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.
Powder-Derived High-Conductivity Coatings for Copper Alloys

Linus U.J.T. Ogbuji

QSS Group, NASA Glenn Research Center
Cleveland, OH 44135
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

A: NiCrAlY ($\lambda_{RT}=106$ W/MK) (cooler substrate)
B: Cu–Cr ($\lambda_{RT}=290$ W/MK)

**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.

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at Lewis Field
## Background

**Pioneer Work:** (K.T. Chiang & Co. (Boeing/Rocketdyne))
- Examined Cu–Cr coatings to protect aerospace Cu alloys
- Demonstrated Cr$_2$O$_3$ protection when Cr $\geq 30$ wt %

**However**
LOx/LH$_2$ 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)

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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)

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Experimental Procedure

Coatings (on GRCop-84)
Cu-xCr \quad (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 % O\textsubscript{2} (1.0 atm.)
- Cyclic TGA in air
- \textit{In-situ} oxidation(air)–reduction(5%H\textsubscript{2}/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

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Oxidation–Reduction Test Apparatus

TGA Balance

Gas Exhaust

Furnace travel

Furnace

Switch Box

Oxidation–Reduction Unit (with Furnace Lowered)

Ar

O–Ring Seal

Air

H₂/Ar

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10/30/2003
Oxidation-Reduction Behavior of Alloys at 800ºC

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.

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Future Work
Ways to Improve Protection With Cu-Cr

(The goal of protection is to form continuous $\text{Cr}_2\text{O}_3$ layer as early as possible.)

- **A**  
  Increase Cr  
  Cu–xCr

- **B**  
  Refine Cu & Cr  
  Cu–xCr

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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.

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Conclusion

- Cu–xCr (x ≥ 21 wt %) can protect Cu alloys from oxidation-related degradation in thrust-cell liner environments.
- The protection derives from a slow-growing Cr₂O₃ 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.

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

20h TGA, 2.2% O₂

Sp. Wt. Gain (mg/cm²)

CuCrNb  8.5Cr  17.1Cr  21.3Cr  25.6Cr

550C  650C  750C

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

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Appendix

SET-UP FOR THE SEBASTIAN PULL TEST

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