HIGH CONDUCTIVITY MATERIALS FOR HIGH HEAT FLUX APPLICATIONS IN SPACE PROPULSION SYSTEMS

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ABSTRACT

The requirements defined for Next Generation Reusable Launch Vehicles (RLVs) target aggressive cost reductions and improved safety goals. Several next generation launch vehicle concepts are being designed with Rocket Based Combined Cycle propulsion systems. High conductivity, high temperature materials have been identified as a major requirement via a joint industry/government activity for defining critical issues for achievement of the vehicle goals. SC/RAMjet engines will need large actively cooled panels especially in the combustor section. GRCop-84 is a new copper base alloy with an excellent combination of strength and conductivity and has been developed to the point that it is a strong candidate for near-term rocket engine applications. The purpose of the present work is to establish feasibility of new alloys with capability beyond GRCop-84. The use of coatings as environmental and thermal barriers adds further capability onto the Cu-base structures. Finally, NiAl based systems have also been explored to achieve further performance gains.

INTRODUCTION

The very challenging cost and safety goals established for next generation RLV's have been addressed by several joint industry/government workshops. The workshops have identified several next generation launch vehicle concepts including Turbine Based (TBCC) and Rocket Based (RBCC) combined cycle propulsion systems. These designs require new high conductivity, high temperature materials for rocket and SC/RAM jet engines to meet design and performance goals. Prominent among these technologies is the need for high conductivity, high temperature materials for use in several high heat flux applications. Combustion chambers, nozzle ramps, large actively cooled panels and heat exchangers, and leading edges can all benefit from the improved material properties.

Copper-base alloys such as NARloy-Z, Glidcop and AMZIRC have previously been used in these applications but limit performance to lower than desired operating temperatures and lives. A new series of alloys based on Cu-Cr-Nb is under development that possesses the potential for dramatically improving the performance of propulsion systems for advanced aerospace vehicles. GRCop-84 is the first alloy in this series and has been developed to a technology readiness level that allows application in near-term engine applications. The purpose of this paper is to review the development and properties of these new alloys and describe the potential for further improvements beyond GRCop-84. The mechanical properties of the new alloys offer up to 300°F improvement in temperature capability over the existing alloys. Even further improvements can be achieved by including environmental barrier and thermal barrier coatings on the copper alloys.

Further improvements beyond the capability of copper were also explored. Nickel aluminide (NiAl) has an excellent combination of high temperature strength and thermal conductivity, combined with low density and excellent resistance to environmental attack. However, it is prone to brittle fracture at low temperatures. A bimetallic concept where an inner layer of NiAl is encased by an outer layer of either a nickel-base superalloy or a copper alloy was investigated as a means to provides both thermal and structural performance.

COPPER ALLOY DEVELOPMENT

NASA GRC has undertaken the development of a series of Cu-Cr-Nb alloys and derivatives over the past sixteen years. The alloys have a nearly pure copper matrix strengthened by Cr_2Nb precipitates. The alloy system has demonstrated high thermal conductivity, tensile strength, creep life and low cycle fatigue (LCF) life in both the as-produced condition and following simulated high temperature braze cycles. GRCop-84 is the most mature member of the emerging alloys under development. This material's manufacturing begins as a pre-alloyed atomized powder and follows conventional powder metallurgy processing. The powder is canned and can be either Hot Isostatic Pressed (HIPed) or extruded. After HIPing, parts can be directly machined or further processed. Similarly, the canned powder can be hot extruded into billets or rod. Large extruded billet sections can be rolled into plate and sheet by a combination of warm and cold rolling. GRCop-84 properties have been well characterized (1). The alloy has been commercially produced in large quantities (800 to 1000 lbs batches) demonstrating manufacturing capability. Suitable manufacturing procedures have been developed and are being optimized. Forming, friction stir welding and other joining techniques are also under development. Manufacturing capabilities are already in place or can be extended to meet desired final size or shape. GRCop-84 is under consideration for use in several current and recent rocket engine programs such as the RS-83 and RS-84 (Rocketdyne), COBRA (Aerojet) and RL-60 (P&W).

New alloys in the GRCop system include GRCop-42, a variation of GRCop-84 with a lower volume fraction of Cr_2Nb. This alloy is intended to achieve reasonable mechanical properties, slightly lower than that provided by GRCop-84, but has a higher thermal conductivity. The alloy would be favored in an application where thermal conductivity is the most critical factor. GRCop-84 + Ag is another variation of GRCop-84 with silver added to enhance creep lives and possibly thermal conductivity. The processing of these alloys is identical to GRCop-84. Typical chemical compositions are presented in Table 1 for each alloy. AMZIRC, NARloy-Z and Glidcop have also been included for comparison where data from either NASA tests or the literature is available.

Table 1. Chemical Composition (wt %) of Copper Alloys used in Rocket Applications

Alloy	Cr	Nb	Ag	Zr	Al¹	O	Cu
GRCop-84	6.5	5.5					Bal.
GRCop-42	3.8	3.6					Bal.
GRCop-84 + 1 Ag	6.5	5.9	0.9				Bal.
GRCop-84 + 5 Ag	6.2	5.0	4.9				Bal.
NARloy-Z			3.0	0.5			Bal.
Glidcop Al 15 (C15715)					0.15	0.17	Bal
Glidcop Al 60 (C15760)					0.60	0.57	Bal
AMZIRC (C15000)			--	0.15			Bal.
Copper (C10100)							99.99 min.

