

TMS Chicago-2003 ABSTRACT II:

Powder-Derived High-Conductivity Coatings for Copper Alloys

by

Linus U. J.T. Ogbuji, QSS Inc., NASA-Glenn Research Center,
Cleveland OH 44135, USA

Abstract

Makers of high-thermal-flux engines prefer copper alloys as combustion chamber liners, owing to a need to maximize heat dissipation. Since engine environments are strongly oxidizing in nature and copper alloys generally have inadequate resistance to oxidation, the liners need coatings for thermal and environmental protection; however, coatings must be chosen with great care in order to avoid significant impairment of thermal conductivity. Powder-derived chromia- and alumina- forming alloys are being studied under NASA's programs for advanced reusable launch vehicles to succeed the space shuttle fleet. NiCrAlY and Cu-Cr compositions optimized for high thermal conductivity have been tested for static and cyclic oxidation, and for susceptibility to blanching – a mode of degradation arising from oxidation-reduction cycling. The results indicate that the decision to coat the liners or not, and which coating/composition to use, depends strongly on the specific oxidative degradation mode that prevails under service conditions.



TMS Fall 2003 *Materials Science & Technology 2003* Chicago, Nov.'03



Powder-Derived High-Conductivity Coatings for Copper Alloys

Linus U.J.T. Ogbuji

QSS Group, NASA Glenn Research Center
Cleveland, OH 44135

Glenn Research Center

at Lewis Field



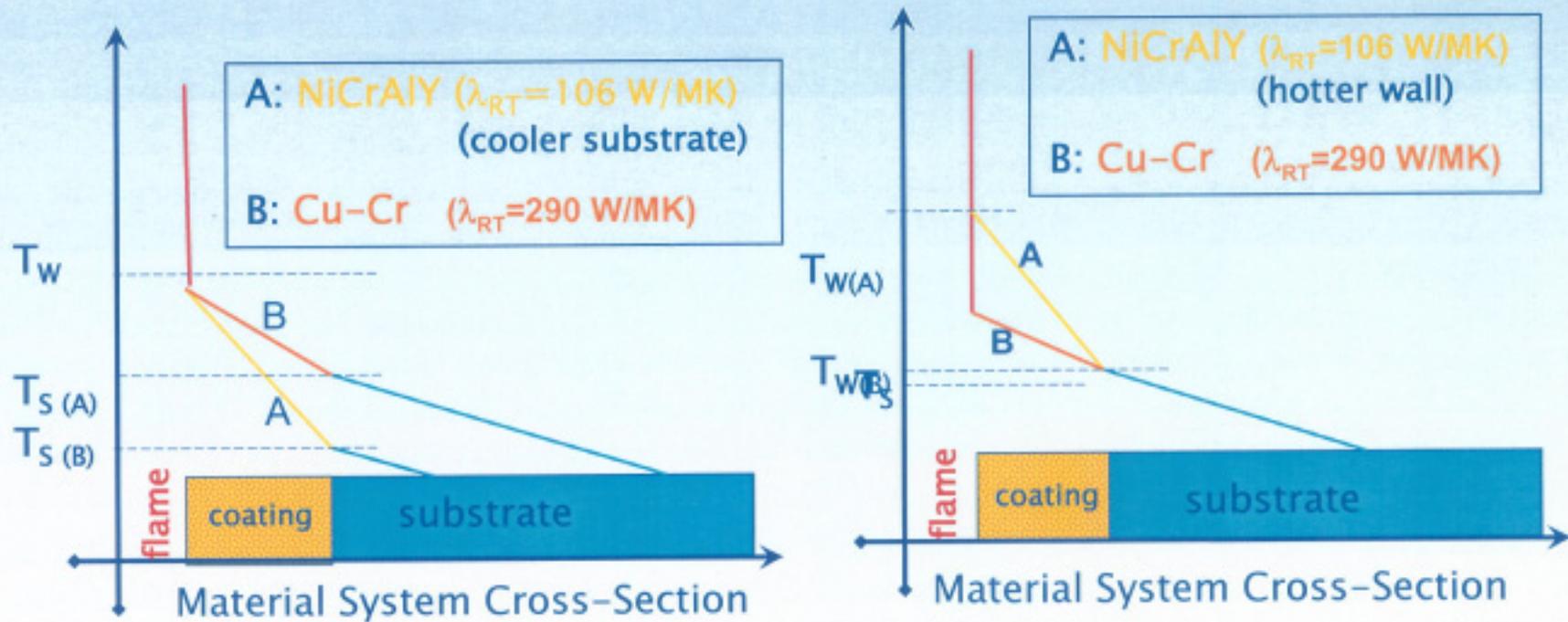
10/30/2003

1

Need for Coating Protection

- Advanced Cu alloys provide excellent mechanical and thermal properties for aerospace applications:
 - They are preferred liners for rocket engine thrust-cells
 - Cu-8Cr-4Nb (“GRCop-84”) is state-of-the-art liner
- But they may be prone to oxidative degradation:
 - Static Oxidation -- in reduced $p_{(O_2)}$
 - Cyclic Oxidation (varying thermal cycles)
 - Blanching (oxidation-reduction cycling)
- They need environmental-barrier coatings (EBC) protection by formation of a stable oxide:
 - Al_2O_3 from NiCrAlY, or
 - Cr_2O_3 from Cu-Cr

Development Efforts Underway for Two Coating Compositions



MERITS

NiCrAlY enables cooler substrate for a given wall temperature (left), or a hotter wall for a fixed substrate temperature (right).

Cu-Cr provides higher thermal conductivity for more efficient dissipation of heat.

Background

Pioneer Work: (K.T. Chiang & Co. (Boeing/Rocketdyne))

- Examined Cu-Cr coatings to protect aerospace Cu alloys
- Demonstrated Cr₂O₃ protection when Cr ≥ 30 wt %

However

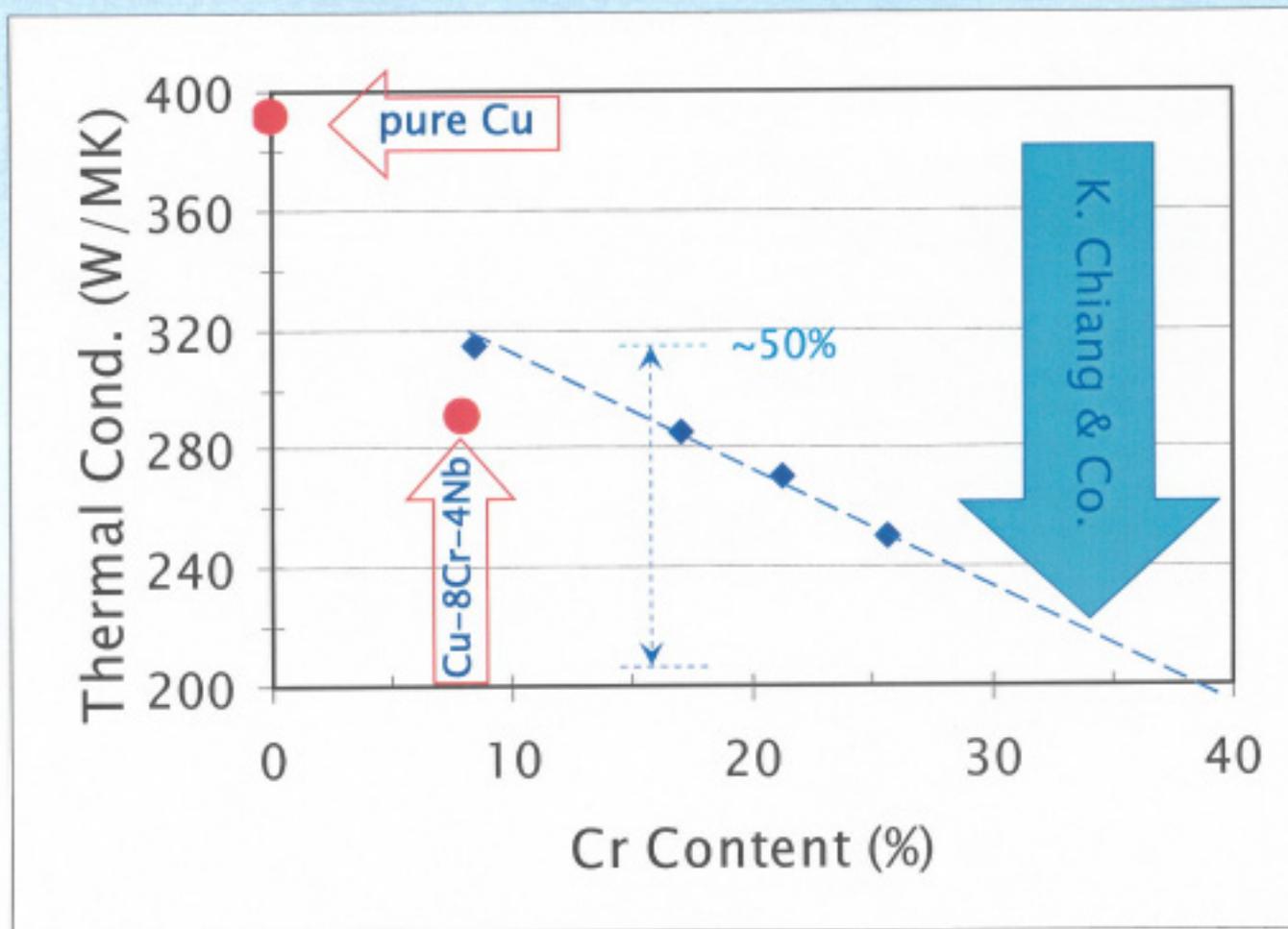
LO_x/LH₂ thrust cell liner coatings need reduced Cr levels to keep thermal conductivity and ductility high.

