OXIDATION BEHAVIOR OF COPPER ALLOY CANDIDATES FOR ROCKET ENGINE APPLICATIONS

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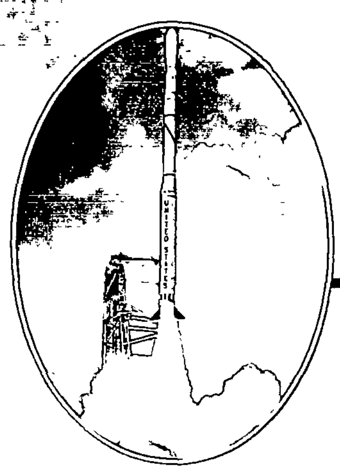
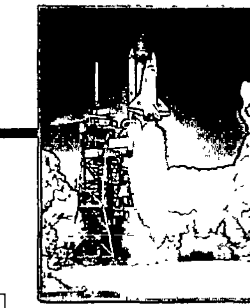




BACKGROUND

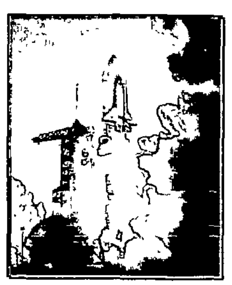
Combustion Chamber Liners for Rocket Engines

- A rocket engine's combustion chamber is lined with material that is highly conductive to heat in order to dissipate the huge thermal load (evident in a white-hot exhaust plume).
- Because of its thermal conductivity, copper is the best choice of liner material. However, the mechanical properties of pure copper are inadequate to withstand the high stresses, hence, copper alloys are needed in this application. But copper and its alloys are prone to oxidation and related damage, especially "blanching" (an oxidation-reduction mode of degradation). The space shuttle main engine combustion chamber is lined with a Cu-Ag-Zr alloy, "NARloy-Z", which exhibits blanching
- A superior liner is being sought for the next generation of RLVs (Reusable Launch Vehicles) It should have improved mechanical properties and higher resistance to oxidation and blanching, but without substantial penalty in thermal conductivity.
- GRCop-84, a Cu-8Cr-4Nb alloy (Cr_2Nb in Cu matrix), developed by NASA Glenn Research Center (GRC) and Case Western Reserve University, is a prime contender for RLV liner material.
- In this study, the oxidation resistance of GRCop-84 and other related/candidate copper alloys are investigated and compared (A parallel investigation of blanching resistance is underway.)

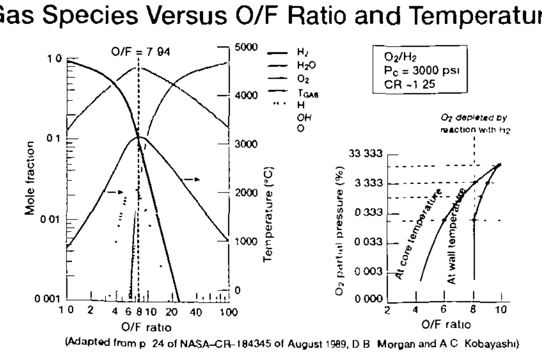
Thermophysical and Thermomechanical Properties of Some Cu Alloys*

Composition	GRCop84 Cu-8Cr-4Nb	GlidCop-AL15** ODS Cu-Al_2O_3	NARloy-Z Cu-3w/oAg	Cu-Zr Cu-0 1%Zr	OFHC-Cu pure Cu
Mean change transfer effeciency (CTE) 500 to 700 °C (ppm/K)	16	16 6			17 7
Thermal conductivity at 20 °C (W/mK)	300	365	350		391
Density (g/cm3)	8 72	8 91			8 94
Elastic modulus (GPa)		130		116	115
Elastic modulus at 600 °C (GPa)	72			65	
Yield strength at 600 °C (MPa)	160	150	62	10	10
R T. yield strength (MPa) After brazing simulation 1 hr at 600 °C (for GRCop, 23 min at 935 °C)	150	400	35	80	40

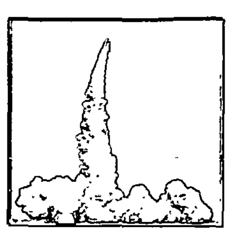
* From GlidCop brochure (except GRCop84).
**AL15 contains 0 15 wt% Al (0 3 wt% Al_2O_3)



