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## **Progress in Additively Manufactured Copper-Alloy GRCop-84, GRCop-42, and Bimetallic Combustion Chambers for Liquid Rocket Engines**

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### **Abstract**

Additive Manufacturing (AM) has significantly evolved over the last decade for use in the aerospace industry, particularly for liquid rocket engines. AM offers a considerable departure from traditional manufacturing to rapidly fabricate components with complex internal features. High performance liquid rocket engine combustion chambers that operate in a high heat flux environment are fabricated using a copper-alloy liner with a series of integral coolant channels. Copper-alloys provide the necessary conductivity and material strength for adequate design margins offering high performance without the need for film coolant. Copper-alloys present unique challenges to properly melt the powder in laser-based AM processes due to their high reflectivity and conductivity. Starting in 2014, NASA's Marshall Space Flight Center (MSFC) and Glenn Research Center (GRC) have developed a process for AM of GRCop (Copper-Chrome-Niobium) alloys using Selective Laser Melting (SLM). GRCop, originally developed at GRC, is a high conductivity, high-strength, dispersion strengthened copper-alloy for use in high-temperature, high heat flux applications. NASA has completed significant material characterization and testing, along with hot-fire testing, to demonstrate that GRCop-42 and GRCop-84 alloys are suitable for use in combustion chambers. Additional development and testing has been completed on AM bimetallic chambers using GRCop-84 liners and superalloy jackets, fabricated using two Directed Energy Deposition (DED) processes: Electron Beam Freeform Fabrication (EBF<sup>3</sup>) and Blown Powder DED. NASA completed hot-fire testing on various AM chambers using GRCop-84, GRCop-42, and bimetallic chambers in Liquid Oxygen (LOX)/Hydrogen, LOX/Methane, and LOX/Kerosene propellants.

**Keywords:** Additive Manufacturing, Laser Powder Bed Fusion (L-PBF), GRCop-42, GRCop-84, Liquid Rocket Engines, Selective Laser Melting (SLM), Combustion Chambers, Channel-Cooled Chambers, Regeneratively-cooled chamber, Regen chamber, Bimetallic Additive Manufacturing, AM, DED

### **Acronyms/Abbreviations**

Additive Manufacturing or Additively Manufactured (AM), Directed Energy Deposition (DED), Electron Beam Freeform Fabrication (EBF<sup>3</sup>), Gaseous hydrogen (GH<sub>2</sub>), Glenn Research Center (GRC), NASA GRC Copper-alloy Cu-Cr-Nb (GRCop), Hot Isostatic Pressing (HIP), thousand pound-force, thrust (K-lb<sub>f</sub>), George C. Marshall Space Flight Center (MSFC), Low Cycle Fatigue (LCF), Low Cost Upper Stage Propulsion (LCUSP), Liquid Oxygen (LOX), Kerosene (RP-1), Laser Powder Bed Fusion (L-PBF), Chamber Pressure (Pc), Pounds Square Inch, Gage (psig), Methane (LCH<sub>4</sub>), Rapid Analysis and Manufacturing Propulsion Technology (RAMPT), Room Temperature (RT), Selective Laser Melting (SLM), Thrust Chamber

Assembly (TCA), United States (US) National Aeronautics and Space Administration (NASA)

### **1. Introduction**

Additive Manufacturing (AM) is an emerging fabrication technology being used across the aerospace industry as a new approach for fabricating complex components. The United States (U.S.) National Aeronautics and Space Administration (NASA) along with U.S. industry partners have been developing the use of AM specific to complex liquid rocket engine components to significantly reduce the lead time and costs associated with their fabrication. Regeneratively (regen) cooled combustion chambers are an ideal application of the AM technology due to the complexities

of the design and an inability of traditional manufacturing to meet desired geometries. AM is also an excellent candidate to apply the structural jacket instead of using traditional brazing. AM processes have been shown to significantly reduce the lead time for thrust chamber fabrication and reduce production costs, making use of alloys that optimize the performance of combustion chambers.

