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GRCop-84: A High-Temperature Copper Alloy for High-Heat-Flux Applications

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February 2005

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Executive Summary

While designed specifically for rocket engine main combustion chamber (MCC) liners, GRCop-84 (Cu-8 at.% Cr-4 at.% Nb) offers potential for high-heat-flux applications up to approximately 700 °C (1292 °F). GRCop-84 is a copper-based alloy with excellent elevated temperature strength, good creep resistance, long low-cycle fatigue (LCF) lives and enhanced oxidation resistance. It also has a lower thermal expansion than copper and many other low-alloy copper-based alloys. GRCop-84 can be manufactured into a variety of shapes such as tubing, bar, plate, and sheet using standard production techniques and requires no special production techniques. GRCop-84 forms well, so conventional fabrication methods including stamping and bending can be used. GRCop-84 has demonstrated an ability to be friction stir welded, brazed, inertia welded, diffusion bonded, and electron beam welded for joining methods. Potential applications include plastic injection molds, resistance welding electrodes and holders, permanent metal casting molds, vacuum plasma spray nozzles, and any high-temperature heat exchanger applications.

Introduction

Cu-Cr-Nb alloys were initially examined under the Earth-to-Orbit Program during the 1980s. Efforts during the 1990s and 2000s under various hypersonic and reusable launch vehicle programs have brought the alloy to commercial-scale production. The desire was to develop an elevated-temperature high-strength copper-based alloy that retained most of the thermal conductivity of copper but which had creep and low-cycle fatigue (LCF) lives that exceeded NARloy-Z (Cu-3 wt.% Ag-0.5 wt.% Zr), the space shuttle main engine (SSME) main combustion chamber (MCC) liner. Initial results with lab scale runs (1 to 25 g) using chill block melt spinning (CBMS) showed that adding 2 to 10 at.% chromium and 1 to 5 percent niobium at a 2:1 atomic ratio produced the high melting point intermetallic compound Cr_2Nb within a nearly pure copper matrix (ref. 1). Mechanical testing of the CBMS ribbons showed a considerable increase in strength at room and elevated temperatures for the Cu-Cr-Nb alloys (ref. 2). Based upon the balance of properties, the Cu-8 at.% Cr-4 at.% Nb alloy was selected for scaleup to commercial production.

The alloy was designated Glenn Research Copper 84 or GRCop-84. GRCop-84 has higher strength, creep resistance, and LCF life than NARloy-Z while possessing a lower thermal expansion and thermal conductivity. GRCop-84 also exceeds the properties of most other competing alloys such as AMZIRC, GlidCop AL-15 low-oxygen grade, Cu-Cr, and Cu-Cr-Zr. The benefits are generally increased when comparing the alloys following a high-temperature thermal exposure such as a braze cycle or diffusion bonding.

Production

Cu-Cr-Nb alloys can only be produced using rapid solidification technology. Conventional casting results in Cr_2Nb precipitates that grow to well over 1 cm (0.39 in.) in diameter during slow cooling. So far the alloys have been successfully produced using CBMS and conventional gas atomization.

Conventional argon gas atomization was chosen because it offered a large industrial base, relatively low cost, volume production capability, and a high cooling rate. Elemental copper, chromium, and niobium are melted to produce a uniform molten alloy. The molten metal is atomized to produce a fine powder. For extrusion and hot isostatic pressing (HIPing), -140 mesh (<106 μm) powder is used. Typically, this powder has a mean powder size around 40 μm . For vacuum plasma spraying (VPSing), a finer powder is desired. The -270 and -325 mesh (<53 and <44 μm) have been used with great success.

Three conventional consolidation techniques have been successfully used to produce GRCop-84. At NASA Glenn Research Center, direct extrusion of the powder to a round or rectangular shape and HIPing to simple shapes have been examined. Both consolidation methods produce fully dense material that has excellent properties. At NASA Marshall, VPS has been used to produce liners with an integral NiCrAlY inner layer and functional gradient material. The sprayed powder was fully densified after spraying and HIPing.

Once the powder is consolidated, the alloy can be processed like any other high-strength copper alloy. For liners, GRCop-84 has been successfully warm and cold rolled, bump formed, stamped, and metal spun. Tube drawing has been successfully demonstrated with tubes as small as 0.3-cm OD by 0.08-cm wall (0.125-in. OD by 0.030-in. wall) being drawn for testing compatibility of GRCop-84 with RP-1 rocket fuel.

To support manufacturing of complex parts by stamping, bending, and other techniques, forming limit diagrams for GRCop-84 at room temperature and 200 °C (392 °F) have been created (ref. 3). The usefulness of the forming limit diagrams was demonstrated by successfully stamping a complex part from flat sheet without significant thinning or any failures.

VPS has been successfully proven for both small and large liner fabrication (refs. 4, 5, and 6). VPS has the advantage of being able to use a functionally graded material (FGM) on the hot wall surface. This allows a gradual transition from pure NiCrAlY or other coating through a mixture of the coating and GRCop-84 to pure GRCop-84. The gradual transition eliminates the traditional sharp interface of overlay coatings and a potential failure point.

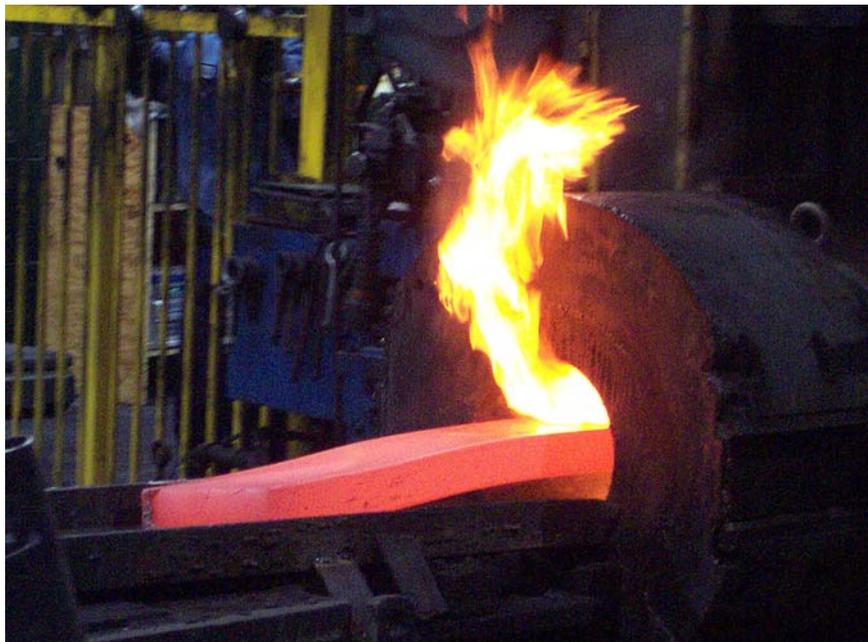


Figure 1.—GRCop-84 can be direct-extruded from powder to make fully dense material. Typically a copper or steel can is used to contain the powder. After extrusion, the can is removed by machining or chemical means. Hot isostatic pressing (HIPing) also produces fully consolidated material with good properties.

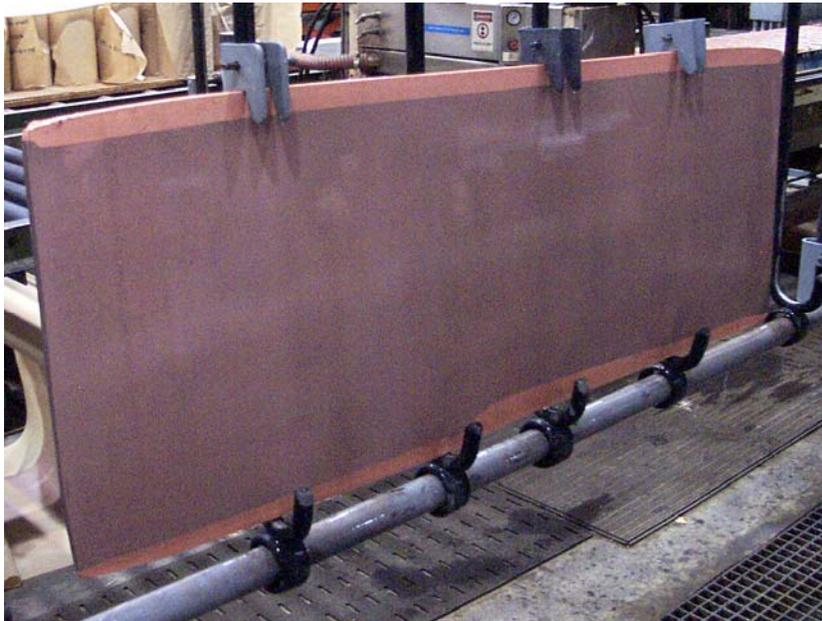


Figure 2.—GRCop-84 can be warm rolled easily to make plate. Rolling results in a small degradation in properties, primarily creep resistance. After rolling the oxide layer is easily removed by an acid dip to give a matte surface finish. The remnants of the copper can be used for this extrusion can be seen at the top and bottom of the plate. GRCop-84 is easily distinguished from the copper by its darker color.