Our Approach

Refine coatings to reduce Cr content, by using improved deposition techniques:

- Low-pressure plasma spray (LPPS)
- **Kinetic Metallization (Variant of Cold Spray)**

Cu-Cr Conductivity vs. Cr Content at R.T.*



Measurements by Thermo-Physical Properties Research Lab. (TPRL), W. Lafayette, IN

(* At 650°C Cu-Cr values are uniformly lower by 30 W/MK ; GRCoP-84 values remain ~same)

Glenn Research Center

at Lewis Field



10/30/2003

Experimental Procedure

Coatings (on GRCop-84)

Cu-xCr (x = 8.5, 17.1, 21.3, and 25.6 w/o)

Deposition

Kinetic Metallization (KM), a cold-spray variant
by Inovati Co., CA

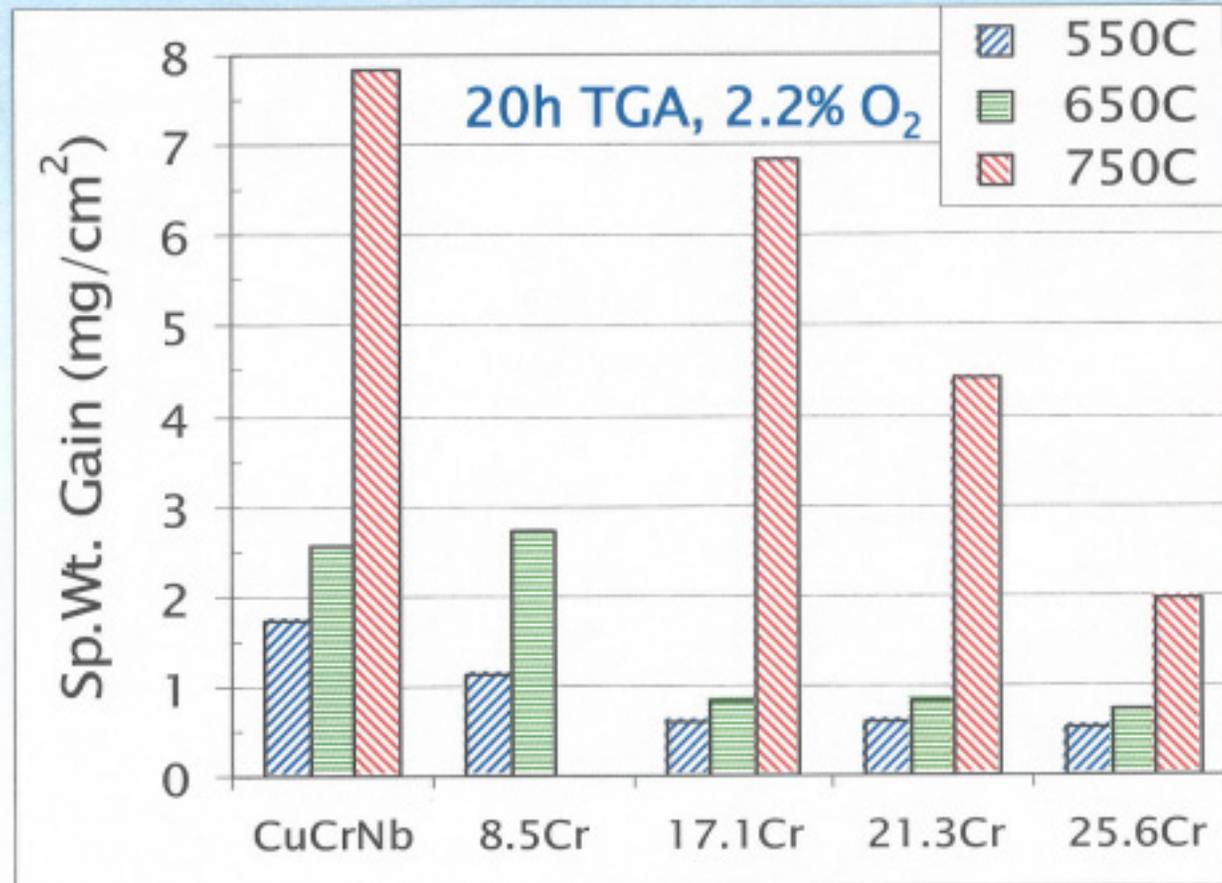
Starting Powders

Ultra-pure Cu & Cr powders (-635 fraction)
Co-atomized by Crucible Research, Pittsburgh, PA

Testing (T= 550 - 800°C)

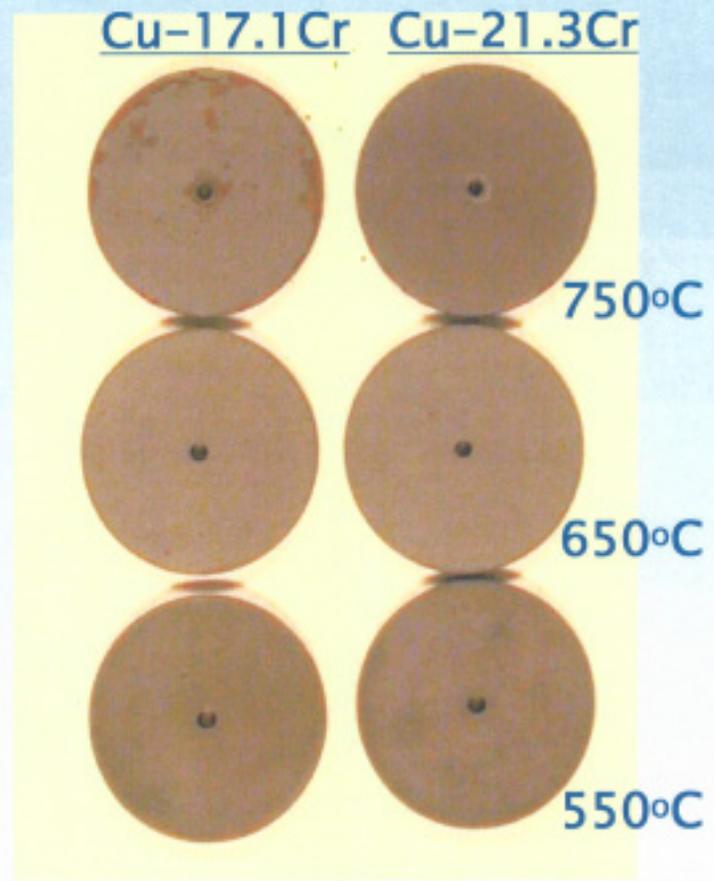
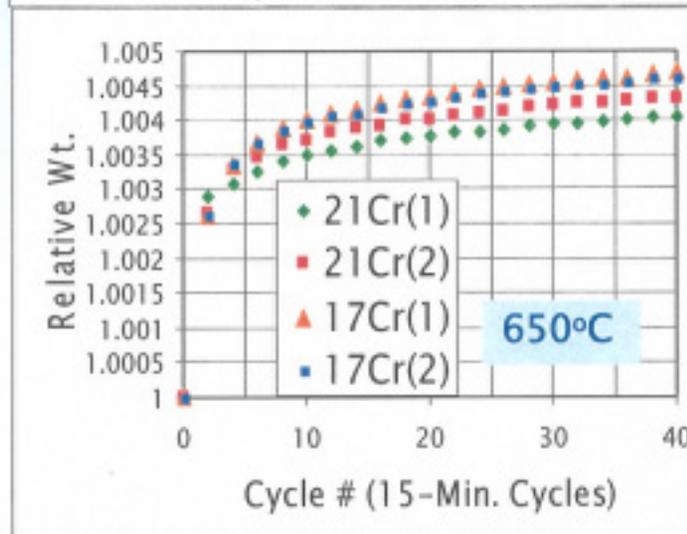
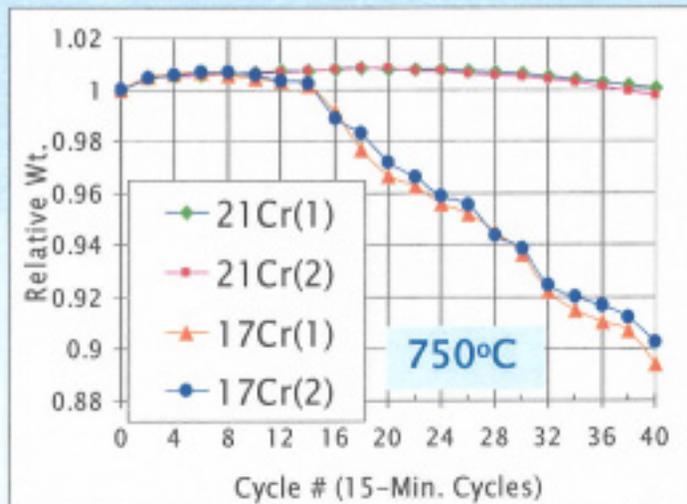
- Static TGA in 0.25 vol% - 100 % O₂ (1.0 atm.)
- Cyclic TGA in air
- *In-situ* oxidation(air)-reduction(5%H₂/Ar) cycling
- High-resolution SEM (Hitachi S4700 - FESEM)