(1)Al present as Al_2O_3

A typical microstructure for extruded GRCop-84 is shown in Figure 1. The structure consists of a nearly pure copper matrix strengthened by Cr_2Nb precipitates. Typical average grain size is 8 μm, and particle size of the Cr_2Nb precipitates range from 0.1 to 0.3 μm. The performance of this alloy is in large part directly related to the microstructure. The grain size is intentionally made small by the powder processing and remains relatively unchanged even after long exposures to elevated temperatures due to the grain boundaries being pinned by the Cr_2Nb precipitates. The Cr_2Nb precipitates themselves remain small due to their limited solubility and diffusivity in copper. The other GRCop alloys function similarly.
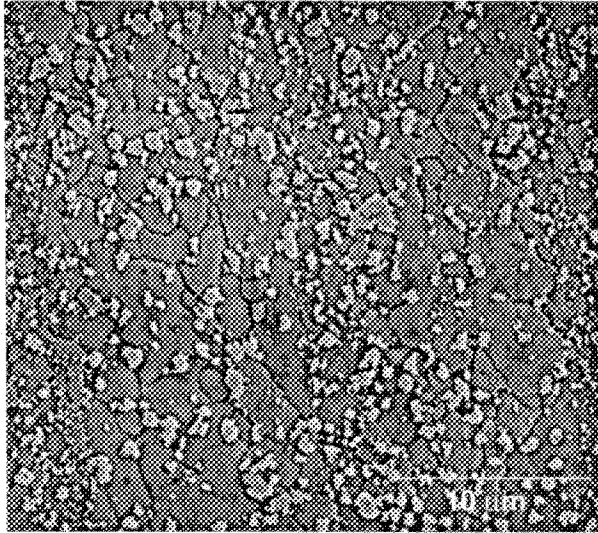
Figure 1. Scanning electron micrograph of GRCop-84. About 15 volume % of Cr_2Nb particles (light gray) are present in a matrix of pure Cu.

A comparison of thermal conductivity of the alloys being examined is presented in Figure 2. GRCop-84 and GRCop-84+Ag have slightly lower thermal conductivities than NARloy-Z especially at elevated temperatures, but they still retain at least 72% of the thermal conductivity of pure copper at and above room temperature. GRCop-42 is similar or slightly better than AMZIRC and is better than NARloy-Z especially at temperatures below 300°C (620°F). The thermal expansion of the alloys is also an important factor influencing component design. The coefficient of thermal expansion (CTE) of the GRCop alloys is lower than the other alloys tested. Lower thermal expansion will lower the thermally induced stresses in a combustion chamber liner and may promote better coating adherence and minimize CTE mismatch with components such as steel jackets when assembled into a thrust cell.
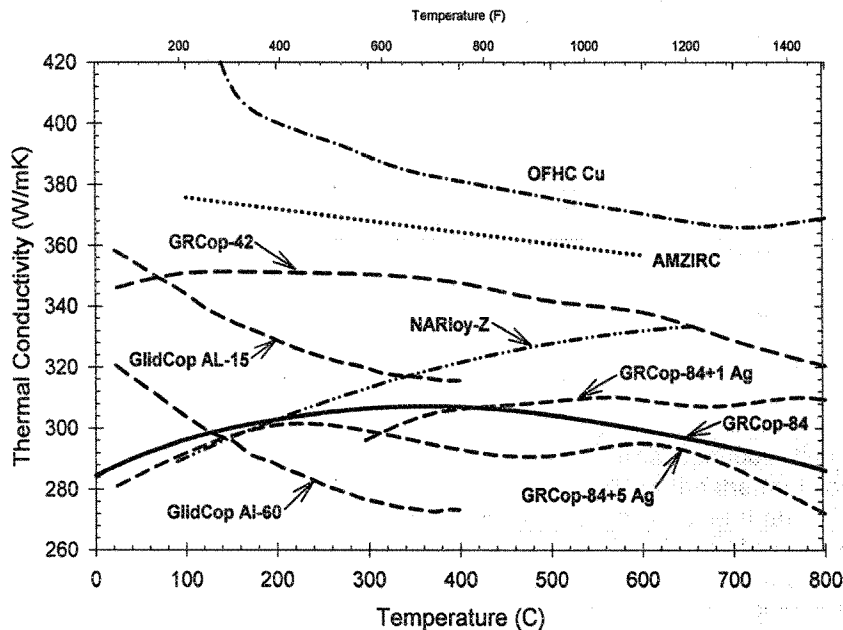

Figure 2. Thermal conductivities of various copper alloys.

Yield strength as a function of temperature are presented in Figure 3; the ultimate tensile strength follows similar trends and is not shown. In the as-produced condition, GRCop-84 has improved strength over Narloy-Z at all temperatures, as does GRCop-42. The 1% and 5% silver additions in GRCop-84 improves strength at temperatures less than 500°C, but at higher temperatures the tensile strengths are equivalent to GRCop-84 or even slightly lower. AMZIRC in the cold worked condition has very high strength at temperatures less than 500 °C, but above this temperature the loss of strength is rapid as the

cold work is annealed out. In addition, the advantage of the cold work will be greatly reduced if the component assembly requires high temperature brazing such as is used to assemble thrust cells.
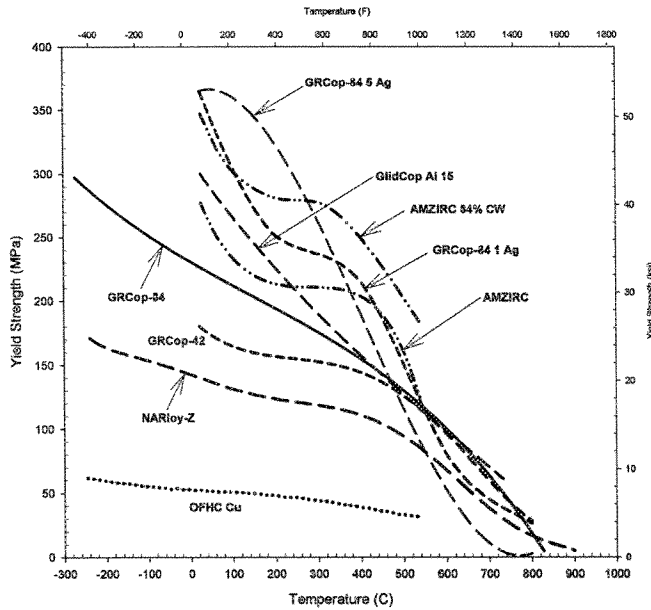

Figure 3.
Yield strength of various copper alloys.