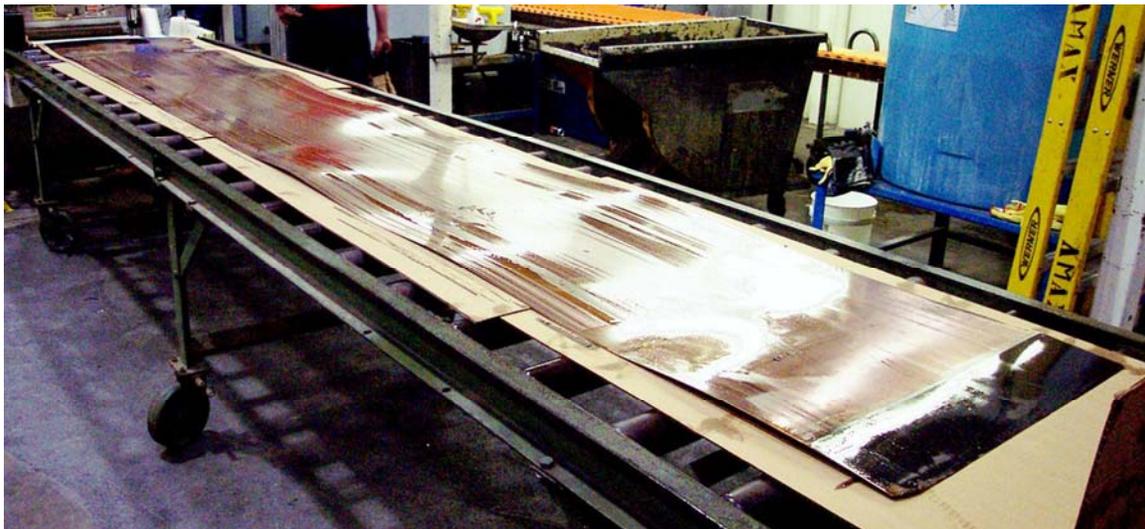


Figure 3.—GRCop-84 can be cold rolled with minimal difficulty. Large reductions without annealing are possible. GRCop-84 foil has been produced on an experimental scale.



Figure 4.—GRCop-84 can be formed into shapes using conventional methods used for copper-based alloys. The cylinder shown on the left was bump formed from two pieces of a plate and friction stir welded together. Another cylinder was hot metal spun into the hourglass-shaped liner preform shown on the right.



Figure 5.—In addition to extrusion and HIPing, GRCop-84 can be vacuum plasma sprayed (VPSed) into complex shapes. NASA Marshall Space Flight Center has successfully used VPS to produce many liner configurations including a full-scale space shuttle main engine (SSME) main combustion chamber (MCC) liner. A major advantage of VPS is the ability to introduce environmental and thermal barrier coatings on the hot wall as a functional gradient material (FGM).

Microstructure

GRCop-84 has a high volume fraction of Cr_2Nb , approximately 14 vol%. The intermetallic compound dispersion strengthens the copper matrix and also acts to refine and control the copper grain size. Approximately two-thirds of the strengthening comes from a Hall-Petch mechanism while one-third is from Orowan strengthening (ref. 7). The Cr_2Nb is extremely stable up to at least $800\text{ }^\circ\text{C}$ ($1472\text{ }^\circ\text{F}$). Because the Cr_2Nb particles do not coarsen significantly, the grain size remains nearly constant and even long-term exposures to temperatures under $800\text{ }^\circ\text{C}$ do not degrade the strength of GRCop-84 much. Most other copper alloys suffer loss of strength and grain growth when exposed to these temperatures. In the cases of precipitation-strengthened alloys such as NARloy-Z and Cu-Cr, either the precipitates grow too large to be effective at strengthening the alloy or they dissolve completely.

Working the alloy through rolling and similar methods produces a slight crystallographic texture. This texture is the same as that seen for pure copper, but is much less than copper rolled to a similar reduction. The macroscopic properties do not exhibit any discernable anisotropy, so the slight crystallographic texture does not appear to be significant for most applications.

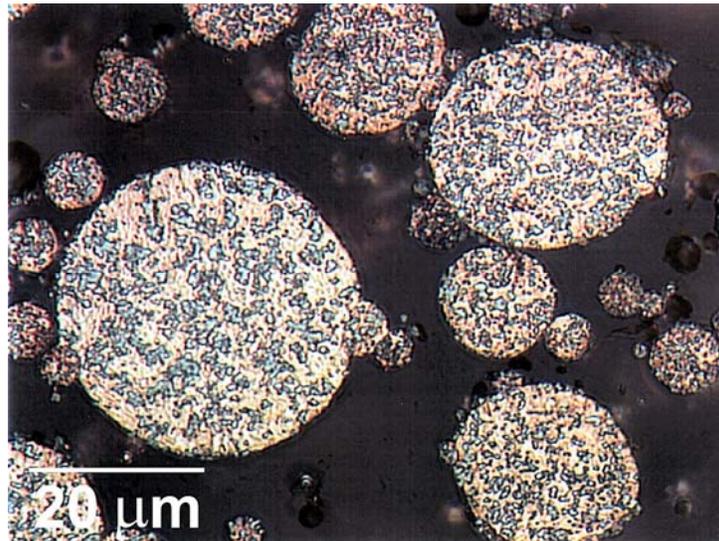


Figure 6.—GRCop-84 powder shows the pure copper matrix and the Cr_2Nb particles (bluish silver phase) that precipitate from the molten solution during atomization. The stability of Cr_2Nb is such that it will immediately precipitate from the molten metal when the melt temperature starts to drop. Even much higher cooling rates than found in conventional gas atomization cannot suppress this precipitation. If rapid solidification is not used, then the Cr_2Nb particles will grow to millimeter or even centimeter size. The volume fraction of Cr_2Nb particles is about 14 percent.

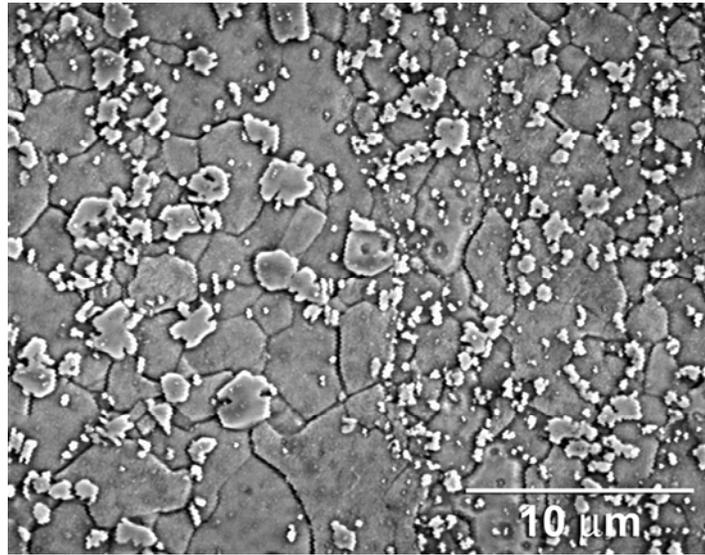


Figure 7.—As-extruded GRCop-84 is a very fine grained (typically, 2 to 7 μm or ASTM grain size 11 to 15) with little texture even after high reductions during extrusion. It also consolidates well with small area reductions during extrusion. The agglomerations of Cr_2Nb particles can be seen standing proud of the etched surface. Rolling and other subsequent working of the material can break up and redistribute the Cr_2Nb particles to produce a more uniform distribution.

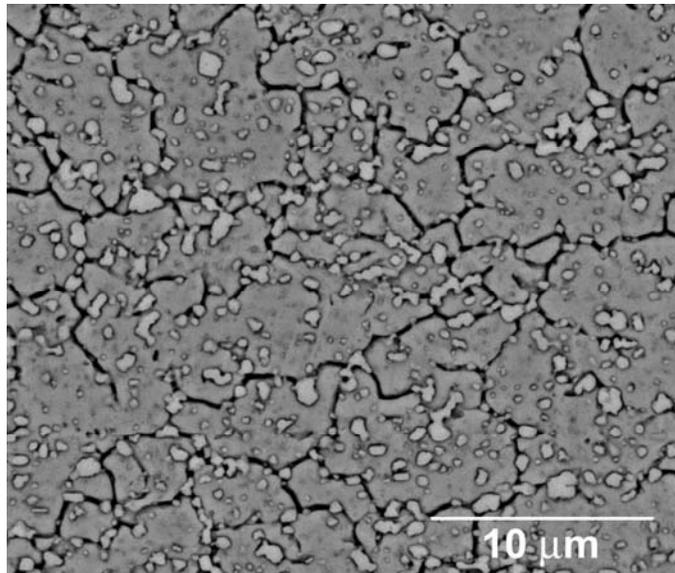


Figure 8.—GRCop-84 shows extremely good stability both for the grain size and the Cr_2Nb particle size. After a 1000 °C (1832 °F) exposure for 30 minutes followed by an air cool, the grains remain pinned by the Cr_2Nb particles and do not show much growth even after exposure to a temperature equal to 94 percent of the melting point. The high melting point intermetallic Cr_2Nb particles also do not show much coarsening.

Thermal Expansion

Thermal expansion is a critical thermophysical property for rocket engine liners. Most stresses and strains are thermally induced rather than mechanically generated. During operation of a typical hydrogen-fueled engine, the hot wall temperature rises to somewhere between 400 and 600 °C (752 and 1112 °F) while the cold wall and lands between the cooling channels remain near room temperature. This produces a large thermal gradient through the wall and considerable strains, typically over 1 percent. This expansion creates plastic deformations and stresses while promoting LCF and creep as the engine is fired repeatedly. Normally either creep or LCF is the life-limiting factor in a liner design.