Several AM processes, specifically laser powder bed fusion (L-PBF) or selective laser melting (SLM), have matured over the last decade for a variety of materials, yet a limited number of metals are available using this process. While the availability of SLM materials for aerospace components is continuing to expand, a majority of the market is primarily focused on superalloys. NASA identified this need for new materials, specifically copper-alloys to make use of the AM process for combustion chambers. High performance, liquid rocket engine, combustion chambers that operate in a high heat flux environment are fabricated using a copper-alloy liner with integral coolant channels. Copper-alloys provide the necessary conductivity and material strength for adequate design margins without the need for film coolant. Yet, copper-alloys present unique challenges to properly melt the powder in laser-based AM processes due to their high reflectivity in the near-IR wavelengths typically used for AM and high thermal conductivity.

Starting in 2014, NASA's Marshall Space Flight Center (MSFC) and Glenn Research Center (GRC) have developed a process for AM of GRCoP (Copper-Chrome-Niobium) alloys using SLM. GRCoP, originally developed at NASA's GRC, is a high conductivity, high-strength, dispersion strengthened, copper-alloy for use in high-temperature, high heat flux applications. NASA's goal was to expand the list of available materials for liquid rocket engines, by providing the development and dissemination of data on GRCoP, specifically GRCoP-42 (Cu-4 at.% Cr-2 at.% Nb) and GRCoP-84 (Cu-8 at.% Cr-4 at.% Nb) alloys.

The SLM process can fabricate a combustion chamber liner with complex internal coolant channels using a monolithic alloy, such as GRCoP. However, some combustion chamber designs require an additional structural jacket due to handle high (axial) thrust and hoop or circumferential loads. An optimized solution is to create a copper liner for the chamber and then apply a second high-strength-to-weight alloy using a secondary AM process with Directed Energy Deposition (DED), specifically Electron Beam Freeform Fabrication (EBF<sup>3</sup>) and Blown Powder DED at NASA's Langley Research Center (LaRC). Under NASA's Low Cost Upper Stage Propulsion (LCUSP) program, these AM techniques were used to deposit a high strength superalloy onto a GRCoP liner, forming a bimetallic mechanical bond and the necessary strength to handle structural loads.

Successful hot-fire testing of this 35,000 (35K) lb<sub>f</sub> bimetallic chamber is shown in Fig. 1.

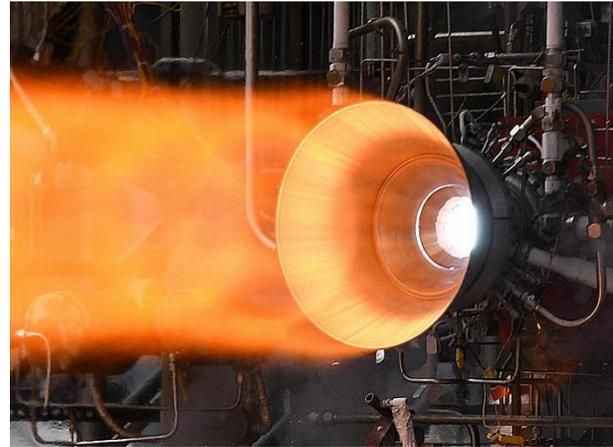


Fig. 1. Hot-fire testing of LCUSP Bimetallic AM Chamber.

In addition to the LCUSP chamber, NASA has completed significant material characterization and testing on these processes, along with additional hot-fire testing, to demonstrate that AM GRCoP-42 and GRCoP-84 alloys are suitable for use in a variety of combustion chambers. Efforts have been completed on AM bimetallic chambers using GRCoP-84 liners with Alloy 625 (Inconel 625) structural jackets. In addition, extensive hot-fire testing on various AM chambers with GRCoP-84, GRCoP-42, and bimetallic chambers using Liquid Oxygen (LOX)/Hydrogen (H<sub>2</sub>), LOX/Methane (LCH<sub>4</sub>), and LOX/Kerosene (RP-1) propellants. Future development and flight programs can make use of these advancements in AM GRCoP-84 and GRCoP-42 alloys for a variety of high performance liquid rocket engine applications. These NASA-led projects have matured the process significantly and also made process parameters and characterization data available to industry to enable commercial supply chains. Several industry partners have continued to advance the GRCoP-84 and GRCoP-42 materials in addition to exploring other copper-alloys such as C-18150, C-18200, C-18000, and Glidcop.