Only limited data is available for tensile strengths following a simulated braze cycle. Figure 4 compares GRCop-84 to NARloy-Z following a simulated braze cycle at 935°C (1725°F) for 15 minutes with a slow heating and cooling rate. Even after a post braze cycle aging step, the NARloy-Z still loses approximately half of its tensile strength. In comparison, the GRCop-84 loses only a minimal amount of strength, typically 20-35 MPa (3-5 ksi). The loss in strength is related to the differences in microstructural stability of the two alloys. In contrast to the Ag-rich precipitates in NARloy-Z, the Cr_2Nb particles in GRCop-84 are inherently very resistant to coarsening even at temperatures approaching the melting point of copper. In the case of AMZIRC, the braze cycle would reduce the strength of heavily worked material to that of the fully annealed state, or even lower if grain growth occurs. Results for GLIDCOP given a similar braze cycle at 980°C (1796°F) showed little or no decrease in tensile strength as well (2).
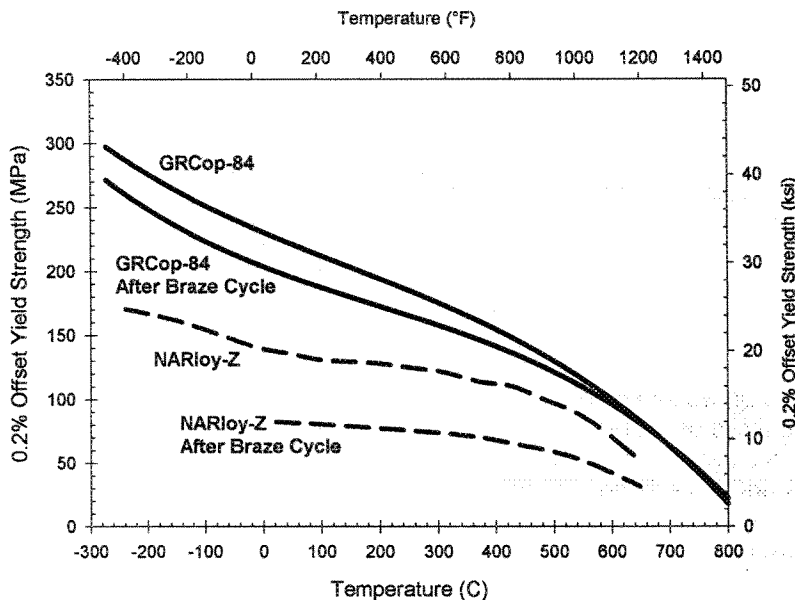

Figure 4.
Effect of simulated brazing heat treatment on the yield strength of various copper alloys.

After a long term thermal exposure GRCop-84 maintains excellent strength at all temperatures. GRCop-84 samples were given a 100 h exposure at 500°C (932°F) to analyze end of life properties for a liner after a typical life and operating temperature. Instead of decreasing, the ultimate tensile strength actually increased by 20-40 MPa (3-5 ksi) above the upper 95% confidence interval for the average strengths at temperatures up to 400°C (752°F). At 600°C (1112°F) and 800°C (1472°F), the strengths fell within the upper 95% confidence interval. Similar results were observed for the yield strength. This again indicates the exceptional microstructural and property stability of the GRCop family of alloys.

Because of the disparity of creep testing conditions in the literature, a Larson-Miller plot must be used to compare the various alloys. As shown in Figure 5, the Glidcop family of alloys performs the best in creep-rupture. This is due to the very fine dispersion of alumina throughout the alloy which gives excellent dispersion strengthening. GRCop-84 in the as-extruded condition is second only to Glidcop.
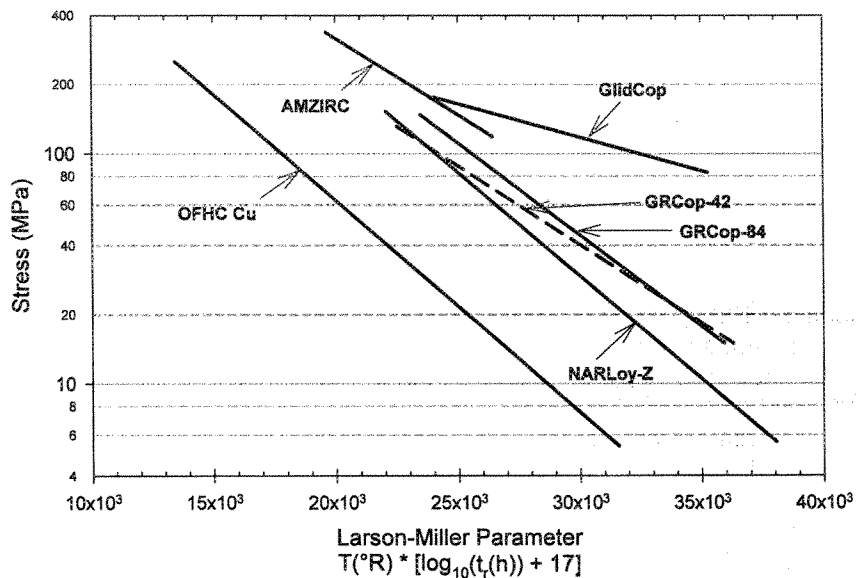

Figure 5. Creep strength of various copper alloys.

AMZIRC is comparable to GRCop-84 in short duration creep tests, but does not hold up as well at lower stresses and higher temperatures. NARloy-Z is significantly lower than all other alloys presented. With the exception of GRCop-84, none of these samples were tested following a high temperature braze cycle. It is expected that the AMZIRC and NARloy-Z would see a significant decrease in creep life following aging based on the decreases in their yield strength. In contrast, even after a simulated braze cycle, the decrease in creep life for GRCop-84 is minimal and mirrors the small, consistent decrease in the yield strength. Glidcop is expected to behave in a similar manner based upon its strengthening mechanism.
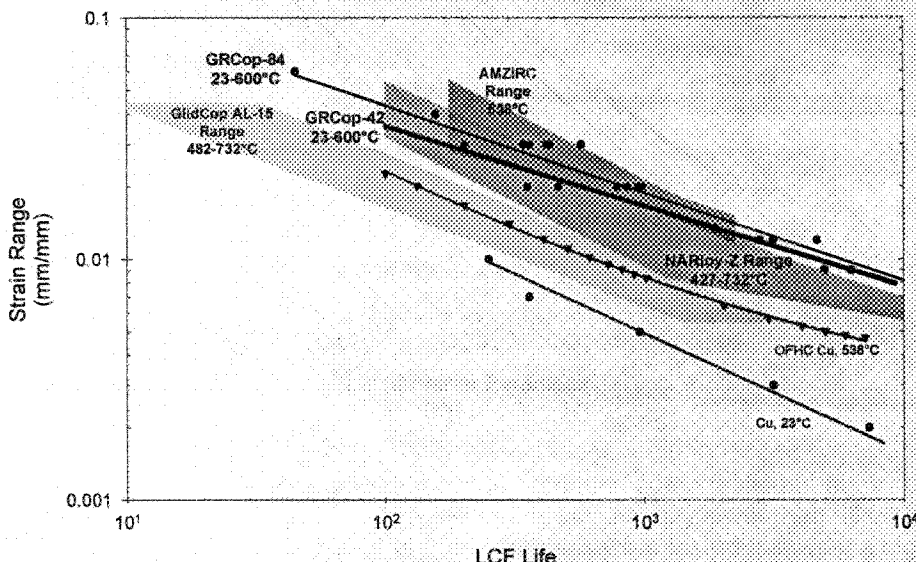

Figure 6. Low cycle fatigue strength of various copper alloys.