Cu-8Cr-4Nb Static Oxidation Weight Gains With and Without Cu-Cr Coatings



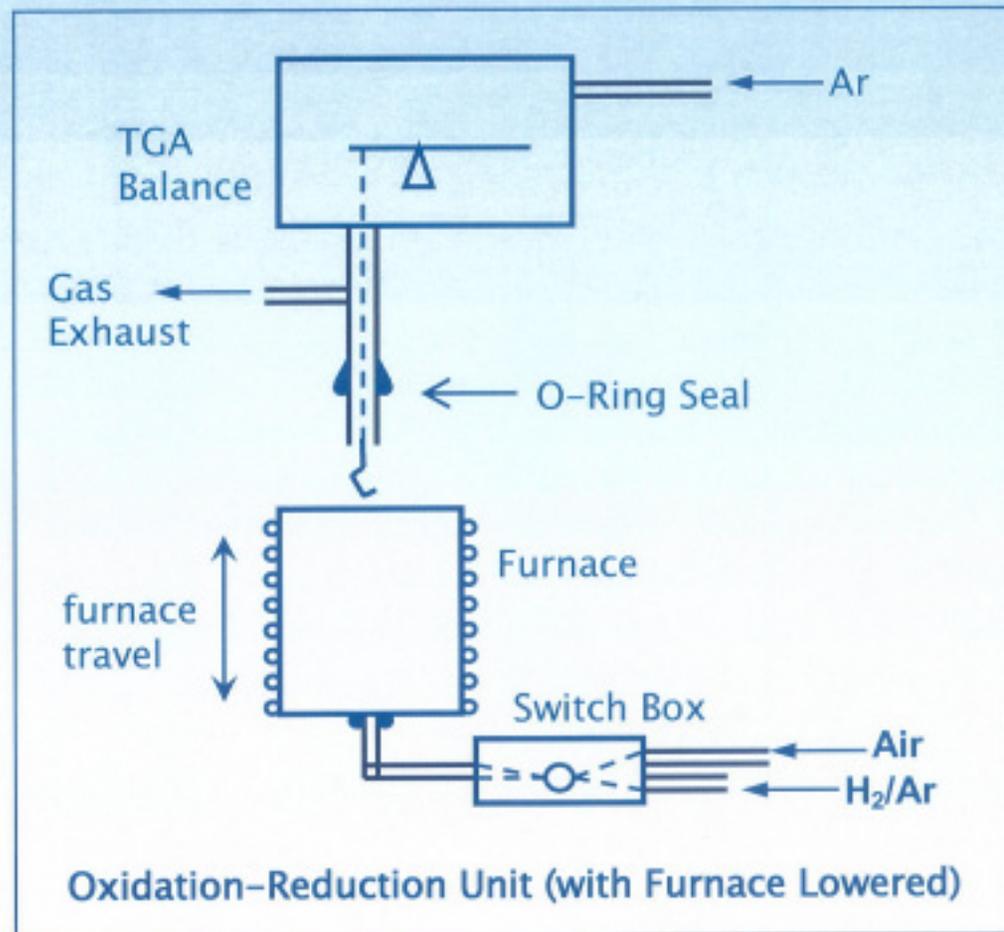
All Cu-Cr compositions reduced Cu-8Cr-4Nb oxidation wt. gain. Extent of protection depended on Cr content and temperature.

Cyclic Oxidation Behavior of Cu-Cr

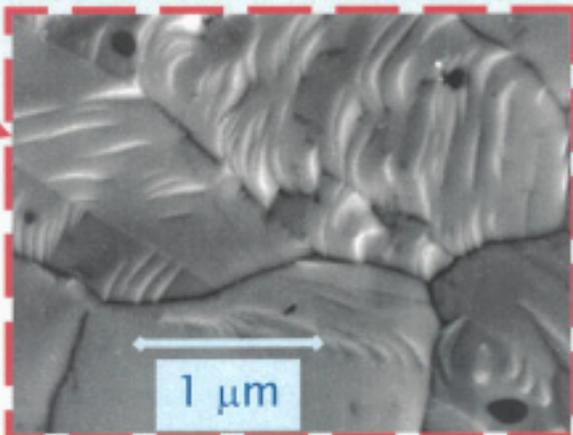
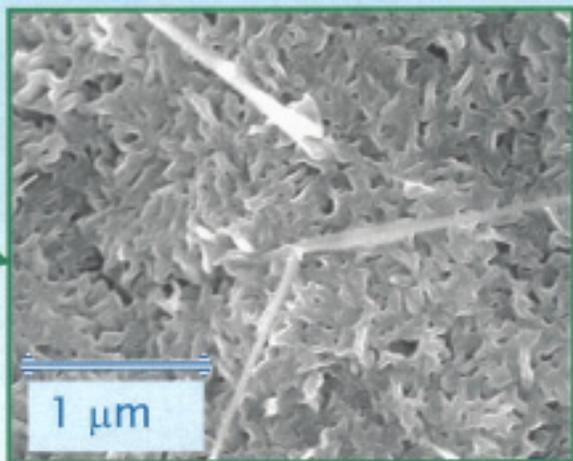
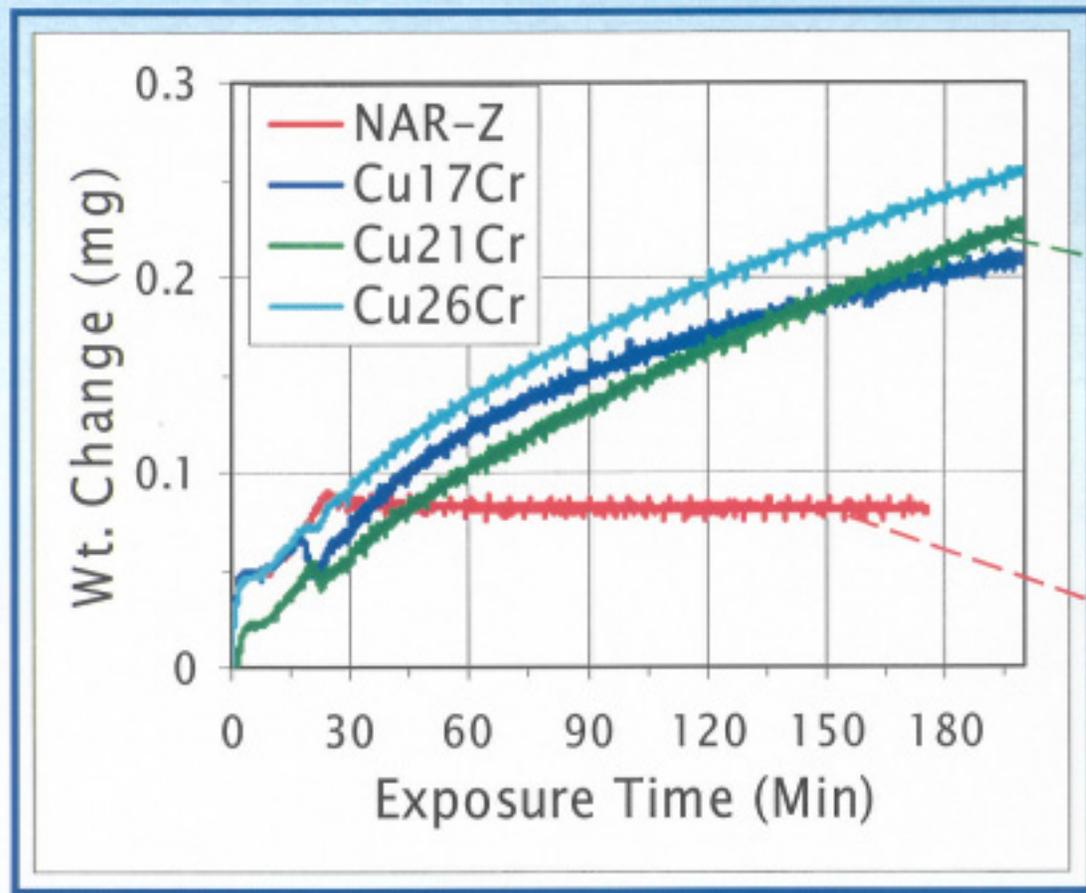