## 2. Process Overview and Development

The GRCoP family of alloys exhibit exceptional high temperature mechanical and good thermophysical properties. The alloys were developed as a high heat flux, high strength alternative to other common aerospace copper alloys, such as NARloy-Z and C-18150 (Cu-1 Cr-0.15 Zr) [1,2,3,4]. The alloys are dispersion strengthened materials with primary strengthening from the Cr<sub>2</sub>Nb phase. The material is preferred for use in combustion chambers due to:

- 1) Oxidation and blanching resistance during thermal and oxidation-reduction cycling [5],
- 2) A maximum use temperature around 800 °C, depending upon strength and creep requirements
- 3) Good mechanical properties at high use temperatures,
- 4) Lower thermal expansion to reduce thermally induced stresses and low cycle fatigue (LCF),
- 5) Established powder supply chain,
- 6) Mature AM process that provides consistent, minimum material properties [6].

GRCop-84 is the most common alloy, having completed substantial process and property development using SLM under the LCUSP program. Recent advancements of GRCop-42 though are showing that it provides a higher conductivity compared to GRCop-84, and its maturity level is rapidly increasing. The conductivity of the wrought (non-AM) GRCop-84 and GRCop-42 materials are compared in Fig. 2.

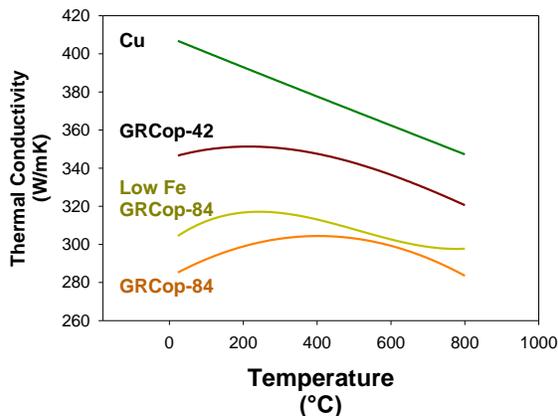


Fig. 2. Thermal Conductivity of Wrought GRCop Alloys and Pure Cu

Both alloys are capable of operating at temperatures up to 800°C, and they have been successfully hot-fire tested in an oxidizing environment to above 750°C. In comparison, pure copper is limited to approximately 200°C, and most copper alloys cannot exceed 500°C [7]. Substitution of GRCop-42 or GRCop-84 for NARloy-Z, C-18150, or another precipitation strengthened copper-alloy, could result in a 200°C or more increase in temperature capability, providing higher performance trades or increased margin. These attributes, in addition to the rapid development of the GRCop alloys using the SLM process, make them an attractive option for use in high performance combustion chambers.

The strengths of GRCop-42 and GRCop-84 exceed almost all other copper-based alloys in the 500-700°C range. They also exceed all other precipitation strengthened copper-based alloys at all temperatures if the part must be given a high temperature heat treatment

or secondary processes such as brazing or other manufacturing steps, and it is not possible to perform subsequent solution and precipitation heat treatments. The advantage is typically on the order of two times the strength of competing alloys such as NARloy-Z (Cu-1 Ag-0.5 Zr). Creep failure modes can occur when the liner material is operated for sustained durations at high temperatures. GRCop alloys typically can withstand 10% to 25% greater stresses than most competing copper alloys with even larger advantages above about 600 °C.

The intrinsic oxidation rates of GRCop-42 and GRCop-84 up to 800 °C are up to one order of magnitude lower than most competing copper-based alloys. GRCop-42 and GRCop-84 have demonstrated exceptional thermal stability up to 1050 °C or 98% of the melting point of copper. Essentially no mechanical property or microstructural changes have been observed up to 800 °C and the alloys retain at least half their tensile strength when exposed up to 1050 °C for 100 hours. Short term thermal exposures to temperatures up to 1050 °C for simulated manufacturing steps such as brazing have resulted in minimal property degradation. In comparison, all precipitation strengthened, low-alloy high conductivity copper-based alloys would return to mechanical properties similar to pure copper at these higher temperatures.