Since LCF life is frequently the primary design criteria for regeneratively cooled rocket engine thrust cell liners, a high LCF life provides a major advantage. Figure 6 presents a spectrum of LCF lives for the alloys of interest. As with the creep data, there is a large disparity in test conditions, mainly temperature. Experience indicates that the temperature tends to have a secondary effect rather than a primary effect on LCF lives, so data from within a fairly wide range of temperatures can be grouped together. Copper and Glidcop have the lowest LCF lives. NARloy-Z tends to be an intermediate performer while GRCop-42 and GRCop-84 along with AMZIRC are the top performers.

In summary, the GRCop family of alloys shows considerable promise. They can be easily produced using conventional manufacturing techniques. GRCop-84 is currently commercially available in quantity, and the other alloys can be easily produced using the same procedures and facilities. As shown in Table 2, these alloys offer an excellent combination of thermophysical and mechanical properties. For all the major physical properties needed for a liner material, GRCop is the best or nearly the best material examined. A major advantage of the GRCop alloys is their high stability. Decreases in properties are minimal following even high temperature braze cycles. The advantages for GRCop alloys in mechanical properties tend to be magnified following a simulated braze cycle or long term thermal exposure. Thermal conductivity of GRCop-84 is slightly lower than the other alloys, but GRCop-42 can be used as a viable substitute if this is a significant design issue. The concept of combining silver additions to GRCop-84 was only partially successful, as strength was improved only at lower temperatures.

Table 2. A summary of the balance of properties required for high heat flux components and the relative rankings of the various alloys. Performance of each alloy is ranked as either High , Medium or Low, where "High" always means preferred.

	GRCop-84	GRCop-42	GRCop-84 + Ag	NARloy Z	Glidcop	AMZirc
Processing	H	H	H	H	L	H
Welding	H	H		M	L	M
Brazing	H	H		M	M	M
Thermal conductivity	M	H	M	H	H	H
Thermal Expansion	H	H	H	M	L	L
Low temperature strength	H	H	H	M	H	H
High temperature strength	H	H	M	L	H	L
Creep	H	M	M	L	H	M
LCF	H	H	M	M	L	H
Stability	H	H	M	L	H	L
Oxidation	H	M	H	L	H	L

COATING DEVELOPMENT

Rocket engine concepts being considered include those designed to use liquid hydrogen (LH) as the fuel and liquid oxygen (LOX) as the oxidizer. Other engine designs will rely on a high purity liquid hydrocarbon such as kerosene (RP-1) as the fuel. Environmental durability of Cu-base alloys is a concern with both types of fuel. GRCop-84 possesses not only excellent high-temperature mechanical properties, but has also been shown to exhibit superior oxidation resistance vis-à-vis other Cu alloys. At temperatures up to 650°C and in oxygen partial pressures of 0.2 to 100 vol %, GRCop-84 undergoes static oxidation with parabolic rate constants that are an order of magnitude lower than that of pure Cu or NARloy-Z [3, 4]. GRCop-84 also has significantly lower weight loss in cyclic oxidation than both NARloy-Z

and AMZIRC[5]. The superior oxidation resistance of GRCop-84 derives from a compact layer of Cr-Nb oxides which functions to slow the oxidation rate through a "reservoir effect" [5] and which is also tenacious enough to suppress loss of the oxide cover by spallation during temperature cycling. Nevertheless, the superior oxidation resistance of GRCop-84 is limited to temperatures up to ~650°C (1200°F). Above that temperature the alloy oxidizes at about the same rate as pure Cu and NARloy-Z [5], most likely owing to a breakdown of the Cr-Nb oxide barrier.

The higher temperature capability of GRCop alloys can be further extended by the application of protective coatings. Important concerns when relying on a coating for protection relate to the intrinsic risk of coating spallation, exposing an unprotected substrate to the hostile engine environment, and the potential for the coating to negatively impact the fatigue life. However, reliable, long-life coatings have been successfully used in the hostile operational environments of the compressor, combustor and turbine components of aircraft and power generation engines.

Developing new coatings is key to protecting the copper-based alloy liners from environmental attack inside a rocket chamber. The coating must be able to provide an environmental barrier and, when required, a thermal barrier. Adhesion to the substrate and/or optimization of the interface properties between multiple layers of the coating (e.g. when easing the transition from the CTE of the substrate to a dissimilar CTE of the coating) may require the use of a bonding layer, typically referred to as a bond coat. It would be highly desirable to develop a coating system versatile enough to be applicable to combustor liners in a range of engines. A successful development and demonstration of a reliable, coated-GRCop-84 liner in hydrogen- and hydrocarbon-fueled engine environments will make possible a reduction in the combustor chamber component maintenance and replacement costs during the operational life of the engine. Four major areas are being explored, and include: (a) new metallic coating compositions; (b) cost-effective coating application techniques; (c) effective test method development; and (d) life prediction design methodology. Laboratory-based characterization and testing is simultaneously being integrated with the development of manufacturing and analytical modeling capabilities. It is expected that the outcome of this integrated effort will lead to the development of new, reliable coating technologies.

