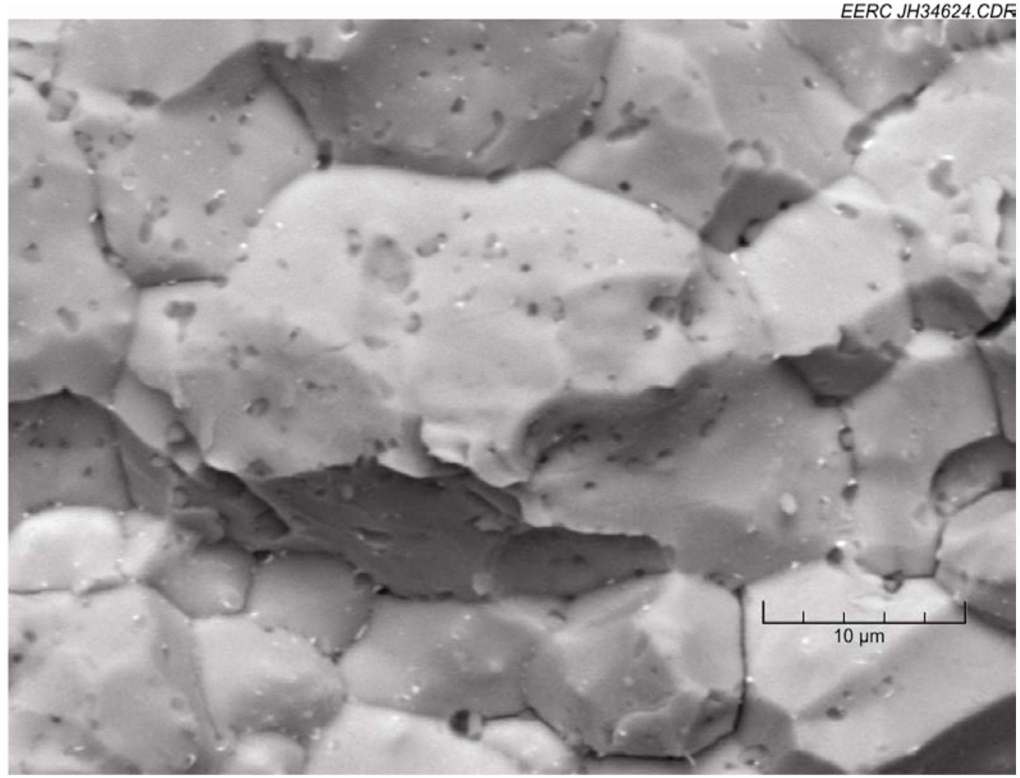


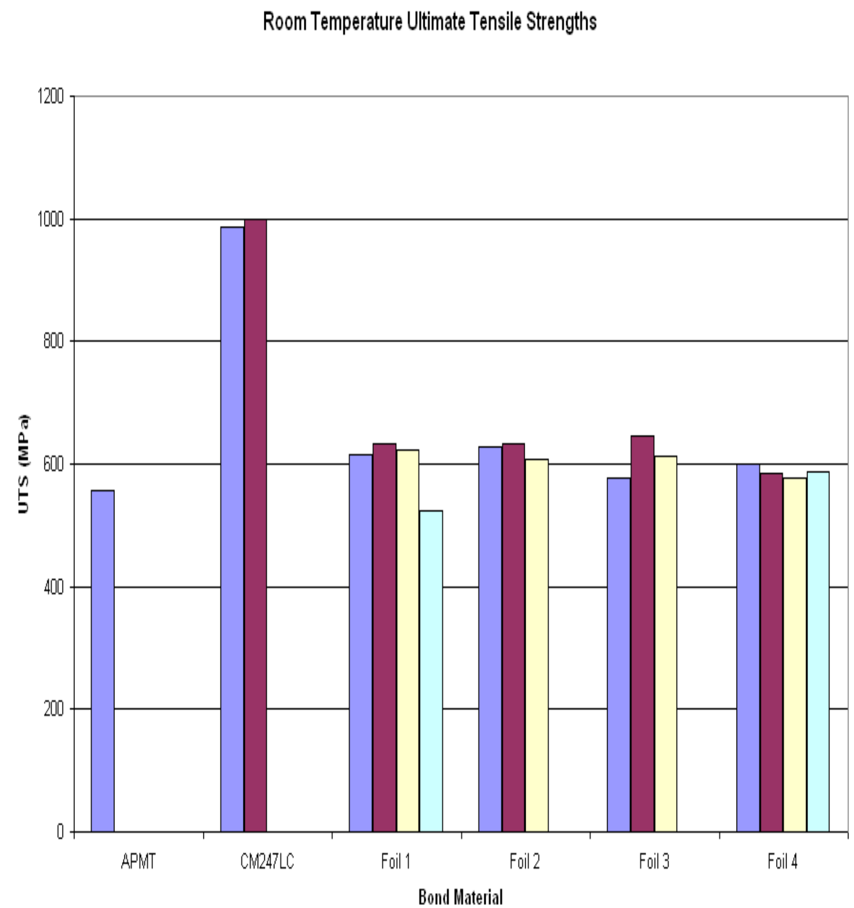
TLP Bonding MA956–MA956

- Oxide dispersions remain in intergranular boundaries.
- Dispersed grains are yttrium aluminum oxides.