Gas Species Versus O/F Ratio and Temperature



(Adapted from p 24 of NASA-CR-184345 of August 1989, D B Morgan and A C Kobayashi)



At oxygen-to-fuel (O/F) ratio of ≅ 7.0
- Combustion efficiency (i e , the yield of H_2O) reaches a maximum
- Flame-core $p(O_2) \leq 0$ 03, rising, $p(H2) \leq 0$ falling fine balance, oxidation ⇔ reduction
- p(O) and p(H) are insignificant (each an order-of-magnitude lower)
- Fluctuations can easily cause oxidation/reduction flip-flop (hence ***blanching***)
- With flame-core $p(O_2)$ at 0 01, the wall $p(O_2)$ is 0 0003 (0 03%), hence $p(O_2)$ of 0 03 to 2 2% were chosen for thermogravimetric analysis (TGA) oxidation studies

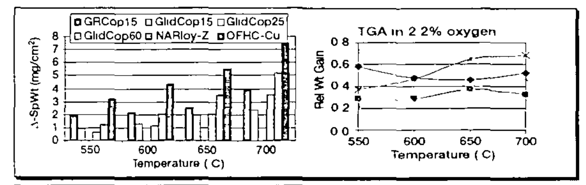
ISOTHERMAL OXIDATION

10-hr TGA Oxidation of Copper Alloys in Reduced $p(O_2)$

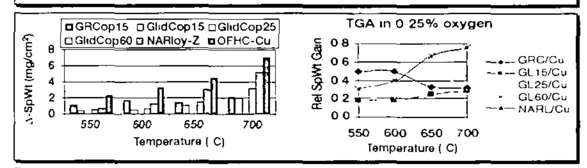
1. GLIDCop-AL15 (ODS alloy) gained the least weight in all cases. Its nanodispersion of 0.3 wt% Al_2O_3 may have suppressed diffusion and slowed oxidation, but this benefit did not scale up with increased Al_2O_3 content (see AL25 and AL60).
2. GRCop-84 weight gains were similarly low in all cases.
3. NARloy-Z and pure Cu gained the most weight.

Ambient

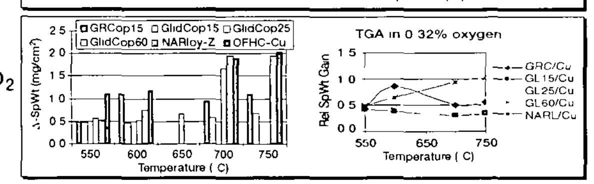
2.2% O_2 (bal Ar)

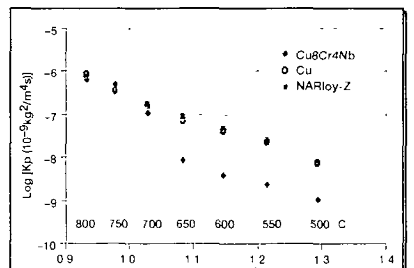


0.25% O_2 (bal Ar)

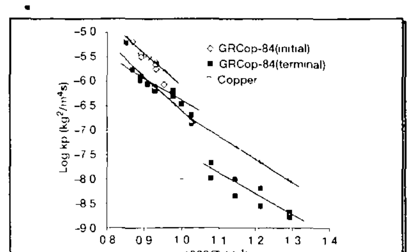


0.032% O_2 (bal Ar)



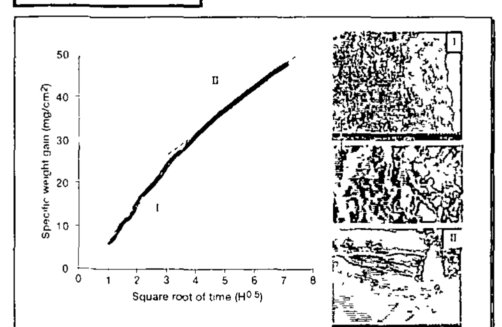


Below 700 °C, GRCop84 resists oxidation better than Cu and NARloy-Z. Above 700 °C, all three materials behave similarly—on a gross scale



On a finer scale, GRCop84 oxidation kinetics is complex above 700 °C, with fast-initial and slow-terminal branches