Compositions Dropped:
 Cu-8.5Cr: inadequate above ~650°C
 Cu-25.6Cr: no advantage over Cu-21.3Cr

Oxidation-Reduction Test Apparatus



Oxidation-Reduction Behavior of Alloys at 800°C



Flat Profile (Cu-3Ag-0.5Zr): Oxidation gain reversed by reduction loss, each cycle
Rising Profile (all Cu-Cr): Steady growth of protective, reduction-resistant Cr₂O₃

Future Work

Glenn Research Center

at Lewis Field

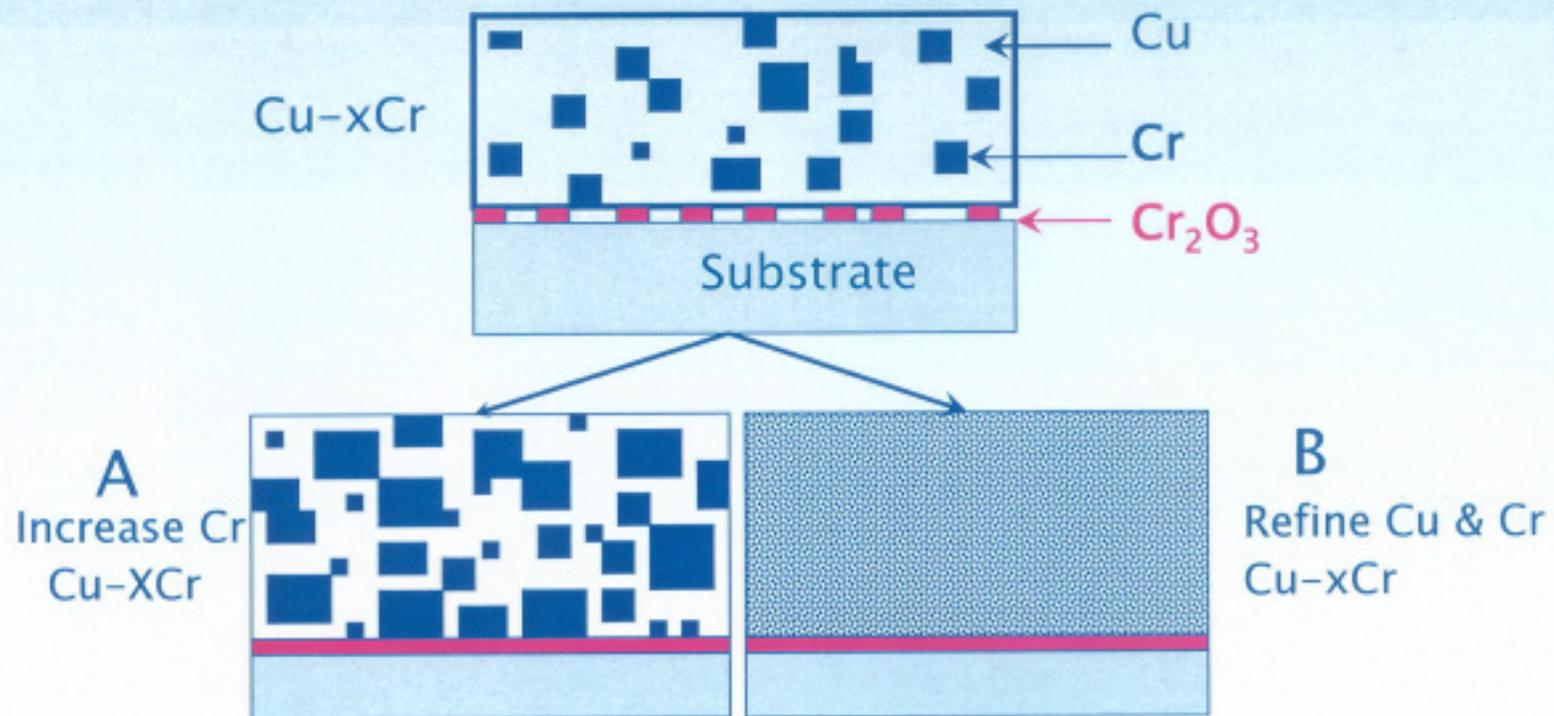


10/30/2003

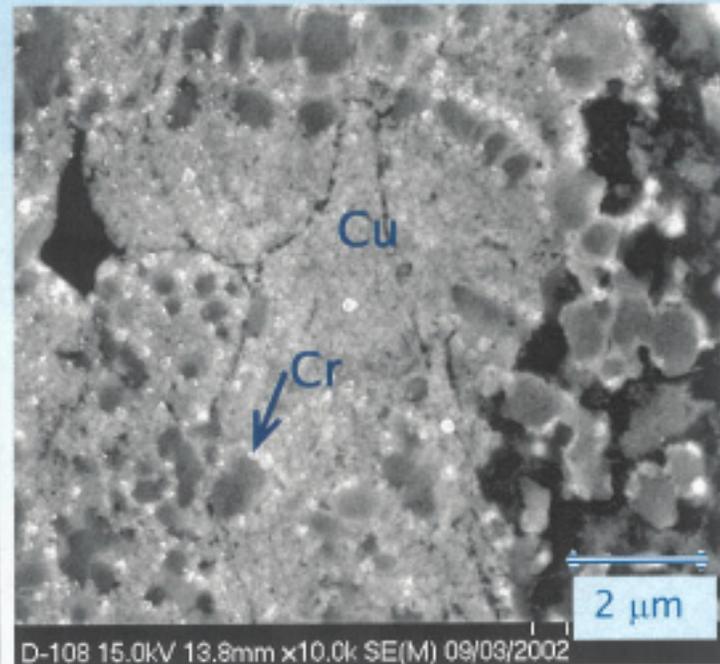
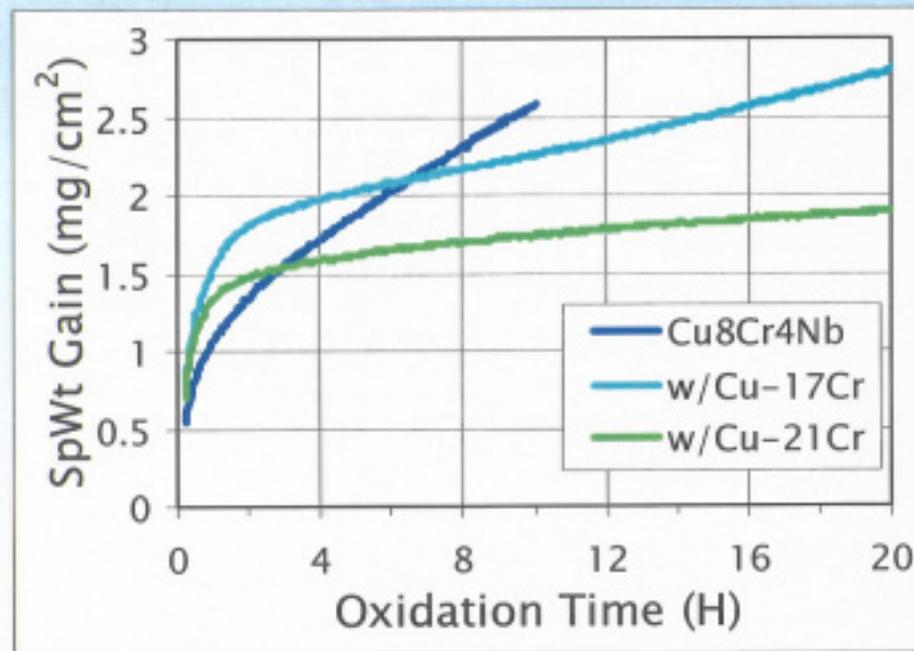
11

Ways to Improve Protection With Cu-Cr

(The goal of protection is to form continuous Cr_2O_3 layer as early as possible.)



Need to Refine Our Starting Powders



In the first few hrs. coatings gain more weight than substrate. This may reflect the time to grow continuous Cr₂O₃ layer due to coating coarseness and inhomogeneity.

Effort is underway to refine the constituent phases (Cu & Cr) further to enable early growth of Cr₂O₃ at lower Cr levels.

Conclusion

- Cu-xCr ($x \geq 21$ wt %) can protect Cu alloys from oxidation-related degradation in thrust-cell liner environments.
- The protection derives from a slow-growing Cr_2O_3 subscale that also resists reduction.
- With further refinement/homogenization of the coating, protection may be achieved at even lower Cr level.

Acknowledgment

D. Ellis	(GRC):	substrate materials
D. Humphrey	(QSS):	static oxidation
C. Barrett	(GRC):	cyclic oxidation
J. Setlock	(CWRU):	oxidation-reduction

This work was done at NASA GRC and was funded under the HOT-PC project of the Propulsion and Power Program.