There are some differences between GRCop-84 and GRCop-42, and they can be traded for various applications. GRCop-42 trades somewhat lower mechanical properties, such as strength, for higher thermal conductivity, and thus a lower wall temperature. The ductility of GRCop-42 is generally superior to that of GRCop-84. With only half the Cr<sub>2</sub>Nb content of GRCop-84, this was expected. Both alloys have sufficient ductility for most applications, and will deform large amounts without failure. The major difference between the alloys is observed in low cycle fatigue (LCF) in the stresses observed during strain control testing. The difference in stresses at the minimum and maximum strains was calculated, and Fig. 3 shows the total stress range for each strain at the three test temperatures. This made GRCop-84 preferable for reusable launch vehicles requiring lives of hundreds of missions.

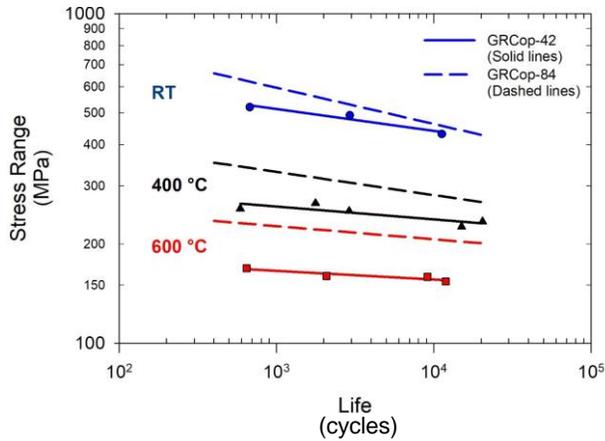


Fig. 3. Low Cycle Fatigue of Wrought GRCop-84 and GRCop-42.

In all cases, GRCop-42 had a lower stress range than GRCop-84, and the difference increased with temperature. This was consistent with expectations as GRCop-84 has a higher strength and requires a higher stress to deform it to these strains. This indicates that the load bearing capability of GRCop-42 in an LCF environment will not be as high as GRCop-84. This will need to be addressed in some designs, but since the LCF is thermally driven for a liner, it is expected that the total thermal expansion driven by the temperature change will be the key determinants for the LCF performance. The analyses will also need to address the higher coefficient of thermal expansion for GRCop-42 relative to GRCop-84 when calculating the thermal stresses and strains. With the increased thermal conductivity, wall temperatures will also be lower and stresses may be equivalent in designs.

All initial SLM development was completed using GRCop-84 since it was the more mature alloy with wrought (extruded, hot rolled, cold rolled and forged) data for comparison. However, after successful development using this alloy, GRCop-42 was pursued for some performance improvements.

The GRCop-42 has the following advantages over GRCop-84, based on the envisioned engine application:

- 1) Improved thermal conductivity,
- 2) Limited and acceptable reduction in strength,
- 3) Simplified powder atomization based on powder supplier comments,
- 4) Less costly fabrication build times based on increased layer height

Development on both alloys has been conducted at NASA, and several commercial print vendors now exist in the U.S. for both GRCop-84 and GRCop-42.

### 2.1 GRCop-alloy SLM Process Development

Fabrication using the SLM process must consider the end to end design, atomization, additive processes, and post-processing requirements to provide repeatable

fabrication of components with desired properties and a sustainable supply chain. In the SLM development of the GRCop alloys, a series of integrated tasks across NASA and industry were considered to mature the material and process, including:

- Establishing and controlling the powder supply chain
- Scalability and transfer of the SLM process to various machines and size scales
- Optimal work flow and processing time of GRCop-42 and GRCop-84
- Characterizing the material and establishing a database of AM properties for design engineers
- Understanding property and microstructural sensitivities to powder supply, print parameters, and design features
- Developing best design practices for the SLM GRCop alloy use in combustion chambers
- Demonstrating component hardware in a relevant environment and testing at aggressive conditions to validate designs and property databases
- Dissemination of data to US industry partners and US commercial print service vendors.