DESIGN CONSIDERATIONS
Although all coatings are expected to fulfill certain generic core requirements, such as the ability to protect the substrate from environmental attack and withstand the operational environment without degradation and spallation, other requirements are likely to be specific to a particular engine design. Thus, coatings for rocket engines using an expander cycle should possess a sufficiently high thermal conductivity for efficient heat transfer to occur from the hot gases to the cold wall so as to preheat the fuel. In other types of engines, a low conductivity coating may be required to reduce the temperature of the substrate by acting as a thermal barrier. Coatings may also be applied in multiple layers or functionally graded architectures. Currently several techniques for depositing coatings on GRCop-84 substrates are under investigation. Although steady progress has been made in improving the quality of coatings, as exemplified in Figure 7, issues remain on coating durability and the application of coatings to real parts.
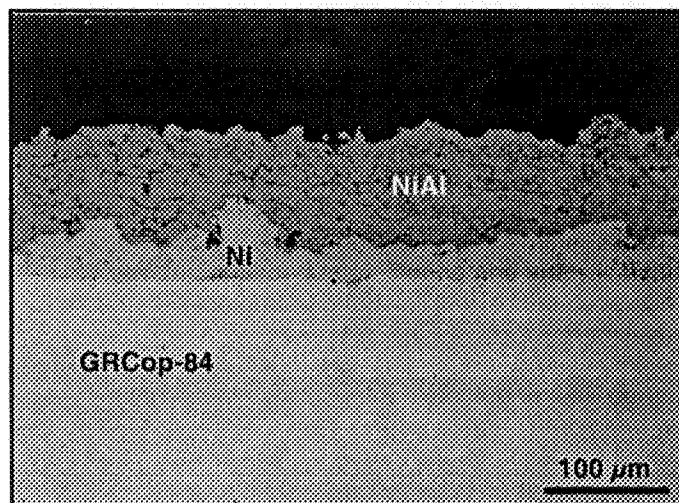

Figure 7. Example of a two-layer coating consisting of a NiAl top coat plus a Ni bond coat.

Table 3 lists several classes of ceramic and metallic coatings being considered for GRCop-84 components along with a tabulation of their generic properties which determine their suitability for RLV engine applications, and the likely process application techniques under consideration.

Table 3: Potential Coatings for GRCop-84

Coating	Thermal conductivity	Hot wall temperature	Ductility[1]	Fuel compatibility		Potential deposition technique[2]
				H$_2$	RP-1	
Yttria-stabilized zirconia	Very low	Very high	0%	Yes	Yes	HVOF; ionic fusion
NiCrAlY	Low	High	> 5 %	Yes	Yes	HVOF; VPS, KM
NiAl	Medium	Moderate	0-1%	Yes	Yes	VPS; ionic fusion
CuCrAl	Medium to high	Low to moderate	> 5%	Yes	unknown	VPS; cold spray
Cu-Cr	Medium to high	Low to moderate	> 5%	Yes	unknown	VPS; cold spray, KM

(1) The ductility values for Cu-Cr and CuCrAl are based on values typical for other copper alloys. The ductility of NiAl increases significantly to > 5% above 400°C.
2) High Velocity Oxy Fuel (HVOF) and Vacuum Plasma Spray (VPS) are well established coating deposition techniques; ionic fusion, kinetic metallization (KM) and cold spray are relatively new deposition processes.

ENVIRONMENTAL DURABILITY

Figure 8 displays the results of cyclic oxidation exposures in air of coated and uncoated GRCop-84. The bare substrate is reasonably resistant to oxidation up to about 600°C, but loses up to 15% of its weight after 20 half-hour cycles at 650°C. Coating with a 100 μm (0.04 in) layer of either Cu-21wt.% Cr, NiAl, or Ni-16Cr-6Al-0.5Y provides good protection for GRCop-84 up to 1000 cycles at the same temperature. Similar experiments have shown that the coatings can provide protection at temperatures up to 850°C with no more than 2% weight loss after 20 cycles. Clearly, coatings can play a beneficial role in improving the environmental durability and life of GRCop-84 liners.
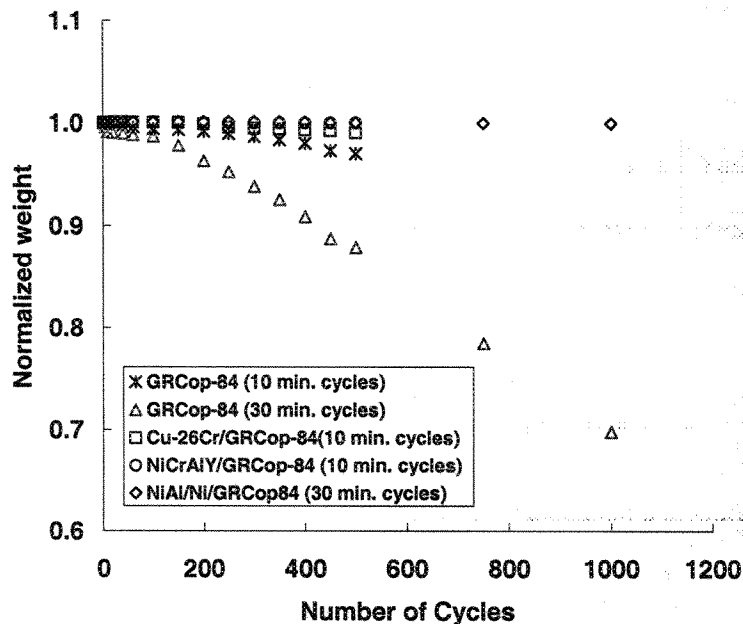

Fig. 8: Plot demonstrating that Cu-26Cr, NiAl and NiCrAlY top coats significantly extend the lives of GRCop-84 disks during cyclic oxidation tests at 600°C.