GRCop-84 has a lower thermal expansion than any of the competitive alloys that have been examined. The decrease is almost 7 percent relative to pure copper in the hot wall temperature range. The lower thermal expansion directly translates into lower creep stresses and smaller LCF strain ranges. For a liner application, a 2- to 100-time increase in life can be expected from the direct substitution of GRCop-84 for other copper alloys depending on the failure mechanism.

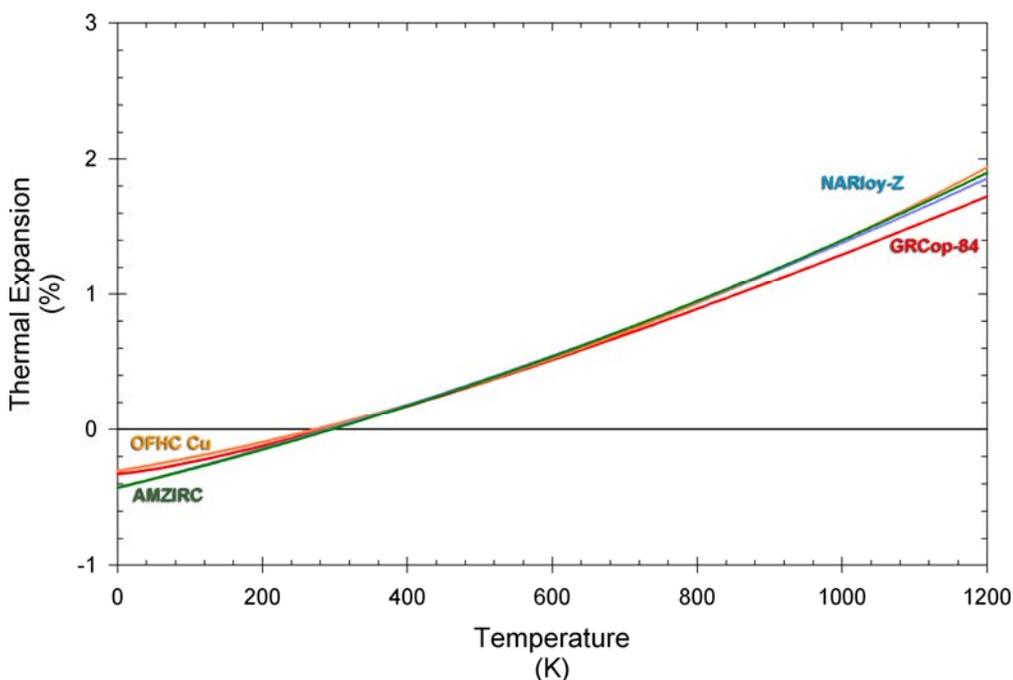


Figure 9.—Most high-temperature, high-heat-flux alloys have a thermal expansion near that of pure copper. However, GRCop-84 has a much lower thermal expansion because of the presence of a large volume fraction of low thermal expansion Cr₂Nb precipitates, which restrict thermal expansion. The lower thermal expansion reduces thermally induced stresses in liners by about 7 percent and can reduce thermal expansion mismatch with other materials such as stainless steels used for jackets and manifolds.

Thermal Conductivity

Thermal conductivity is a key design factor for liner applications. This drove the decision to use precipitation and/or dispersion strengthening for the next generation of liner alloys. While materials such as stainless steel may have much greater strengths and temperature capabilities than copper-based alloys, their low thermal conductivity would result in much higher temperatures and probably melting when exposed to the multimewatt per square meter heat fluxes typical of rocket engines.

GRCop-84 has a thermal conductivity of between 305 and 320 W/m·K (176 to 185 BTU/h·ft·°F) or 75 to 84 percent of the value of pure copper over the operating temperature range of an MCC liner. This is comparable to NARloy-Z near room temperature but lower at higher temperatures such as those experienced at the hot wall. The lower thermal conductivity of GRCop-84 does result in an increase in temperature, but analysis for rocket engine applications indicate the increase is typically 35 °C (65 °F) or less. Given the nearly 200 °C (360 °F) increase in temperature capability of GRCop-84 over NARloy-Z, this small increase can be handled easily by GRCop-84.

Iron from the chromium used to make the powder was determined to be detrimental to the thermal conductivity. As a result, the specifications have been changed to <50 ppm Fe required and <20 ppm Fe desired. This resulted in a significant increase in thermal conductivity at lower temperatures.

As part of the modified Kohlrausch thermal conductivity measurements, the electrical resistivity of GRCop-84 was measured from -186 °C (-303 °F) to 200 °C (392 °F). At room temperature, the electrical conductivity of as-extruded GRCop-84 is approximately 67 percent IACS.

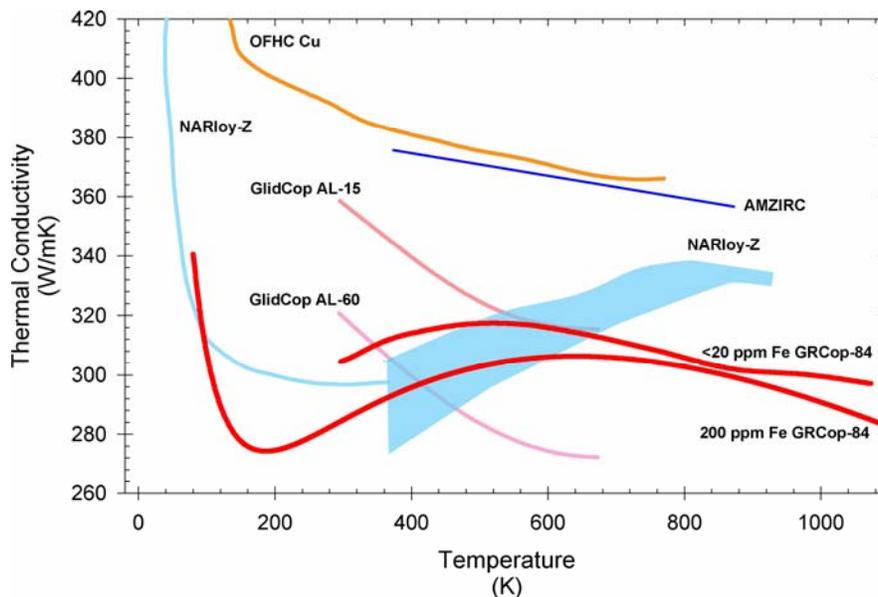


Figure 10.—The high loading of Cr₂Nb reduces the thermal conductivity of GRCop-84 compared to pure copper. Compared to other high-temperature copper-based alloys, GRCop-84 compares favorably to most especially when the entire range of properties are considered. It was discovered that the presence of 200 ppm iron in the initial GRCop-84 powders also reduced the thermal conductivity significantly, especially at lower temperatures. The source of the iron was eliminated, and the thermal conductivity increased 7 percent at room temperature.

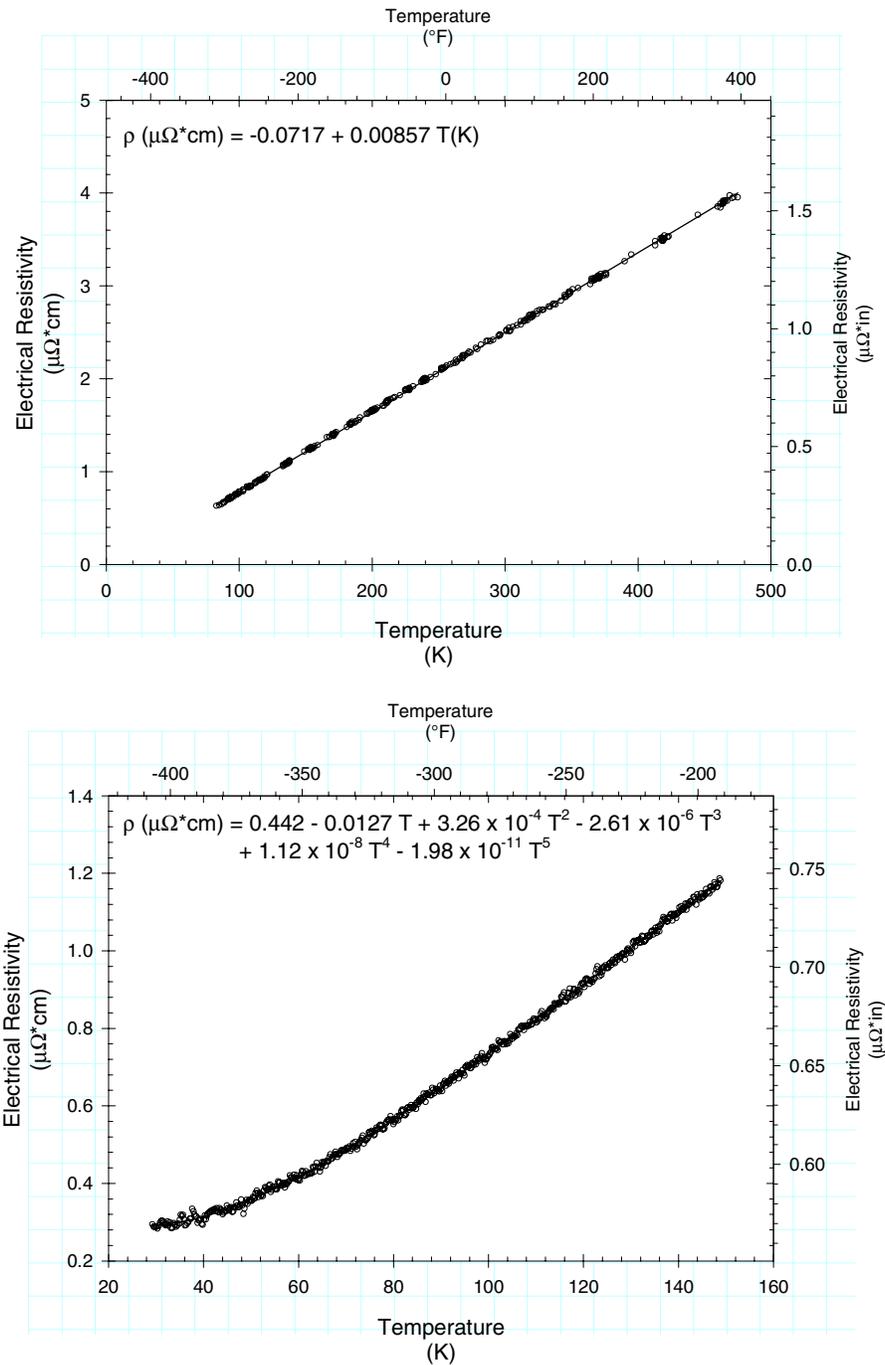


Figure 11.—Limited testing has been conducted on the electrical resistivity of GRCop-84. The resistivity is higher than pure copper, but it is comparable to many high-strength copper alloys near room temperature. At cryogenic temperatures, the electrical resistivity is approximately twice that of pure copper.