50H TGA

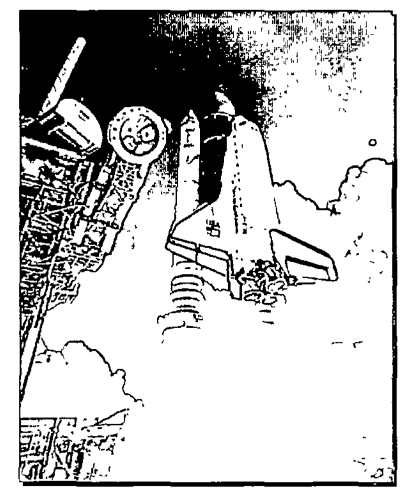


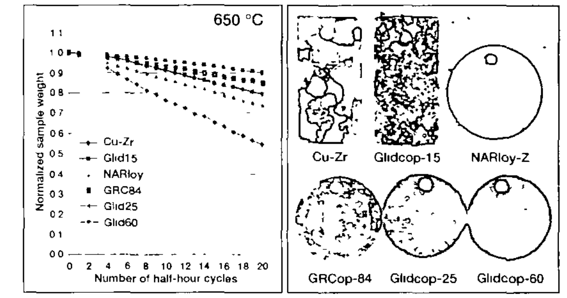
The GRCop84 oxidation rate change, from fast-initial to slower terminal kinetics above 700 °C is caused by morphological changes in the oxide scale, from spongy to dense

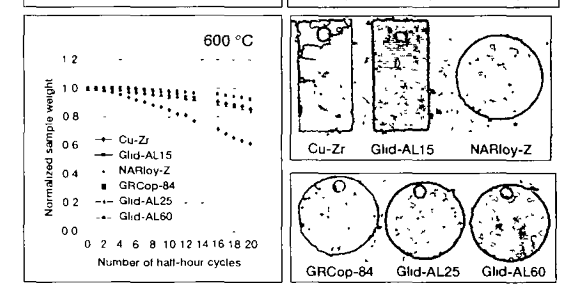
CYCLIC OXIDATION

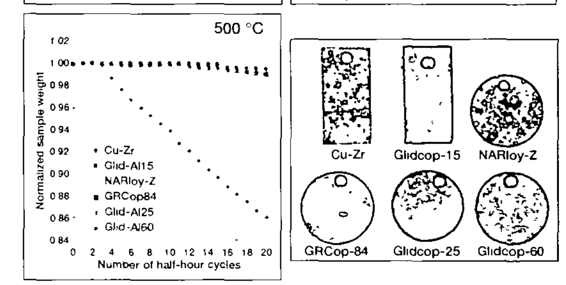
Cyclic Oxidation of Copper Alloys at 500 to 650 °C in Air

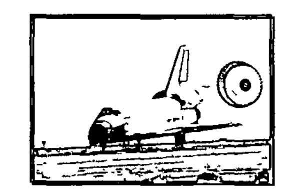
- The images show the sample surfaces following 20 half-hour exposures, and after gentle tapping to dislodge loose oxide (spalls)
- Weight was gained by oxidation and lost by spallation (during cooling)
- Sample weights were measured after each oxidation cycle
- GRCop-84 and the three GlidCop materials showed the least weight gain and the most adherent oxide scales (as the images show).
- Cu-Zr showed the least resistance to cyclic oxidation, followed by NARloy-Z.

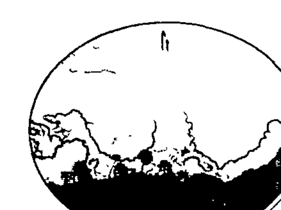












Summary and Conclusion

Oxidation resistance of three advanced copper alloys was studied at 500 to 800 °C, the expected temperature range of RLV liner service: **"GRCop-84" (Cu-8Cr-4Nb)**, three variants of "GlidCop" (ODS Cu-Al_2O_3), and **"NARloy-Z" (Cu-3%Ag-0.5%Zr)**.

Three types of oxidation exposure were employed:
1. Long-term (50-hr) TGA in oxygen and air,
2. Short-term (10-hr) TGA in low $p(O_2)$,
3. 10-hr cyclic oxidation in air.

From the standpoint of oxidation resistance alone, **GRCop-84 and GlidCop are** superior to the current space shuttle main engine liner NARloy-Z; and Cu-Zr is unsuitable as RLV liner.

Acknowledgment
This work was performed at NASA GRC under contract **NAS3-98008**, and funded under the HOT-PC and RLV-Gen2 programs of NASA.