In hydrogen-fueled engines, blanching is of great concern [5]. Blanching is caused by cyclic oxidation followed by rapid reduction of thin oxide films at spots where the local environment fluctuates between oxidizing and reducing conditions [5]. Blanching results in surface roughening due to the development of interconnected porosity and cracking which leads to the formation of hot spots on the liner walls. To resist blanching a material must resist oxidation and its oxide must be highly stable in a hydrogen reducing environment. Figure 9 illustrates the differing behavior during oxidation-reduction cycling, in a simplified simulation of the blanching process. The substrate alloy NARloy-Z and the monolithic coating materials Cu-21Cr, and Ni-16Cr-6Al-0.5Y were cycled in-$situ$ 45-50 times between 0.1-minute oxidation in air and 5-minute H_2/Ar reduction at various temperatures. The NARloy-Z, which is known to undergo blanching during liner service in the Space Shuttle Main Engine, forms a Cu_2O/CuO scale [5] which is easily reduced by H_2. The weight-change profile for NARloy-Z in Figure 9 shows that the weight is gained during the oxidation part of a cycle and is lost during the reduction cycle, leaving a net zero change. In contrast, the two coating materials form slow-growing oxides which resist reduction by H_2 after the initial transient stage. Post-exposure scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS) indicated that the NARloy-Z surface was oxide-free, with scars and pits similar to features seen after blanching in service. In contrast, Cu-21Cr and NiCrAlY surfaces were covered with a near continuous layer of Cr_2O_3 and Al_2O_3, respectively. The slow but steady growth of these protective oxides resulted in a monotonic increase in weight, implying resistance to the oxidation-reduction phenomenon.
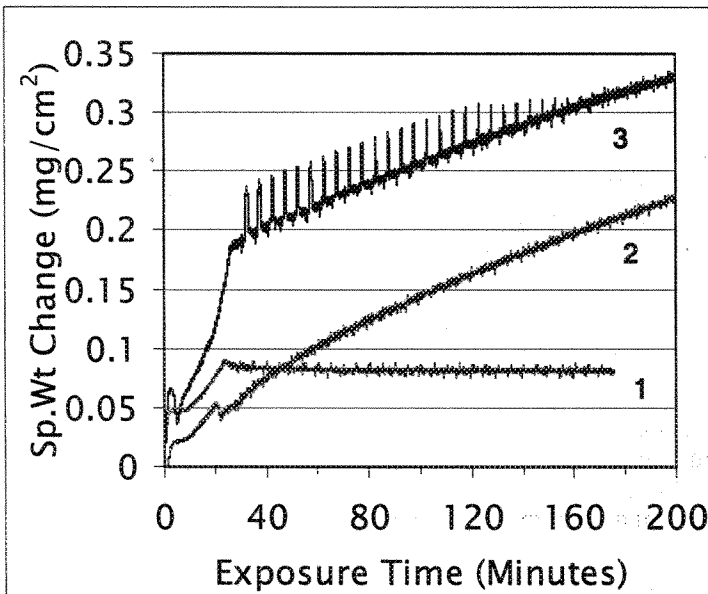

Fig. 9   The effects of oxidation-reduction cycling (air-H_2/Ar) illustrating good behavior (rising weight) and bad (flat profile): (1) uncoated NARloy-Z exposed at 800°C; (2) Cu-21Cr at 800°C; and (3) NiCrAlY at 1100°C

It is well known that sulfur found in commercial hydrocarbon fuels can contribute to metallic corrosion. The durability of GRCop-84 in an RP-1 combustion environment is not yet known. However there are concerns for sulphidation attack. Thermodynamic calculations predict the formation of Cu_2S when the sulfur content in the fuel exceeds 5 ppm [6]. Preliminary studies have shown that GRCop-84 is prone to sulfur attack at 600°C in a rig burning JP-8 fuel containing approximately 1700 ppm sulfur. The typical sulfur content of RP-1 is 30 ppm. It is conceivable that environmental attack of the GRCop-84 liners can be minimized by using a modified RP-1, which contains lower concentration levels of sulfur. Two modified RP-1 blends are available with sulfur contents of 0.1 ppm and 5 ppm. Detailed tests are planned using the lowest sulfur RP-1 fuel to determine the susceptibility of GRCop-84 to sulphidation.

THERMAL ISSUES

Thermal issues are as important as environmental issues when considering coatings in a high heat flux application. Although the thermal conductivity of the coating is an important and necessary property that must be considered in selecting a suitable coating for a specific engine design, it is important to note that coated substrates using coatings of vastly different thermal conductivities can perform almost identically with respect to their heat transfer capabilities. This conclusion stems from the

fact that the coating thickness and the properties of a bond coat also influence the heat transfer efficiency across the thickness of the coated substrate. In other words, it is the heat transfer efficiency of the entire coated system that is relevant in engineering design and not just that of the top coat.

Figure 10 compares the predicted temperatures through the thickness of a coated GRCop-84 sheet substrate and the corresponding heat fluxes for top overlay coatings with different thermal conductivities for a high heat flux engine. The temperature of an uncoated substrate is also shown. The thicknesses (t) of the substrate, a bond coat and the top coat were assumed to be 1.0 mm, 50 μm and 100 μm, respectively, in these calculations. The hot gas and coolant temperatures and their convective heat-transfer coefficients (h) assumed in these calculations are also indicated in the figures. The results of the thermal analyses shown in Figure 10 reveal that the heat transfer capabilities are fairly similar and independent of the thermal conductivity of the top coat when it exceeds 25 W m^{-1} K^{-1}.
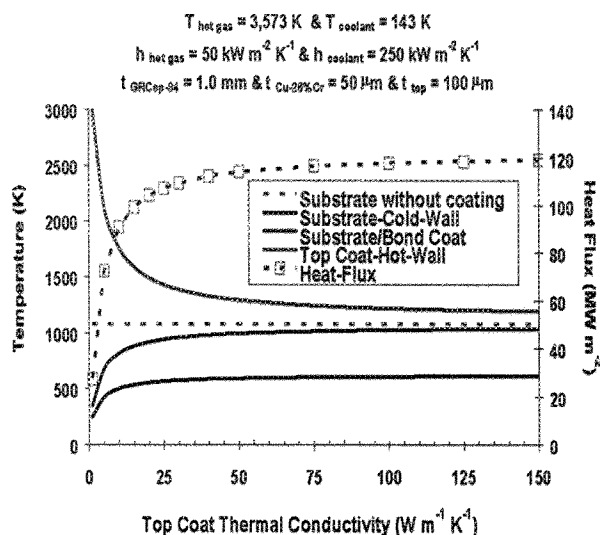

Figure 10. Predicted temperature distributions across the cross-sections of an uncoated and a coated GRCop-84 sheet substrate for a high heat flux engine as a function of top coat conductivity.