Tensile Strength

GRCop-84 was optimized for high-temperature strength. As a result, its low-temperature strength is inferior to Cu-Be and most other precipitation-strengthened copper-based alloys. However, unlike those alloys, GRCop-84 retains good strength to above 700 °C (1292 °F) while other precipitation-strengthened copper-based alloys generally lose most of their strength between 300 and 450 °C (572 and 842 °F) (refs. 8 and 9).

Once the other alloys are exposed to the high temperatures, their strength remains low until they are given another precipitation heat treatment, and even this may not be sufficient to restore their mechanical properties. In some cases such as AMZIRC where cold work is also used to strengthen the alloys, full strength cannot be restored regardless of the thermal treatment used if annealing occurs. In contrast, GRCop-84 shows little decrease in strength even after exposure to very high temperatures in the range of 935 to 1000 °C (1715 to 1832 °F). The strength decrease is not only small, typically 20 to 35 MPa (3 to 5 ksi), it is almost uniform over the usable temperature range.

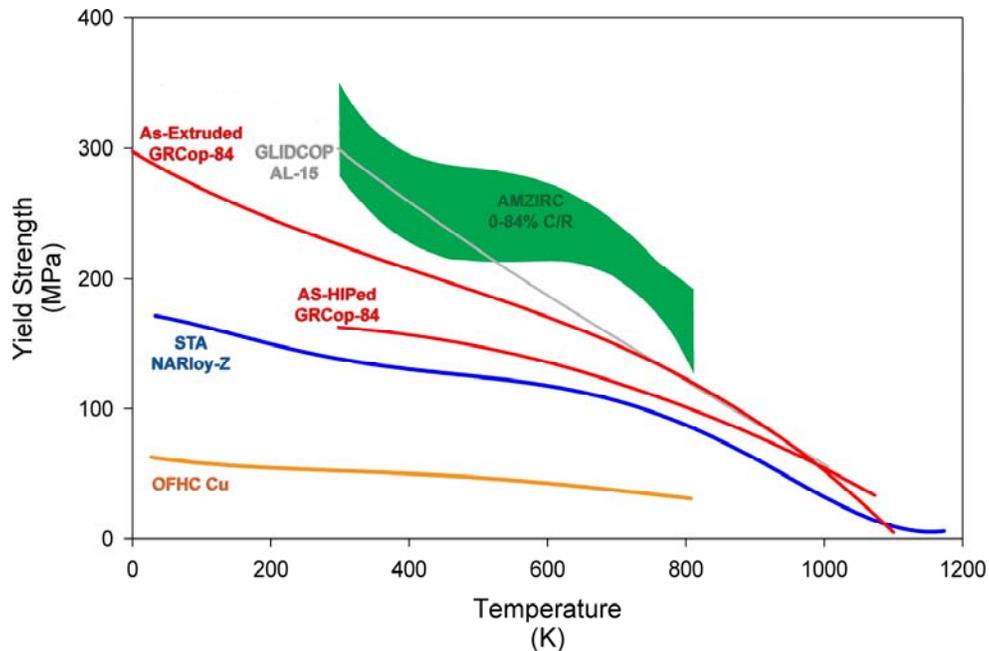


Figure 12.—Compared to other copper-based alloys, GRCop-84 in either the as-extruded or HIPed condition is among the highest strength alloys in the 673 to 973 K (752 to 1292 °F) temperature range, the typical hot wall temperature range for rocket engine liners. Cold or warm working GRCop-84 can increase the yield strength to over 400 MPa (58 ksi) at room temperature. GRCop-84 has a yield strength 50 to 100 MPa (7 to 17 ksi) higher than NARloy-Z, the current SSME MCC liner material and the baseline alloy for comparison.

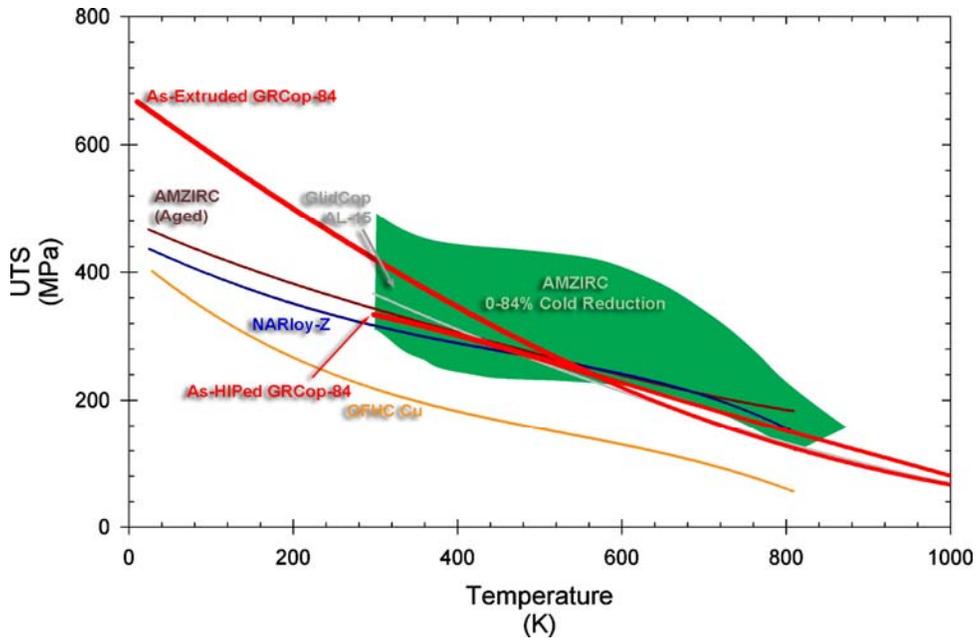


Figure 13.—The ultimate tensile strength of GRCop-84 in the as-extruded and as-HIPed conditions is comparable to other high-temperature, high-conductivity copper alloys.

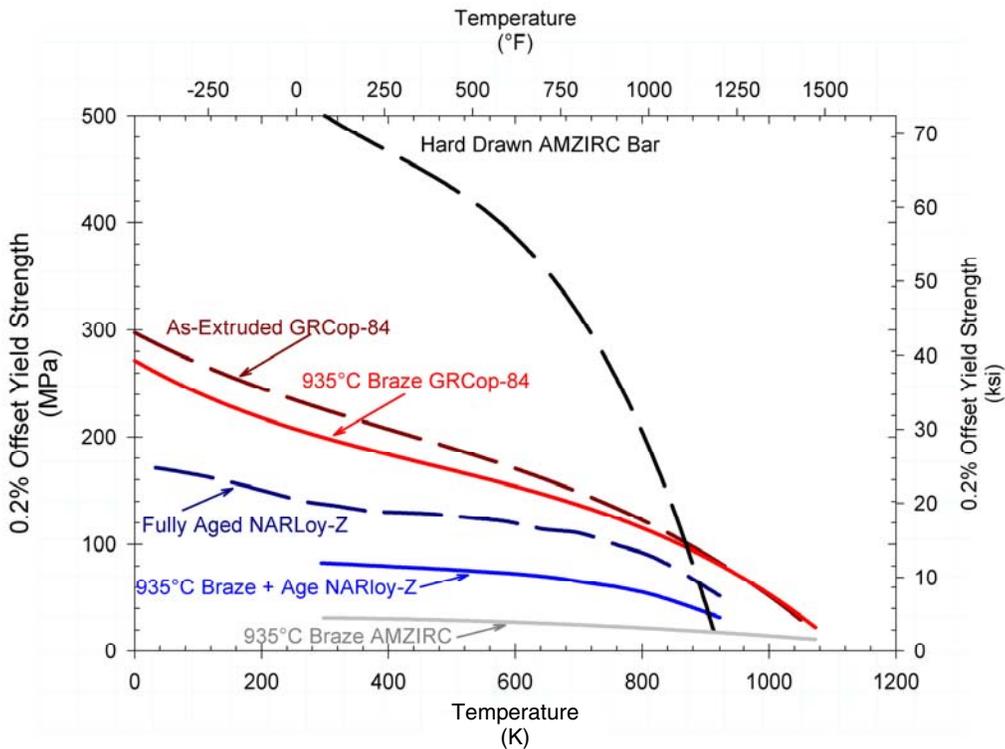


Figure 14.—A major advantage of GRCop-84 is its stability after exposure to long high-temperature thermal cycles such as a simulated braze cycle at 935 °C (1715 °F). After a simulated 935 °C braze cycle, GRCop-84 loses a small and fairly uniform amount of strength corresponding to 30 MPa (4 ksi) or less. AMZIRC (Cu-0.15 Zr) recrystallizes completely after the Cu_5Zr precipitates dissolve and loses all of its advantage in strength. In fact, it becomes comparable to pure copper. NARloy-Z can regain some strength after the braze cycle by being given an aging heat treatment, but the yield strength of NARloy-Z is still only half that of GRCop-84 across the entire temperature range.