Glenn Research Center

at Lewis Field



Powder-Derived High-Conductivity Coatings for Copper Alloys

Linus U.J.T. Ogbuji

QSS Group, NASA Glenn Research Center
Cleveland, OH 44135

Glenn Research Center

at Lewis Field

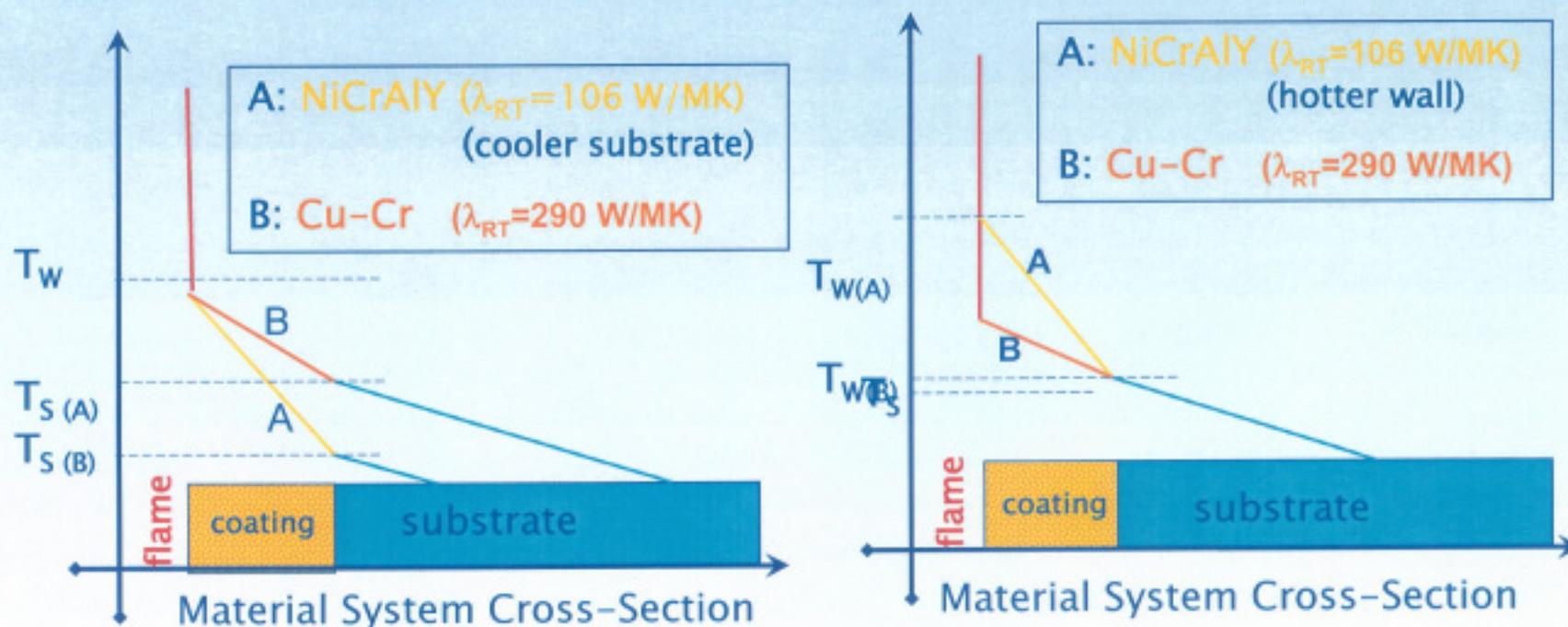


Need for Coating Protection

- Advanced Cu alloys provide excellent mechanical and thermal properties for aerospace applications:
 - They are preferred liners for rocket engine thrust-cells
 - Cu-8Cr-4Nb ("GRCop-84") is state-of-the-art liner
- But they may be prone to oxidative degradation:
 - Static Oxidation -- in reduced $p_{(O_2)}$
 - Cyclic Oxidation (varying thermal cycles)
 - Blanching (oxidation-reduction cycling)
- They need environmental-barrier coatings (EBC) protection by formation of a stable oxide:
 - Al_2O_3 from NiCrAlY, or
 - Cr_2O_3 from Cu-Cr



Development Efforts Underway for Two Coating Compositions



MERITS

NiCrAlY enables cooler substrate for a given wall temperature (left), or a hotter wall for a fixed substrate temperature (right).

Cu-Cr provides higher thermal conductivity for more efficient dissipation of heat.

Background

Pioneer Work: (K.T. Chiang & Co. (Boeing/Rocketdyne)

- Examined Cu-Cr coatings to protect aerospace Cu alloys
- Demonstrated Cr_2O_3 protection when Cr \geq 30 wt %

However

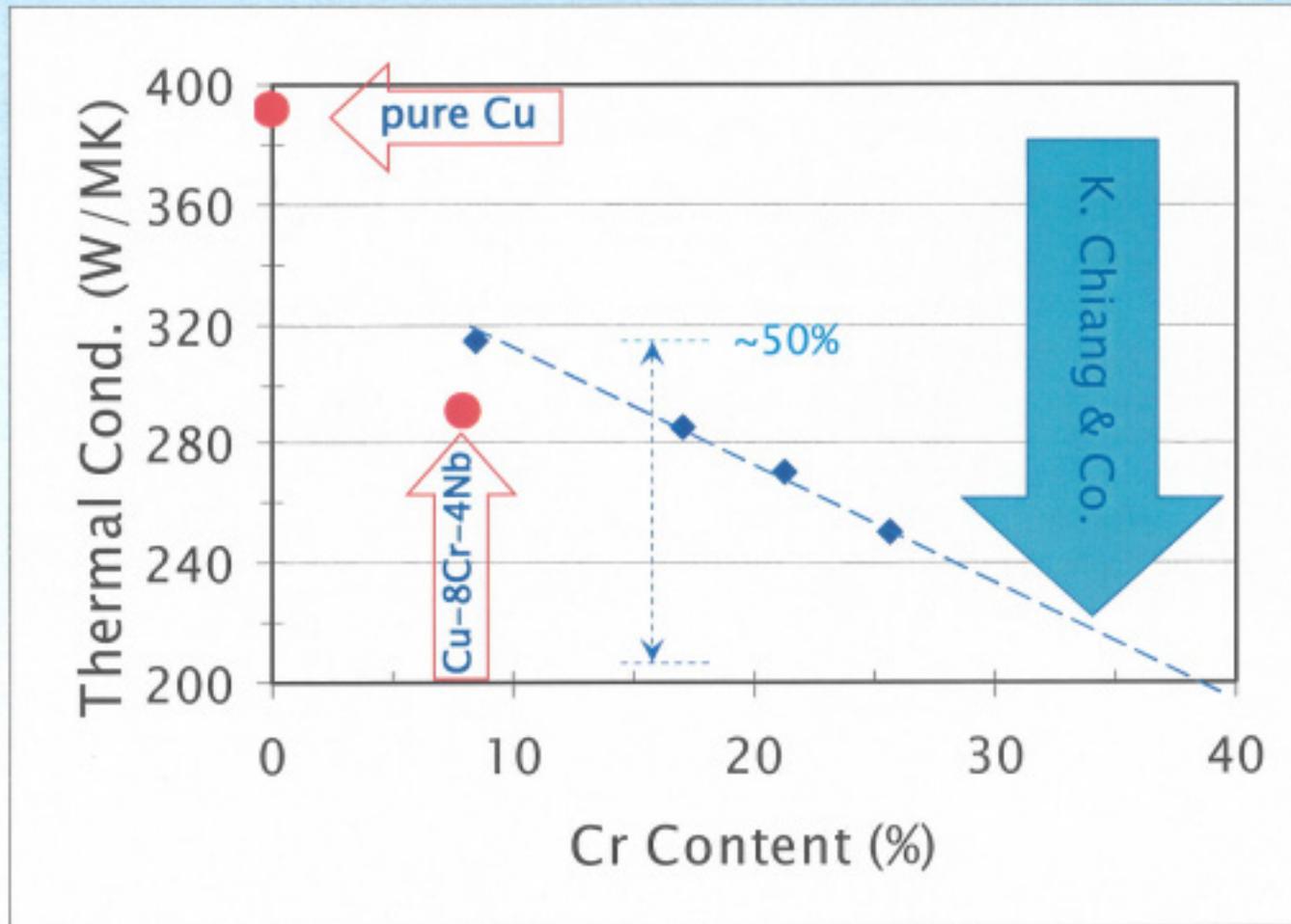
LOx/LH₂ thrust cell liner coatings need reduced Cr levels to keep thermal conductivity and ductility high.