Joining APMT to CM247LC Tests of Multiple Joining Alloys

- Room-temperature ultimate tensile strength results for joints made with four joining alloys.
- All samples broke within the APMT, showing the joints are stronger than the APMT.
- One of the foils evaporates from the structures – patent application filed.



Joining APMT to CM247LC 950°C Stress Rupture Tests of Rods

- Two joints for each of the four joining alloys were tested at 950°C using the 100-hour APMT rupture stress.
- All samples broke similarly, within the APMT, not the joint.
- APMT was much weaker than anticipated.

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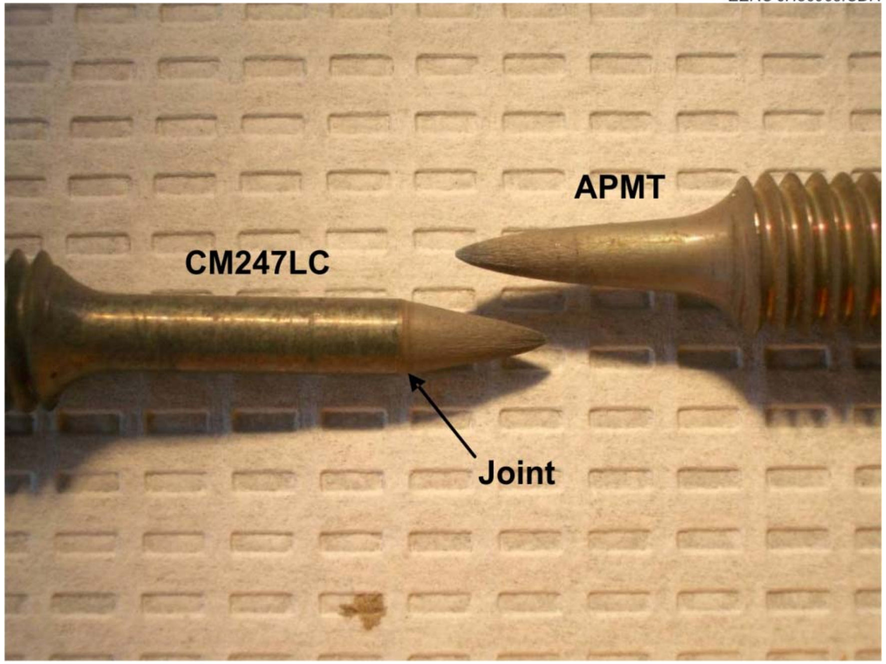
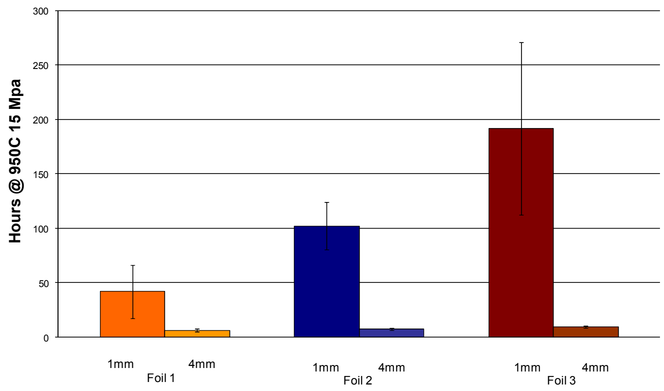