This predicted behavior is significant since it permits several types of top and bond coat systems to be considered for the same engine design. Thus, GRCop-84 substrates coated using a top coat of either Cu-26 wt% Cr (~250 W m^{-1} K^{-1} [i]), CuCrAl (~65 W m^{-1} K^{-1}), or NiAl (~75 W m^{-1} K^{-1} [ii]) are likely to possess similar thermal characteristics. This flexibility in the choice of the top and bond coat system is potentially advantageous in overcoming any manufacturing or integration difficulties.

Once the choice of one or more candidate coating systems has been made, the required thickness of the top coat can be determined from detailed thermal analyses of the coated substrate for a suitable bond coat of constant thickness. Figure 11 shows an example for the predicted temperature and
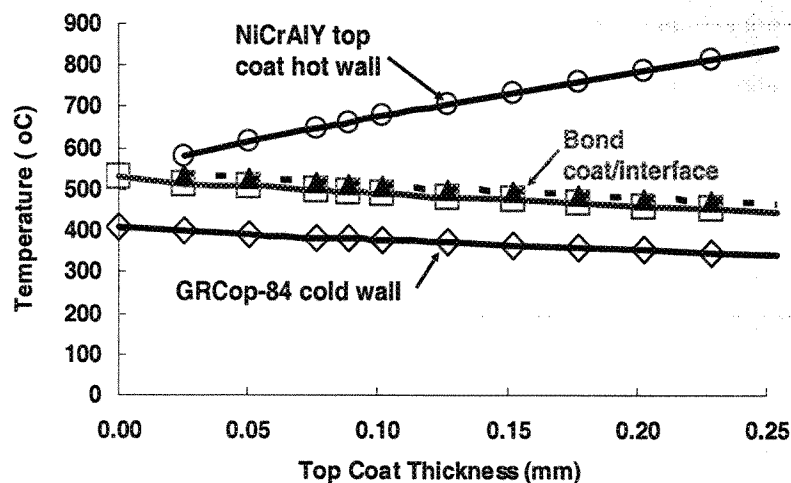

Figure 11. Predicted temperature distributions for a NiCrAlY/Cu-26Cr/GRCop-84 coated system in medium heat flux engines.

heat flux variations through the cross-section of a coated GRCop-84 substrate using a 0.050 mm thick Cu-26Cr bond coat for the NiCrAlY top coat with a thickness varying between 0.025 and 0.23 mm. This figure shows that a top coat thickness of about 0.05 – 0.10 mm would be preferred in order to keep the coating from getting too hot. As shown in Table 3, NiCrAlY is a medium conductivity coating so that there is a substantial increase in the hot wall temperature and the temperature differential between it and the cold wall with increasing top coat thickness.

Given the thermo-mechanical property differences between the coating and substrate materials, a significant build-up in residual stresses during coating deposition and post-spraying processing treatments is possible, and can result in coating spallation under certain conditions. Based on this criterion, Cu-Cr and NiAl top coats, with higher thermal conductivities than NiCrAlY, produce a much lower thermal differential through the cross-section of the coated substrate with lower hot wall stresses and lower residual processing stresses. In some applications, such as for injector plates, the function of the top coat is to provide environmental and thermal barrier protection. NiCrAlY and yittria-stabilized zirconia (YSZ) top coats may represent a desirable choice. However, NiAl top coats provide a reasonable optimum choice for a wide range of possible applications, where the degree of thermal barrier effect could be conceivably controlled by relatively small composition and thickness modifications.

NIAL BIMETALLIC CONCEPTS

The use of NiAl as a coating for copper was also extended to a concept utilizing the structural properties of this material. NiAl is one of the best materials in terms of high temperature strength and thermal conductivity. It also has a low density and good resistance to environmental attack. However, it is brittle at low temperatures and is therefore difficult to fabricate and prone to fracture under moderate tensile loads at low temperatures. To overcome these issues, a bimetallic rocket nozzle design which employs a thick inner layer of NiAl encased by an outer layer of nickel-base superalloy, such as Haynes 230, is proposed for nozzle applications requiring high temperature strength with moderate thermal conductivity. The outer layer of superalloy provides structural reinforcement and helps prevent fracture of the NiAl at low temperatures while the inner layer of NiAl provides enhanced thermal conductivity and resistance to environmental attack near the hot gas path. The NiAl layer also provides high temperature strength above 1000ºC and reduces the weight of the nozzle as NiAl is significantly less dense than conventional superalloys.

A second bimetallic rocket nozzle design which also employs an inner layer of NiAl is proposed for nozzle applications requiring higher thermal conductivity but lower strength than the NiAl/superalloy design described in the previous paragraph. In this design a copper or copper alloy outer layer provides structural reinforcement and helps prevent fracture of the NiAl at low temperatures. The copper layer also provides excellent thermal conductivity at the lower temperatures encountered on the outer wall of cooled rocket nozzles. The inner layer of NiAl provides good thermal conductivity, high temperature strength, and resistance to environmental attack near the hot gas path. Further, overall weight of the nozzle is reduced as NiAl is less than two-thirds the density of copper. Thermal analyses have shown that the total cooling required for a NiAl bimetallic design is lower than that required for a monolithic copper design, thus justifying the experiments described below.

In both bimetallic designs the inner layer of the nozzle is formed by plasma spraying a pre-alloyed NiAl powder onto a steel mandrel. Once cooled, the outer diameter of the NiAl can be machined using EDM or low stress grinding to obtain the desired wall thickness. As the NiAl is still backed by the steel mandrel, machining of the NiAl is simplified compared to a free standing NiAl thin walled tube. The outer layer of superalloy or copper is then applied over the NiAl layer by plasma spraying powder of the desired composition. After completion, final machining of the outer layer by conventional means can be employed to establish the desired features and dimensions on the exterior face of the nozzle. Finally, chemical leaching of the steel mandrel reveals the finished hot wall. HIPing of the nozzle can be employed after each spraying operation to provide complete densification of the layers.

An example of small bimetallic tubes is shown in Figure 12 and 13. Each tube is 32 mm in diameter and 125 mm long with a 3 mm wall thickness, As seen in Figure 12, the tubes have a throat segment where the diameter drops to 22 mm. A microsection of the wall from a NiAl/Haynes 230 tube is shown in Figure 13. In general the tubes were well bonded with minimal porosity.