Our Approach

Refine coatings to reduce Cr content, by using improved deposition techniques:

- Low-pressure plasma spray (LPPS)
- Kinetic Metallization (Variant of Cold Spray)

Cu-Cr Conductivity vs. Cr Content at R.T.*



Measurements by Thermo-Physical Properties Research Lab. (TPRL), W. Lafayette, IN

(* At 650°C Cu-Cr values are uniformly lower by 30 W/MK ; GRCoP-84 values remain ~same)

Glenn Research Center

at Lewis Field



10/30/2003

20

Experimental Procedure

Coatings (on GRCop-84)

Cu-xCr (x = 8.5, 17.1, 21.3, and 25.6 w/o)

Deposition

Kinetic Metallization (KM), a cold-spray variant
by Inovati Co., CA

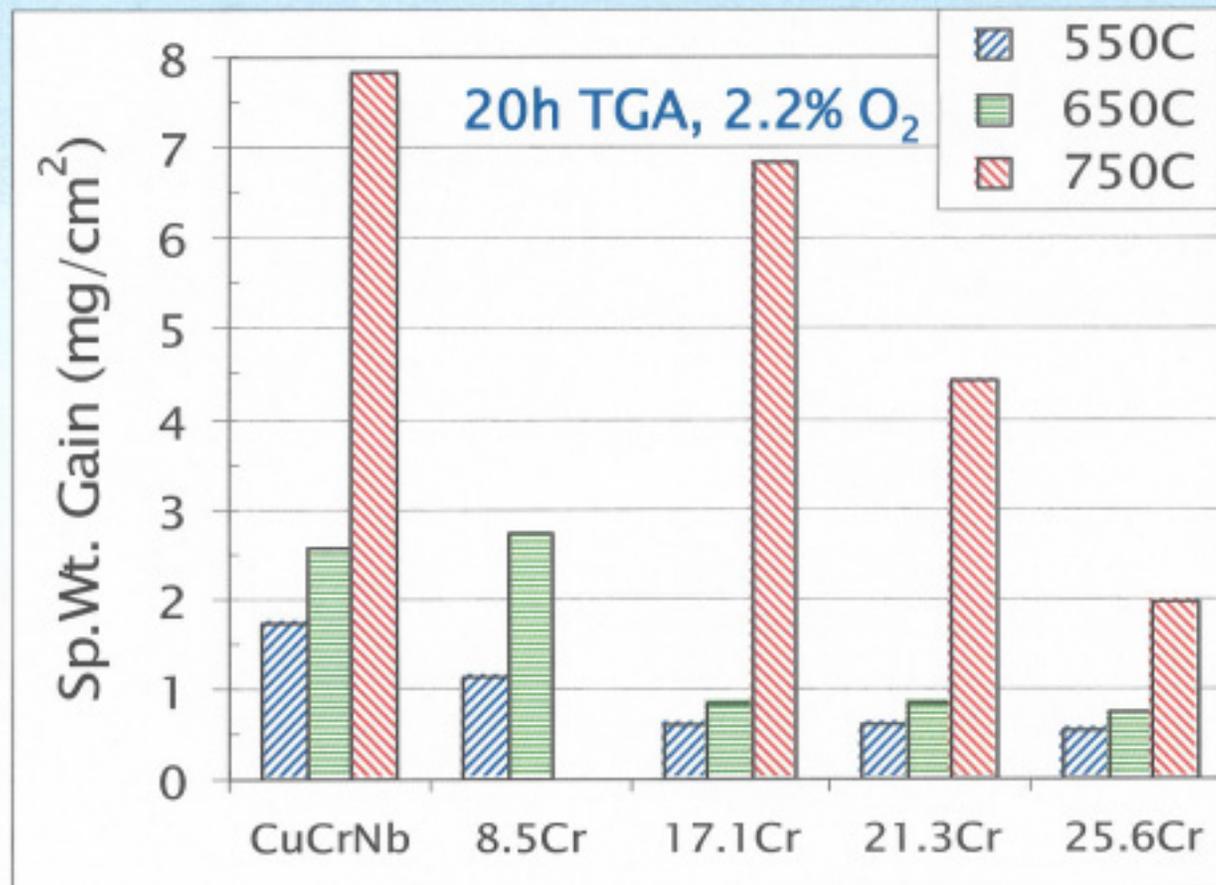
Starting Powders

Ultra-pure Cu & Cr powders (-635 fraction)
Co-atomized by Crucible Research, Pittsburgh, PA

Testing (T= 550 - 800°C)

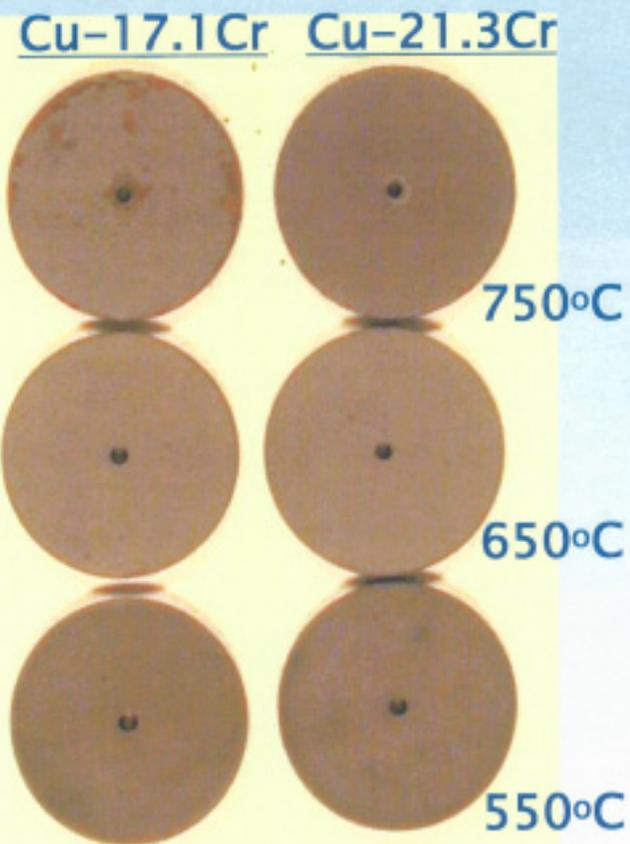
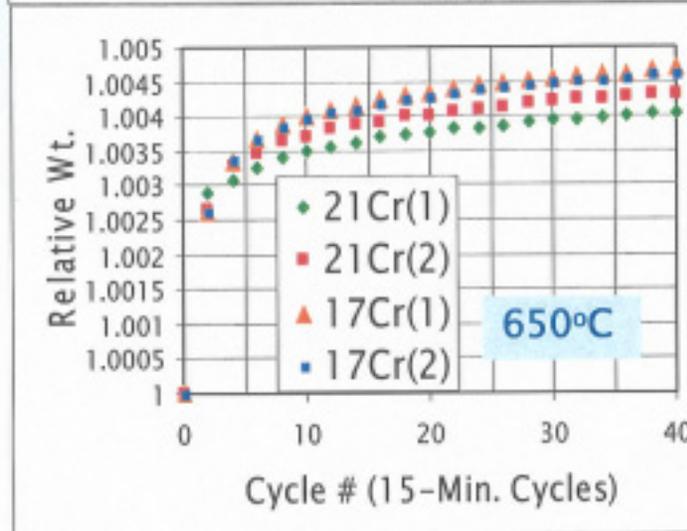
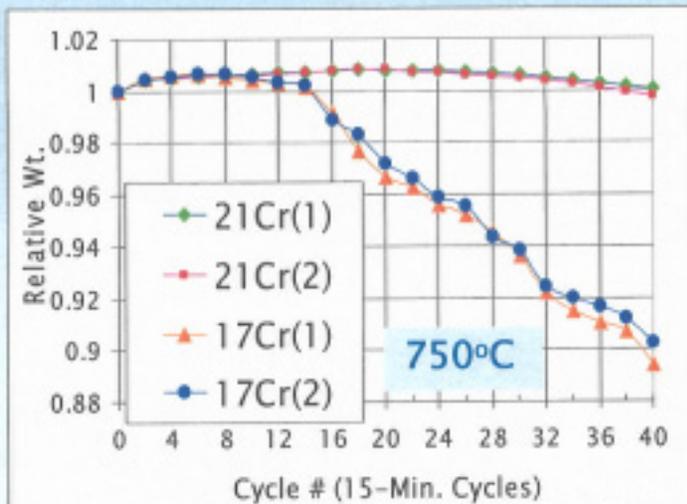
- Static TGA in 0.25 vol% - 100 % O₂ (1.0 atm.)
- Cyclic TGA in air
- *In-situ* oxidation(air)-reduction(5%H₂/Ar) cycling
- High-resolution SEM (Hitachi S4700 - FESEM)