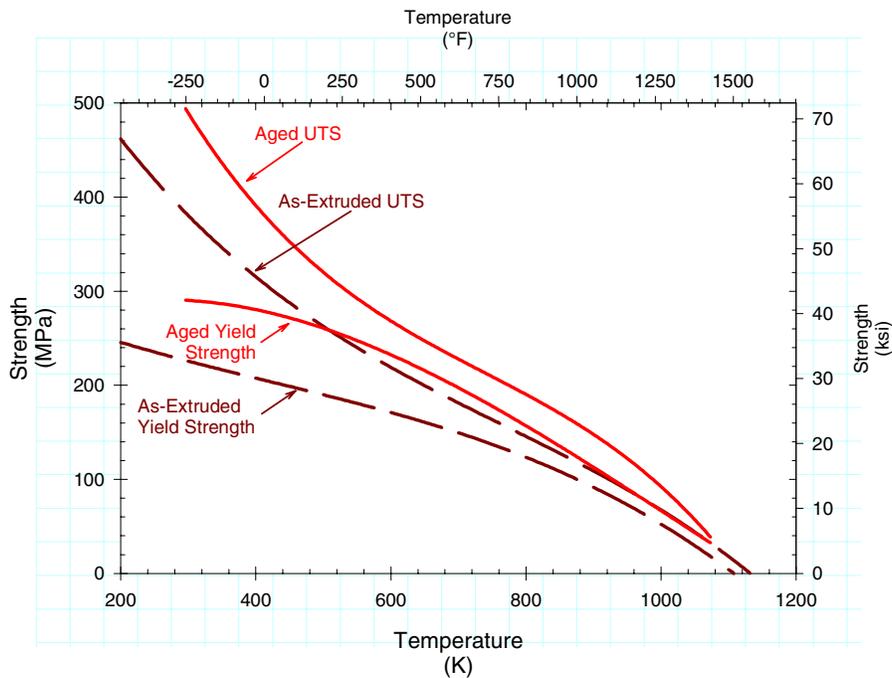


Figure 15.—To determine the end-of-life retention in strength for GRCop-84 samples were exposed at 500 °C (932 °F) for 100 hr to simulate 400 SSME missions. Instead of losing strength, the samples showed a statistically significant increase in both yield and ultimate strength. This again illustrates the stability of GRCop-84 at elevated temperatures.

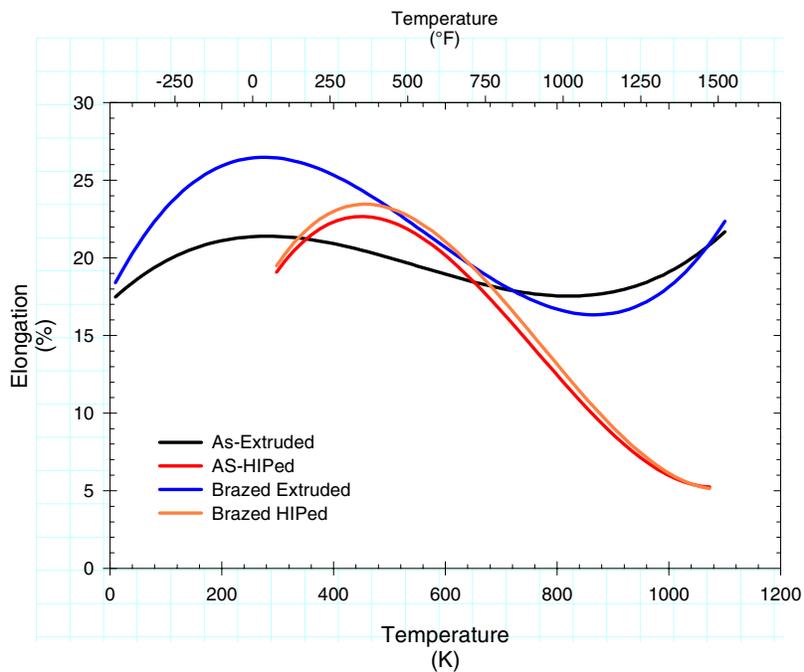


Figure 16.—While the elongation of GRCop-84 is less than many other low-alloy copper-based alloys, it retains good and nearly constant elongation over the entire temperature range tested. Furthermore, thermal exposures do not degrade the elongation. The loss in ductility for the HIPed GRCop-84 above 400 °C (752 °F) was traced back to poor consolidation for some samples. Even with this problem the elongation remained over 5 percent.

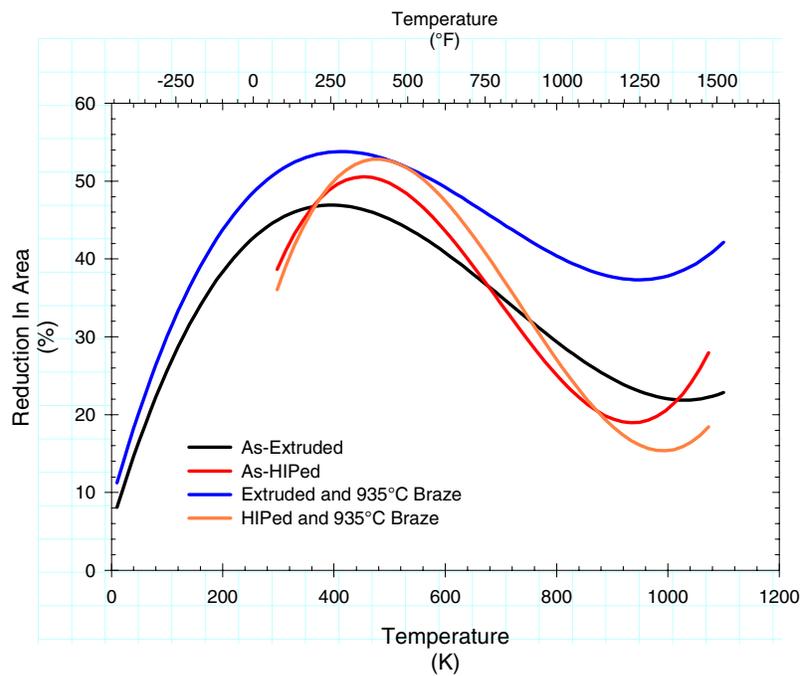


Figure 17.—As with the elongation, the reduction in area for GRCop-84 is less than many other low-alloy copper-based alloys, but it does remain good even at cryogenic temperatures.

Creep Rates and Lives

Creep of GRCop-84 has been tested extensively between 500 and 800 °C (932 and 1472 °F) primarily in the as-extruded and as-HIPed conditions but more recently using production plate and sheet samples. The creep lives are one to three orders of magnitude longer than NARloy-Z tested at the same temperatures. Alternatively, for the same creep life, GRCop-84 can support approximately 15 percent more load than NARloy-Z. Similar benefits are seen over other copper-based alloys in this temperature range.

GRCop-84 exhibits a lower creep rate and extended steady-state or secondary creep. Typically in creep, GRCop-84 will spend most of its creep life in secondary creep with a gradual transition to tertiary creep with a slowly increasing creep rate up until the point of failure. Creep elongations at failure are typically 8 to 14 percent.

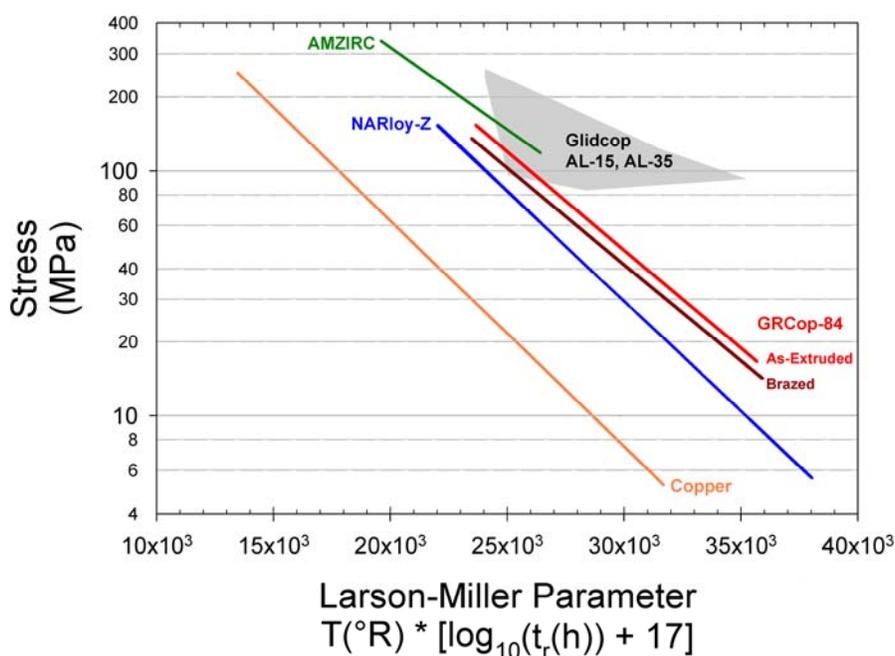


Figure 18.—While the Larson-Miller plot suffers several problems, it does allow the comparison of data sets encompassing a wide range of temperatures and stresses to establish a relative ranking for different alloys. GRCop-84 before and after undergoing a 935 °C (1715 °F) simulated braze cycle is superior to NARloy-Z. GlidCop alumina dispersion strengthened alloys AL-15 and AL-35 are equal to or superior to GRCop-84. Only limited data for AMZIRC could be found, and it was all from low temperatures. It is anticipated that the curve will drop to below that of NARloy-Z when data at high temperatures is generated and added to the plot.