To assess the integrity of the bimetallic concept for nozzle applications, the tubes were subjected to repeated flame testing in GRC's QARE facility. The facility is designed to produce a hydrogen-oxygen flame of prescribed stochiometry at atmospheric pressure. The QARE facility with a bimetallic tube in test is shown in Figure 14. The heating and cooling rates, at the throat, were measured with an embedded thermocouple and achieved ~650°C in about 10 sec.
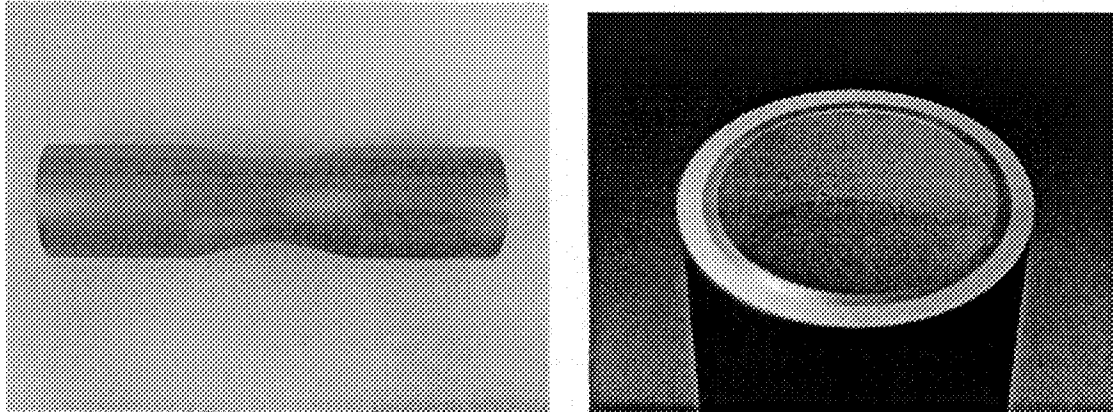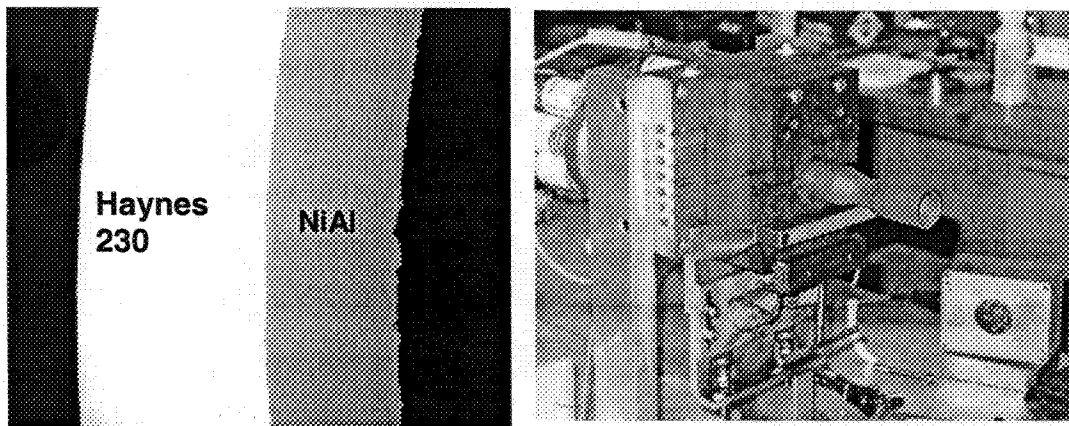

Figure 12. NiAl bimetallic tube.

Figure 13. Microsection of bimetallic tube wall.   Figure 14. QARE facility with NiAl bimetallic tube
Total thickness is 3mm.

Results from the hot fire tests indicated that the bimetallic tubes held up to repeated testing with no evidence of cracking or spallation of the NiAl layer. Additional testing of these tubes is planned at the highest possible flow rates in the QARE facility to achieve a faster heating rate. After these tests the tubes will be examined and sectioned to check for damage on a macroscopic and microscopic level. If the tubes pass these tests, the next step would be a higher fidelity test in a high pressure combustion facility [9].

SUMMARY

This paper summarizes materials development strategies for extending the performance of next generation reusable launch vehicles. In extremely high heat flux applications, materials based primarily on copper are preferred for their high conductivity and ductility. Means for extending the capability of the

state of the art are described: new alloys, new coatings, and bimetallic design concepts. Recent experimental results show that all three areas have considerable potential for improving engine performance at tolerable risk levels.

REFERENCES

1. D.L. Ellis and G. Michal, Aerospace Structural Materials Handbook Supplement, submiitted for publication, (10/2000)
2. J.J. Stephens, R.J. Bourcier, F.J. Vigil, D.T. Schmale, Sandia National Laboratories Report SAND88-1351, (Sept. 1988)
3. L.U. Ogbuji, "The General Isothermal Oxidation behavior of Cu-8Cr-4Nb" (to appear in *Materials at High Temperatures*).
4. L.U. Ogbuji, D.L. Humphrey, and J.A. Setlock, "Comparison of the Oxidation Rates of Some New Copper Alloys" *Oxidation of Metals*, vol. 60, Nos. 3 / 4, pp. 271-291 (2003).
5. L.U. Ogbuji, D.L. Humphrey, and J.A. Setlock, "Oxidation-Reduction Resistance of Advanced Copper Alloys," paper H071, in Proc. of "Corrosion Science in the 21st Century", a conference held at Manchester, UK, July 6-11 2003.
6. N. S. Jacobson, unpublished research, NASA Glenn Research Center, Cleveland, OH (2003).
7. L.J. Ghosn and S. V. Raj, Ceram. Eng. Sci. Proc. 23, 409-416 (2002).
8. S. V. Raj, L. J. Ghosn, A. Agarwal and T. P. Lachtrup, "An Assessment of the Residual Stresses in Low Pressure Plasma Sprayed Coatings on Advanced Copper Alloys", Surface Engineering: In Materials Science II (edited by S. Seal, N. B. Dahotre, J. J. Moore, C. Suryanarayana and A. Agarwal) The Minerals, Metals & Materials Society, Warrendale, PA, pp.49-56 (2003).
9. M.J. Bur, "A Combustion Research Facility for Testing Advanced Materials for Space Applications," AIAA Paper 2003-0282, Jan 2003