Cu-8Cr-4Nb Static Oxidation Weight Gains With and Without Cu-Cr Coatings



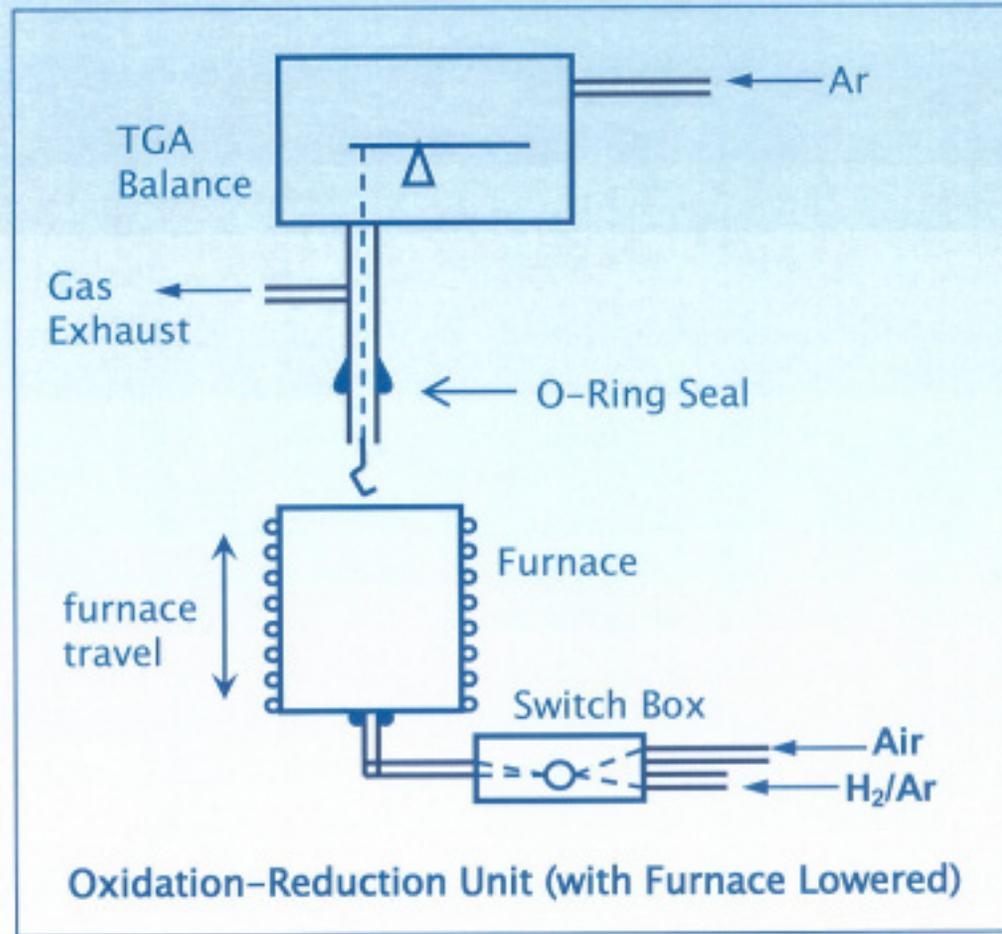
All Cu-Cr compositions reduced Cu-8Cr-4Nb oxidation wt. gain. Extent of protection depended on Cr content and temperature.

Cyclic Oxidation Behavior of Cu-Cr

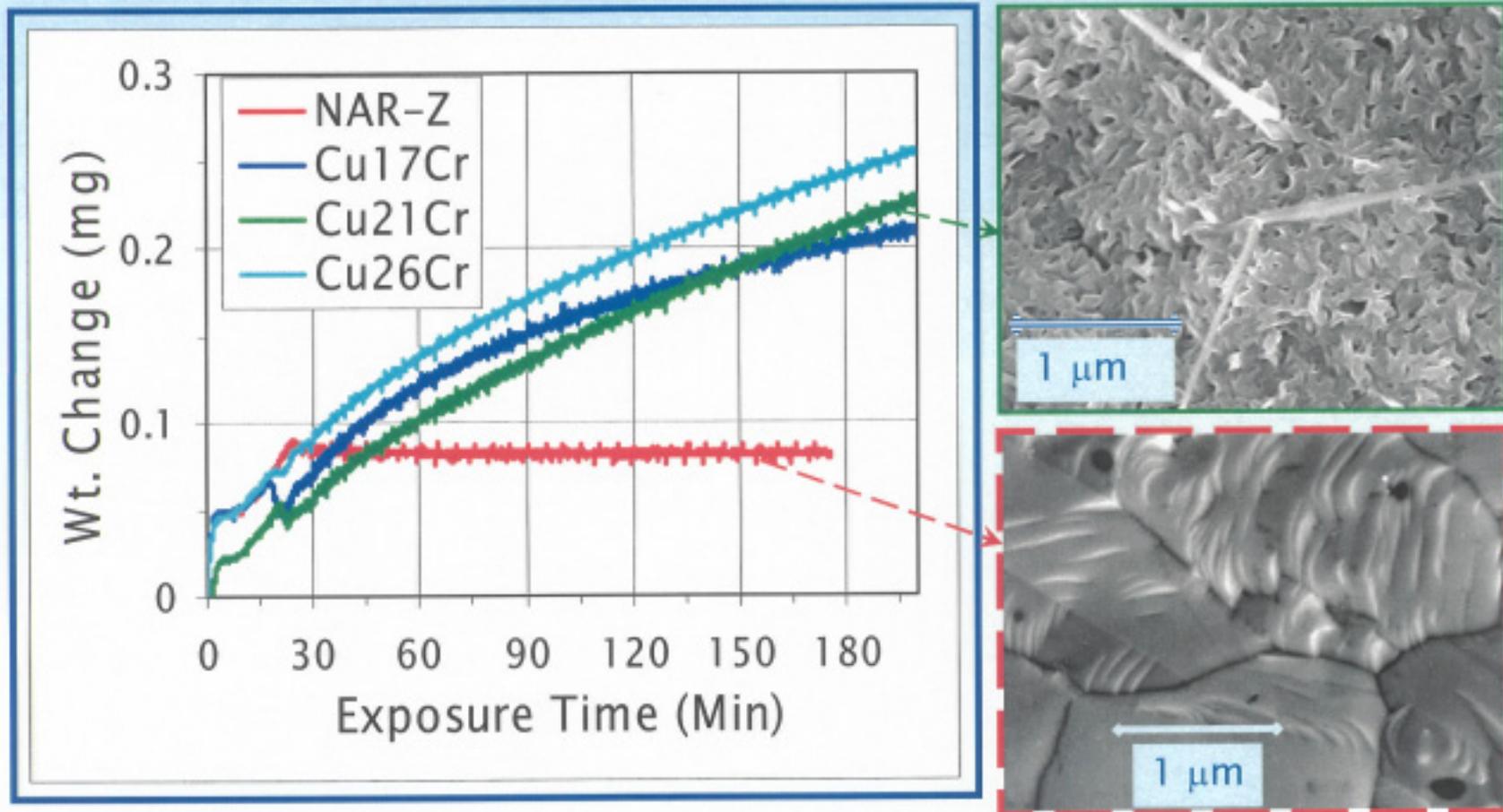


Compositions Dropped:
 Cu-8.5Cr: inadequate above ~650°C
 Cu-25.6Cr: no advantage over Cu-21.3Cr

Oxidation-Reduction Test Apparatus



Oxidation-Reduction Behavior of Alloys at 800°C



Flat Profile (Cu-3Ag-0.5Zr): Oxidation gain reversed by reduction loss, each cycle
Rising Profile (all Cu-Cr): Steady growth of protective, reduction-resistant Cr_2O_3