Low-Cycle Fatigue (LCF) Lives

GRCop-84 exhibits long LCF lives at room and elevated temperatures. The lives are minimally influenced by temperatures up to 600 °C (1112 °F), the highest temperature tested to date. The Cr₂Nb precipitates appear to retard or minimize the development of persistence slip bands and extend the life far above pure copper and most competitive alloys. Processing and environment are known to affect the LCF lives in other material, and testing involving both parameters is underway.

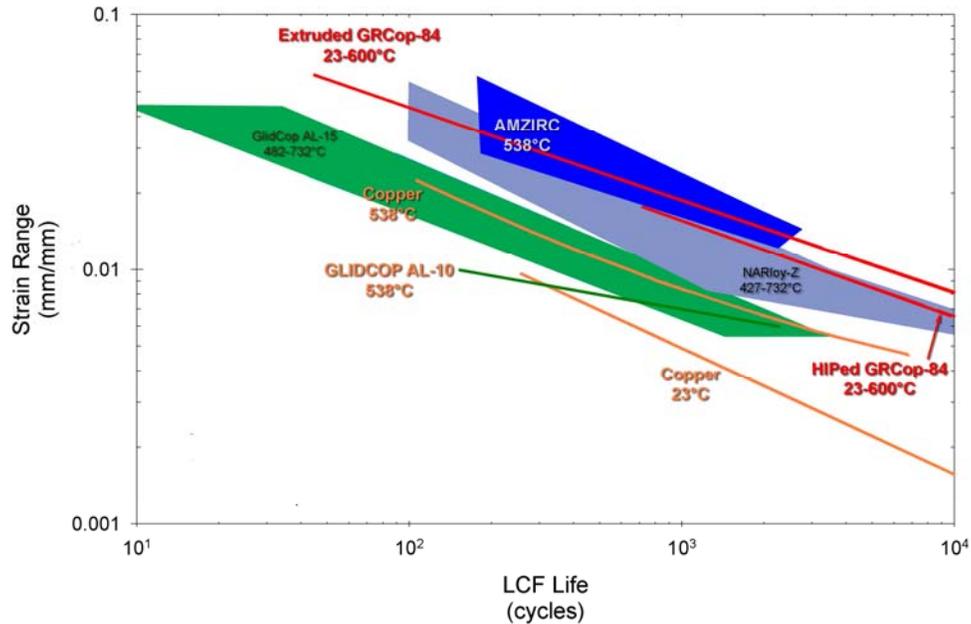


Figure 19.—Low-cycle fatigue (LCF) is the primary property driving design of most liners for reusable launch vehicles (RLVs). It also plays an important role in expendable launch vehicle (ELV) engines as well. GRCop-84 shows no statistically significant difference in LCF lives between room temperature and 600 °C (1112 °F). AMZIRC has a comparable LCF life, but GRCop-84 is clearly superior to NARloy-Z, GlidCop, and copper, in some cases by over an order of magnitude.

Oxidation Resistance and Coatings

GRCop-84 has enhanced oxidation resistance up to 650 °C (1202 °F) because it forms a layer of chromium-niobium oxides underneath the much thicker copper oxide layer. This inhibits diffusion and lowers the oxidation rate of GRCop-84 almost a full order of magnitude below that of pure copper. Above 700 °C (1292 °F) the oxidation rate increases to that of pure copper as the oxidation mechanism undergoes a change.

MCCs for hydrogen-fueled vehicles have a unique environmental failure mechanism called blanching (ref. 10). Local conditions on the liner hot wall undergo rapid oscillations between oxidizing and reducing conditions. For NARloy-Z and other copper-based alloys, copper oxide forms and is then reduced to develop a copper sponge on the hot wall. The poor thermal conductivity of the sponge leads to local hot spots that can exceed the melting point of the alloy and promote cracking. GRCop-84 has been shown to be inherently more resistant to blanching than NARloy-Z, but a coating is still required for multiuse missions or extended life.

To stop blanching either the oxidation or reduction portion of the cycle needs to be minimized or stopped. Cu-Cr offers a high thermal conductivity coating that forms a relatively stable chromia layer and will stop or slow blanching depending on the operating conditions of the engine. NiCrAlY forms an adherent alumina layer and has proven to be a more reliable and effective coating especially when thermal cycling is considered. Other copper-based protective coatings that hold the promise of higher conductivities than NiCrAlY but with the same environmental resistance are under development at NASA Glenn Research Center.

GRCop-84 samples coated with Cu-Cr and NiCrAlY coatings were tested in a hydrocarbon fuel combustion environment to determine if the coatings were susceptible to sulfidation, oxidation, or more complex modes of attack. High-sulfur JP-8 fuel was used in a test rig capable of generating 5 atmospheres of pressure. This is an environment similar to a jet engine combustor section but could be representative of a natural gas or oil-fired furnace environment as well. Cu-Cr coatings improved the initial resistance but were susceptible to failure over long exposures. As expected, NiCrAlY coatings, which was developed for these jet engine environments were virtually unaffected after hundreds of hours of exposure.

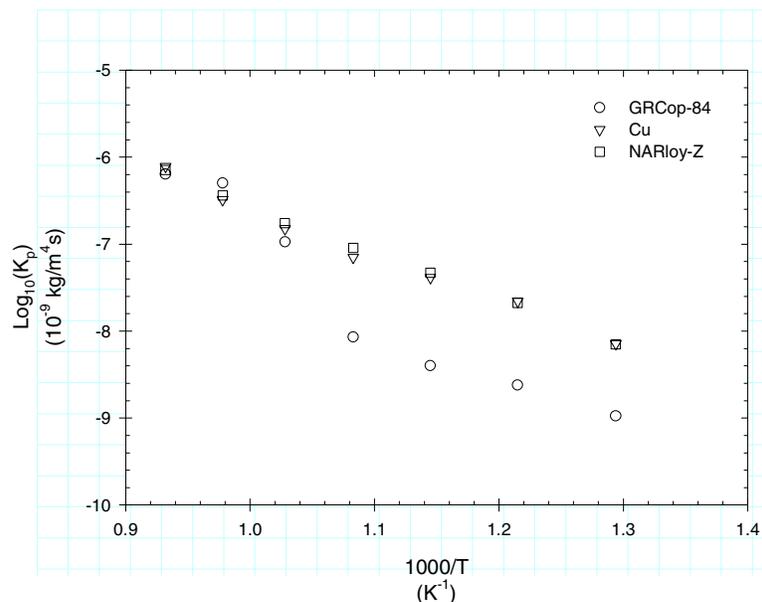


Figure 20.—Compared to pure copper, NARloy-Z has an almost identical oxidation rate as measured by the parabolic rate constant. Below 700 °C (1292 °F) GRCop-84 forms a protective complex Cr-Nb-O layer beneath the outer CuO and Cu₂O layers, which reduces the rate of oxidation by almost an order of magnitude. Above 700 °C the oxidation mechanism changes and GRCop-84 exhibits oxidation behavior equivalent to copper and NARloy-Z.