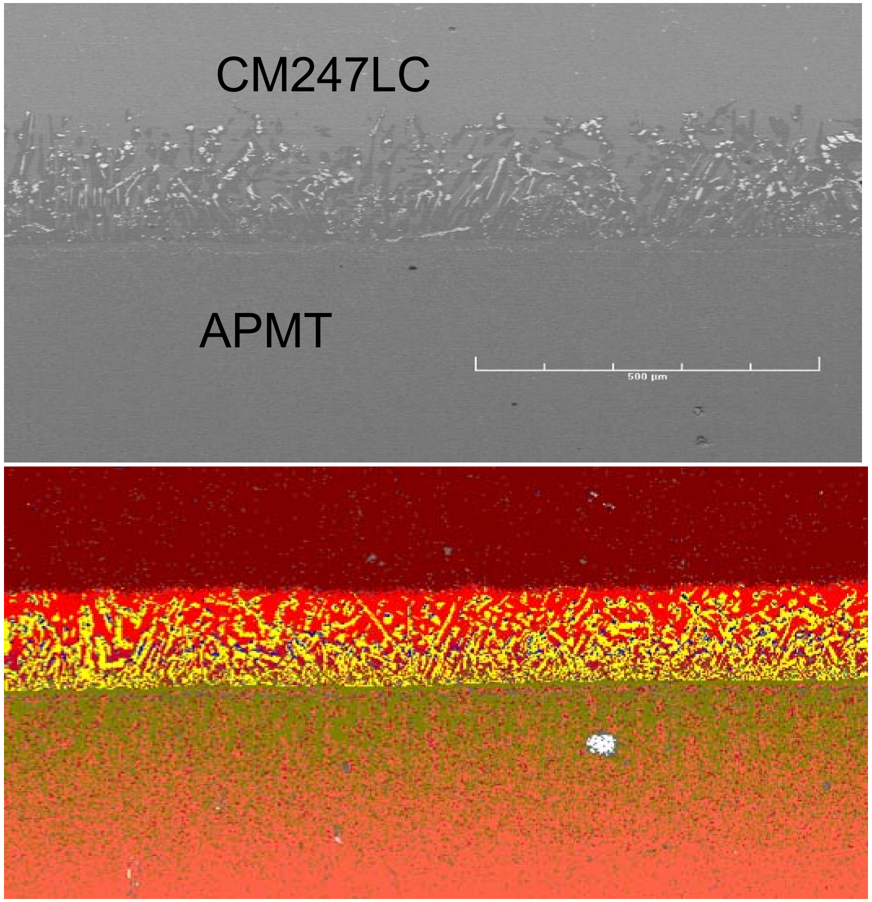
Joining APM to CM247LC Thin-Layer Sandwiches

- 1-mm- and 4-mm-thick layers of APM (not dispersion-strengthened) were sandwiched between rods of CM247LC.
- All high-temperature ruptures occurred in the APM.
- APM strengthened by metal diffusion from the CM247LC.
- Thick layers (4 mm) were not strengthened all the way through, but thin layers (1 mm) were.
- Diffusion increased lifetime of thin layer by 20 times or more.
- Different joining alloys had different effects on interdiffusion.



Joining APMT to CM247LC Microstructure of Joints

- SEM photo top, x-ray map on bottom.
- Needle growth and interdiffusion create a joint stronger than the APMT.
- Nickel diffuses up to 700 μm into APMT.
- Iron diffuses 200 μm into the CM247LC.



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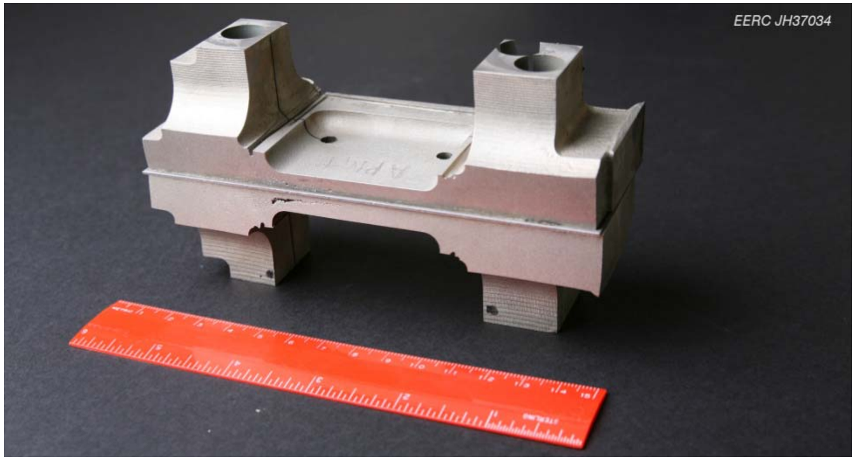
Joining Thin APMT Layers to Actual CM247LC Turbine Structures

- Joined actual turbine ring segments of CM247LC with APM and APMT sheet in between.
- Surfaces were curved.
- Joints were stronger than the APM or APMT.
- APM sheet was not strengthened as rods were.



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CM247LC to APMT Bonding Conclusions

- TLP bonding has been successfully used to bond CM247LC to APM and APMT.
- Articulation of the joints is necessary because of the very thin nature of the joining foil.
- All failures were within the FeCrAl, usually well away from the diffusion-affected zone.
- APM tubing was dramatically strengthened within the diffusion-affected zone, but APM and APMT plate were not.
- Some joining alloys diffuse through the structures and evaporate from their surfaces in what we call evaporative metal bonding.

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