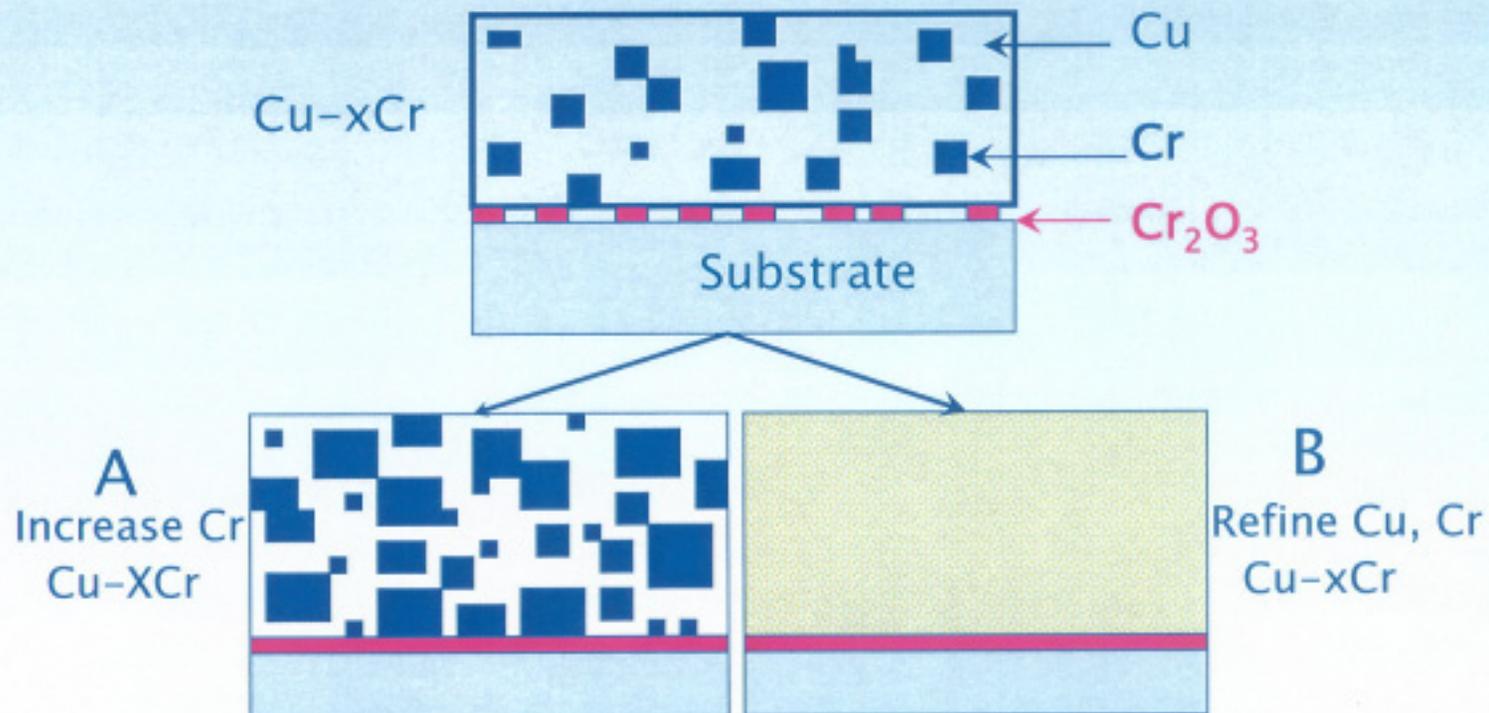
Future Work

Glenn Research Center

at Lewis Field

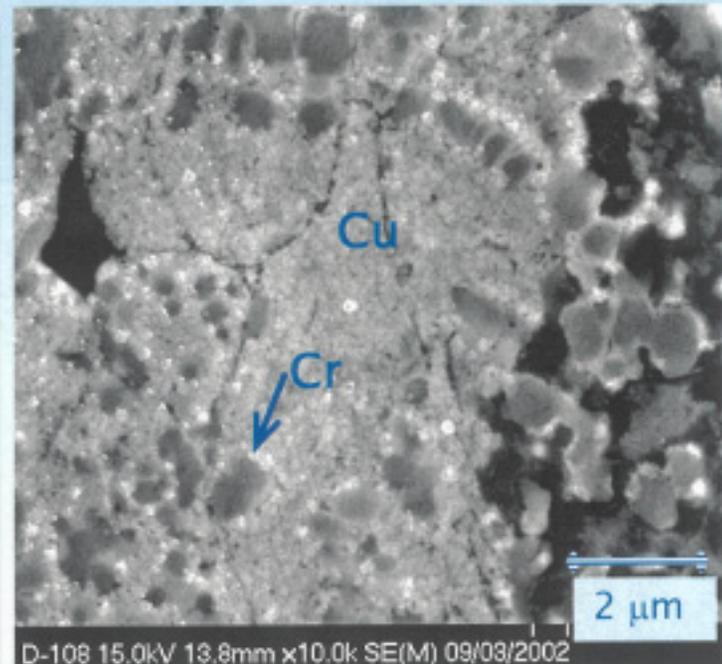
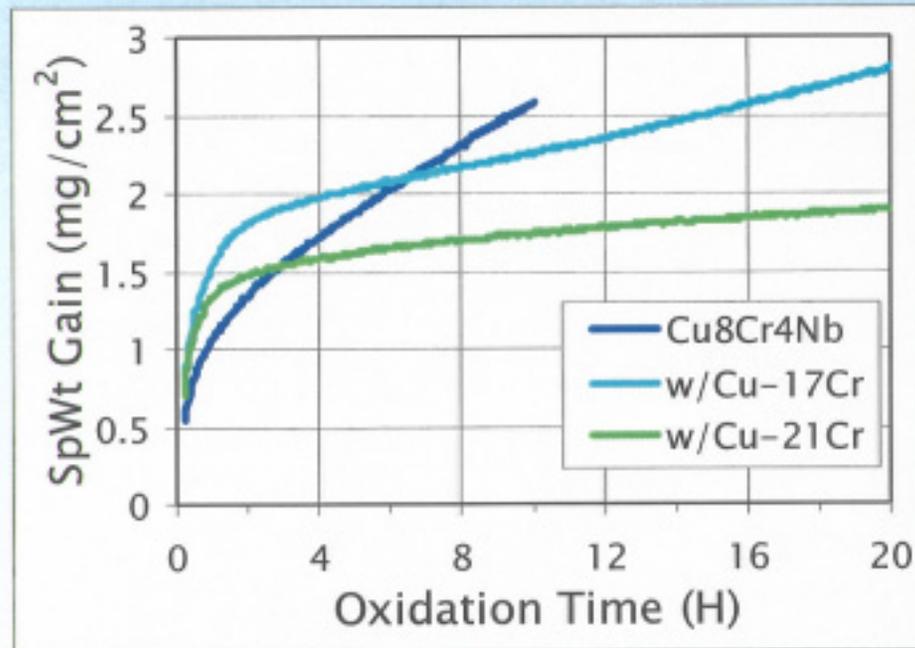


Ways to Improve Protection With Cu-Cr



The goal of protection is to form a continuous Cr₂O₃ layer as early as possible.

Need to Refine Our Starting Powders



In the first few hrs. coatings gain more weight than substrate. This may reflect time to grow continuous Cr₂O₃ layer due to coating coarseness and inhomogeneity. Effort is underway to refine the constituent phases (Cu & Cr) further to enable early growth of Cr₂O₃ at lower Cr levels.

Conclusion

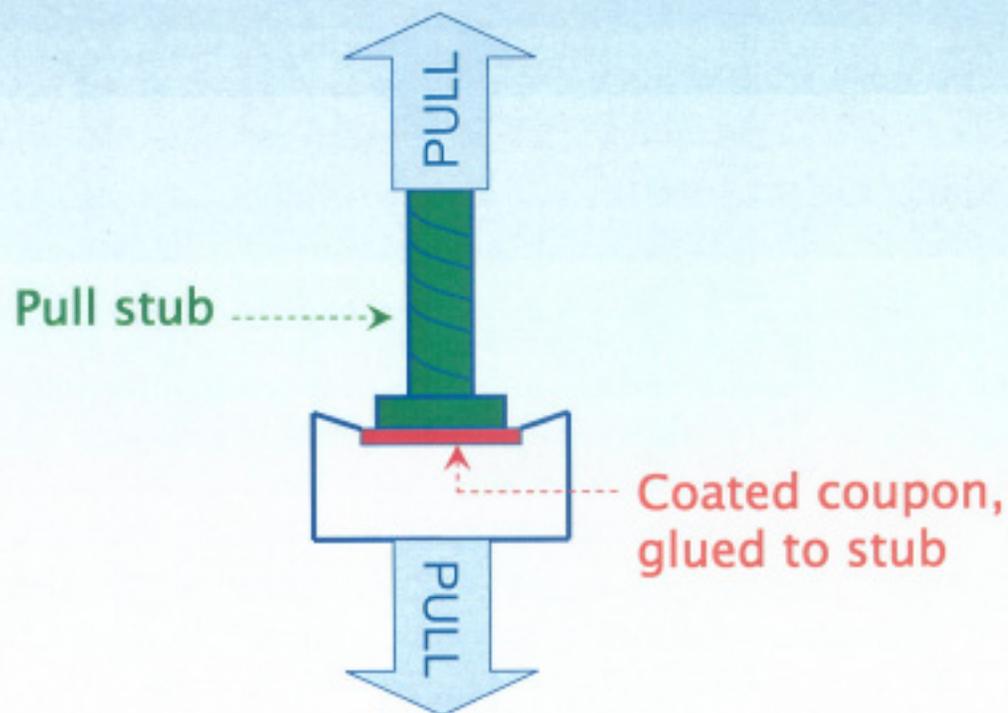
- Cu-xCr ($x \geq 21$ wt %) can protect Cu alloys from oxidation-related degradation in thrust-cell liner environments.
- The protection derives from a slow-growing Cr_2O_3 subscale that also resists reduction.
- With further refinement/homogenization of the coating, protection may be achieved at even lower Cr level.

Acknowledgment

D. Ellis	(GRC):	substrate materials
D. Humphrey	(QSS):	static oxidation
C. Barrett	(GRC):	cyclic oxidation
J. Setlock	(CWRU):	oxidation-reduction

This work was done at NASA GRC and was funded under the HOT-PC project of the Propulsion and Power Program.

Appendix



SET-UP FOR THE SEBASTIAN PULL TEST