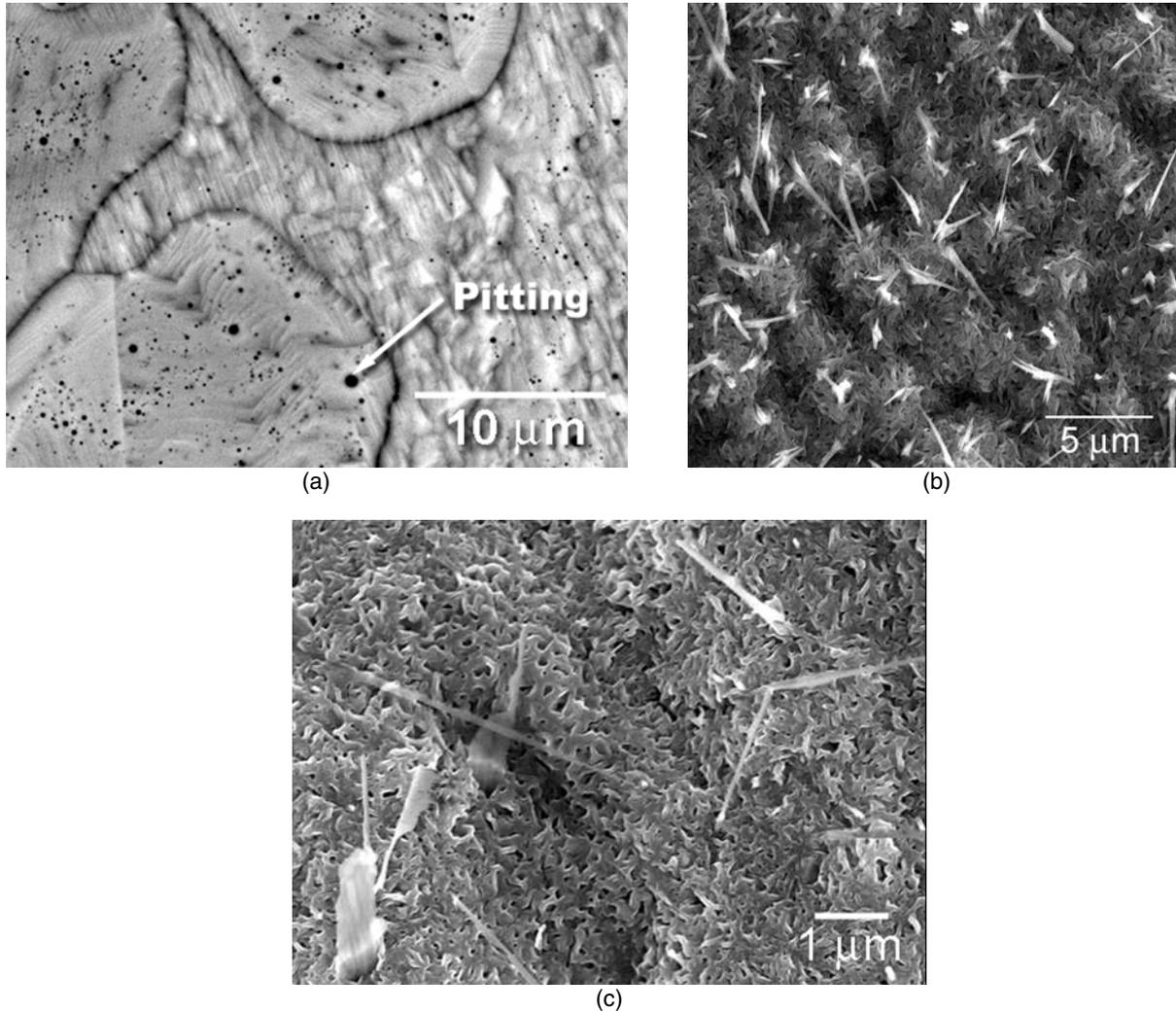


Figure 21.—Blanching typically results in the formation of copper sponge, pits, and grooves at the grain boundaries for NARloy-Z. A simulated blanching experiment where samples were cycled between oxidizing and reducing environments in a furnace was developed. The surface of NARloy-Z samples (a) are nearly identical to published micrographs of SSME liner hot walls that have experienced blanching. In comparison, GRCop-84 (b) exhibits a covering of chromium-niobium oxides which are not reduced in the hydrogen environment. The presence of these oxides partially breaks the oxidation-reduction cycle and imparts better inherent blanching performance to GRCop-84. The best performance is achieved with an environmental barrier coating such as Cu-17 Cr (c) or NiCrAlY, which forms a stable oxide layer that completely covers the sample surface. In most instances NiCrAlY is preferred based upon superior cyclic oxidation performance and generally better resistance to more environments than Cu-Cr coatings.

Joining

Limited joining experimentation has been conducted. Friction stir welding has proven to be an extremely robust joining method (ref. 11), but it is limited to joining GRCo-84 to itself. Tensile tests indicate that the welds retain almost all of the base metal strength. Inertia welding has been used to attach 310 and 316 stainless steel ends on GRCo-84 LCF specimens. During LCF testing the samples failed in the GRCo-84 rather than at the weld joint. Electron beam welding has shown success in joining GRCo-84 to itself and has potential for joining to dissimilar materials. Limited brazing has been conducted, but it appears to be possible to braze GRCo-84 to a variety of materials using brazes normally used for copper. Diffusion bonding of GRCo-84 to itself with and without a nickel layer has been demonstrated, and it can likely diffusion bond to metals that are amiable to diffusion bonding to pure copper.

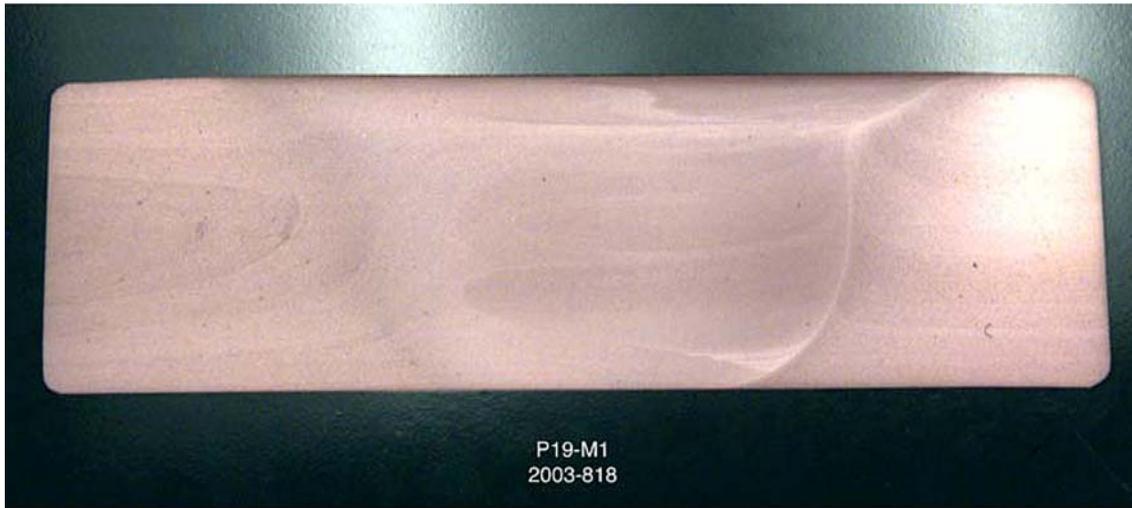


Figure 22.—Friction stir welding (FSW) of GRCo-84 has been developed at NASA Marshall Space Flight Center. GRCo-84 can be welded using a butt joint with ease by FSW. Unlike NARloy-Z, which did not exhibit a good weld, GRCo-84 shows full penetration and a void-free weld zone. GRCo-84 also has a wide processing window, which allows successful friction stir welding under a large variety of conditions. As shown in the tables below, the FSW welds retain almost all of the strength of the parent plate material and can actually exceed the strength of the parent plate in some cases.

TABLE I.—ROOM TEMPERATURE TENSILE STRENGTH AND DUCTILITY OF FRICTION STIR WELDED JOINTS

Material	0.2% offset yield strength	Ultimate tensile strength	Elongation, %	Reduction in area, %
1.27-cm plate—round samples (average of three welds and six tests)	203.6 MPa (29.5 ksi)	403.4 MPa (58.5 ksi)	18.0	20.3
1.27-cm plate—full-thickness samples (average of two welds and eight tests)	203.7 MPa (29.5 ksi)	404.6 MPa (58.6 ksi)	17.8	N/A
As-rolled GRCo-84 1.27-cm thick plate	225.6 MPa (32.7 ksi)	403.1 MPa (58.4 ksi)	23.8	41.9
FSW properties as percent of baseline properties	90.3%	100.2%	75.2%	48.4%

**TABLE II.—TENSILE STRENGTH OF METAL SPUN GRCop-84
LINER PREFORMS IN THE WELD REGION**

Material	0.2% offset yield strength	Ultimate tensile strength
FSW and metal spun— room temperature	246.3 MPa (35.7 ksi)	419.5 MPa (60.8 ksi)
FSW and metal spun— 538 °C (1000 °F)	157.3 MPa (22.8 ksi)	176.6 MPa (25.6 ksi)
As-rolled GRCop-84 plate— room temperature	225.6 MPa (32.7 ksi)	403.1 MPa (58.4 ksi)
As-rolled GRCop-84 plate— 538 °C (1000 °F)	107.8 MPa (15.6 ksi)	138.9 MPa (20.1 ksi)

Component Testing

VPS has been used to make several small liners that have been hot fire tested for various durations at both Glenn Research Center and Marshall Space Flight Center. One liner tested had no protective coating and provides a baseline. The remaining liners had a NiCrAlY functional gradient material on the hot wall.

The uncoated liner test at NASA Glenn accumulated 142 seconds of hot fire time during 11 hot fire tests lasting up to 30 seconds each. The mixture ratio (oxygen to hydrogen by weight) was limited to 7:1 to prevent blanching. Visual examination of the hot wall revealed no detectable changes to the surface.

Much more extensive testing of VPS liners with NiCrAlY functional graded material on the hot wall has been conducted. After the successful testing of a coated liner at NASA Glenn that accumulated 340 seconds of hot fire testing in 17 hot fire tests, a nominal 5000-lb thrust liner with a NiCrAlY functional gradient coating was produced and tested at NASA Marshall. The liner proved to have excellent capabilities. Larger liners have been produced, and plans are underway to evaluate them through hot fire testing.



Figure 23.—NASA Marshall Space Flight Center produced and hot fire tested a GRCop-84 5000-lb thrust cell with a NiCrAlY functionally graded material on the hot wall. Despite two injector failures and 108 hot fire tests, the NiCrAlY coating remained intact and showed no visible wear or degradation. Hot wall cracks were produced in similar NARloy-Z liners tested in the 1970s. No such cracks were observed in the GRCop-84 liner even though it was tested at a higher hot wall temperature. The liner was also tested at a stoichiometric oxygen to hydrogen ratio, which would degrade an uncoated NARloy-Z liner in a few seconds due to blanching with no detectable damage. The GRCop-84 liner survived eight stoichiometric hot fire tests.

Summary

GRCop-84 has demonstrated stable mechanical properties at elevated temperatures that almost always are better than other high-conductivity copper-based alloys especially after high- temperature exposures. The alloy can be processed from powder using a variety of conventional, commercially available techniques. It has been demonstrated that GRCop-84 can be joined using friction stir welding, brazing, inertia welding, brazing, diffusion bonding, and electron beam welding.

In short, GRCop-84 demonstrates a combination of a large variety of highly desirable mechanical and thermophysical properties that makes it a very attractive material to use at temperatures up to 700 °C (1292 °F).

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References

1. D.L. Ellis and G.M. Michal, *Ultramicroscopy*, vol. 30, nos. 1/2, pp. 210-216.
2. D.L. Ellis and G.M. Michal, "Precipitation Strengthened High Strength, High Conductivity Cu-Cr-Nb Alloys Produced by Chill Block Melt Spinning," NASA CR-185144, NASA LeRC, Cleveland, OH, (Sept. 1989).
3. A. Adallah, G.M. Michal, D.L. Ellis, and J.J. Lewandowski, "Formability of a High Performance Dispersion Strengthened Cu-Cr-Nb Composite," Proc. of 2003 Annual TMS Meeting.
4. S. Elam, R. Holmes, T. McKechnie, R. Hickman, and T. Pickens, 52nd JANNAF Propulsion Meeting/1st Liquid Propulsion Subcommittee Meeting, Las Vegas, NV, May 2004.
5. R. Hickman, T. McKechnie, S. Elam, and R. Holmes, 39th AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit, Huntsville, AL, July 2003, AIAA Paper 2003-4612.
6. S. Elam, J. Lee, R. Holmes, and F. Zimmerman, 52nd International Astronautical Congress, Toulouse, France, October 2001.
7. K.R. Anderson, J.R. Groza, R.L. Dreshfield, and D.L. Ellis, "High Performance Dispersion Strengthened Cu-8 Cr-4 Nb Alloy," *Met. Trans A*, vol. 26A, (Sept. 1995), pp. 2197-2206.
8. T. Nagai, Z. Hanmi, and S. Koda, *J. Japan Copper and Brass Assn.*, vol. 14, (1975), pp. 60-73 (CDA Extract 13298).
9. T. Nagai, Z. Henmi, T. Sakamoto, and S. Koda, *Trans. Japan. Inst. Metals*. vol. 14, no. 6, (Nov. 1973), pp. 462-469.
10. L. Ogbuji, D. Humphrey, and J. Setlock, *Affordable Metal-Matrix Composites*, A. Pandey, et al., eds., TMS, Warrendale, PA, (2003), pp. 25-33.
11. C. Russell, R. Carter, D. Ellis, and R. Goudy, AIAA-2004-1995, 45th AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics and Materials Conference, Palm Springs, California, (Apr. 19-22, 2004)

Bibliography

1. L.J. Ghosn and S.V. Raj, "Residual Stresses in Thermal Barrier Coatings for a Cu-8Cr-4Nb Substrate System," *Ceramic Engineering Science Proceedings* 23, pp. 409–416 (2002).
2. 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 an Advanced Copper Alloy," *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).
3. L.J. Ghosn and S.V. Raj, "Residual Stresses in Thermal Barrier Coatings for a Cu-8Cr-4Nb Substrate System," NASA/TM—2002-211561, NASA Glenn Research Center, Cleveland, OH (2002).
4. S.V. Raj, L.J. Ghosn, and C.A. Barrett, "NiAl Coatings Investigated for Use in Reusable Launch Vehicles," 2002 Research and Technology, NASA/TM—2003-211990, pp. 43–45.
5. S.V. Raj and L.J. Ghosn, "Coating Development for GRCop-84 Liners for Reusable Launch Vehicles Aided by Modeling Studies," 2003 Research and Technology, NASA/TM—2004-212729, pp. 35–37.
6. L.U. Thomas-Ogbuji, and D.L. Humphrey: Oxidation Behavior of GRCop-84 (Cu-8Cr-4Nb) at Intermediate and High Temperatures. NASA/CR—2000-210369, Aug. 2000.
7. L.U.J.T. Ogbuji, and D.L. Humphrey: Oxidation Properties of Cu-8Cr-4Nb. *Electrochemical Society Proceedings*, vol. 2001–12, pp. 77–83.
8. L. Ogbuji: Powder-Derived High-Conductivity Coatings for Copper Alloys. *Powder Materials: Current Research & Industrial Practices III*, F.D.S. Marquis, ed., TMS, Warrendale, PA, pp. 293–300.
9. L. Ogbuji, and D.L. Humphrey: Comparison of the Oxidation Rates of Some New Copper Alloys. *Oxidation of Metals*, vol. 60, nos. 3/4, Oct. 2003, pp. 271–291.
10. L. Ogbuji, Humphrey, D., and Setlock, J., A Simplified Test for Blanching Susceptibility of Cu Alloys. *Affordable Metal-Matrix Composites*, A. Pandey, et al., eds., TMS, Warrendale, PA, 2003, pp. 25–33.
11. S.V. Raj, Ghosn, L.J., Agarwal, A., and T.P. Lachtrupp, An Assessment of the Residual Stresses in Low Pressure Plasma Sprayed Coatings on an Advanced Copper Alloy. *Surface Engineering: In Materials Science II*, S. Seal, N. B. Dahotre, J. J. Moore, S. Suryanarayana, and A. Agarwal, eds., TMS (The Minerals, Metals & Materials Society), 2003, pp. 49–56.
12. D.L. Ellis and D.J. Keller, "Thermophysical Properties of GRCop-84," NASA/CR—2000-210055, NASA GRC, Cleveland, OH, (June 2000).
13. D.L. Ellis and H.M. Yun, "Progress Report on Development of a Cu-8 Cr-4 Nb Alloy Database for the Reusable Launch Vehicle (RLV)," *Copper 1999* (Fourth International Conference), Phoenix, AZ, (Oct. 10–13, 1999).
14. R. Holmes, D. Ellis, and T. McKechnie, "Robust Low Cost Aerospike/RLV Combustion Chamber by Advanced Vacuum Plasma Process," 36th Annual Space Congress, Cocoa Beach, FL, (April 27–29, 1999).
15. D.L. Ellis, "Mechanical Properties of Cu-Cr-Nb Alloys," PPM Conference Proceedings, NASA Lewis Research Center, Cleveland, OH (1997).
16. D.L. Ellis, A.K. Misra, and R.L. Dreshfield, "Effect of Hydrogen on Cr₂Nb and Cu-Cr-Nb Alloys," Effect of Hydrogen on the Behavior of Materials, Proc. of Fifth International Conference, Moran, WY, Sept. 11–14, 1994, eds. A.W. Thompson and N.R. Moody, TMS, Warrendale, PA (Oct. 1996).
17. D.L. Ellis and G.M. Michal, "Mechanical and Thermal Properties of Two Cu-Cr-Nb Alloys and NARloy-Z," NASA CR—198529, NASA Lewis Research Center, Cleveland, OH (Oct. 1996).
18. K.R. Anderson, J.R. Groza, R.L. Dreshfield, and D.L. Ellis, "High Performance Dispersion Strengthened Cu-8 Cr-4 Nb Alloy," *Met. Trans A*, vol. 26A, (Sept. 1995), pp. 2197–2206.
19. D.L. Ellis, G.M. Michal, and R.L. Dreshfield, "A New Cu-8 Cr-4 Nb Alloy for High Temperature Applications," *Materials Technology*, vol. 5, no. 5/6, (May/June 1995).

20. D.L. Ellis, R.L. Dreshfield, M.J. Verrilli, and D.G. Ulmer, "Mechanical Properties of a Cu-8 Cr-4 Nb Alloy," Earth-to-Orbit Conference, Huntsville, AL (May 1994).
21. K.R. Anderson, J.R. Groza, R.L. Dreshfield, and D.L. Ellis, "Microstructural Evaluation of Precipitation-Strengthened Cu-8 Cr-4 Nb Alloy," Materials Science and Engineering, A169, (1993), pp. 167–175.
22. D.L. Ellis and R.L. Dreshfield, "Preliminary Evaluation of a Powder Metal Copper-8 Cr-4 Nb Alloy," Proc. of the Advanced Earth-to-Orbit Conference, NASA MSFC, Huntsville, AL, (May 19–21, 1992).
23. D.L. Ellis, G.M. Michal, and N.W. Orth, "Production and Processing of Cu-Cr-Nb Alloys," Scripta Metallurgica et Materialia, vol. 24, pp. 885–890.
24. D.L. Ellis and G.M. Michal, "Formation of Cr and Cr₂Nb Precipitates in Rapidly Solidified Cu-Cr-Nb Ribbon," Ultramicroscopy, vol. 30, nos. 1/2, pp. 210–216.
25. D.L. Ellis, "Precipitation Strengthened High Strength, High Conductivity Cu-Cr-Nb Alloys Produced by Chill Block Melt Spinning," Doctoral Dissertation, Case Western Reserve University, Cleveland, OH (June 1989). Also available as NASA CR-185144, NASA LeRC, Cleveland, OH, (Sept. 1989).
26. K.R. Anderson, "Effects of Thermal and Mechanical Processing on Microstructures and Desired Properties of Particle-Strengthened Cu-Cr-Nb Alloys," Doctoral Dissertation, University of California at Davis, Davis, CA. Also available as NASA/CR—2000-209812, NASA GRC, (Feb. 2000).

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