The high level process flow for SLM GRCop development can be seen in Fig. 4. The powder supply chain was expanded and matured, but it required some variations on printing and lessons learned to be fed back to the powder atomization suppliers. In parallel, mechanical test specimens and design databases were being developed to capture the data and apply it to the chamber designs. Hot-fire testing was conducted in parallel, as the overall process was matured to understand early performance characteristics of the GRCop materials.

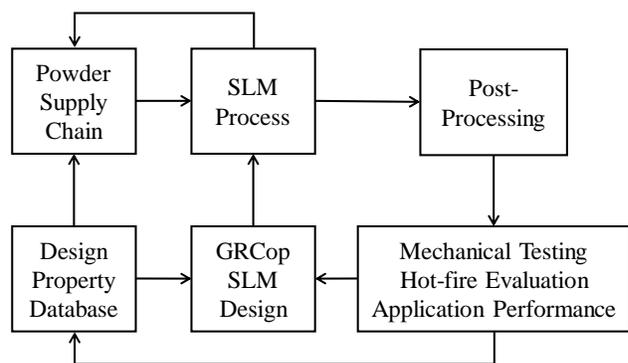


Fig. 4. High-level process flow of SLM GRCop-alloy development.

### 2.2 GRCop SLM Powder Supply Chain

An important aspect of the GRCop alloy development was establishing and controlling powder sources to ensure that the GRCop powders met all requirements. The GRCop alloys are atomized using high purity

elemental charges under argon gas atomization. Handling within an inert or vacuum environment is critical for the GRCo<sub>p</sub> powder to avoid oxygen contamination. Undesired trace elements such as aluminium and silicon that may indicate non-metallic inclusions and iron which reduces thermal conductivity (Fig. 2) must be limited. The ratio of Cr:Nb is also critical as a slight excess of Cr is required to prevent hydrogen embrittlement. The powder chemistry for GRCo<sub>p</sub>-84 and GRCo<sub>p</sub>-42 are provided in Table 1.

Table 1. Powder chemistry comparison of GRCo<sub>p</sub>-42 with GRCo<sub>p</sub>-84.

Element	GRCo <sub>p</sub> -42 Wt %	GRCo <sub>p</sub> -84 Wt %
Cr	3.1 – 3.4	6.2 – 6.8
Nb	2.7 – 3.0	5.4 – 6.0
Fe	Target <50 ppm	Target <50 ppm
O	Target <400 ppm	Target <400 ppm
Al	<50 ppm	<50 ppm
Si	<50 ppm	<50 ppm
Cu	Balance	Balance
Cr:Nb Ratio	1.12 – 1.15	1.12 – 1.15

Various vendors were established to produce the GRCo<sub>p</sub>-84 and GRCo<sub>p</sub>-42 powders for SLM. While it took some iterations early in development, all vendors were able to successfully melt these alloys and meet the chemistry specifications, including oxygen and trace elements. Another driver behind maturing the powder supply chain was cost reduction. Over the course of 5 years in maturing the AM process with several suppliers, the cost was reduced by 3x. There were some minor differences between the vendors for mechanical properties, although they all performed as expected and could be used for SLM processing. The number of vendors has been increased with additional vendors indicating interest. This prevents a single-point loss of capability if a vendor chooses to no longer make GCo<sub>p</sub> alloys or ceases operations.

Early development and powder lots were specified to a more traditional SLM sieve size at -325/+1250 mesh (10-45 μm). It was determined through further development that the fines could be included in the SLM powder, which helped improve yield. The specification was later changed to provide -325/down mesh. The change had the additional benefit of increasing the observed elongations, but the increase might be confounded by processing parameter changes.

An additional powder study with the GRCo<sub>p</sub>-42 was completed during development and produced identical results [8]. SLM build parameters were developed to optimize the infill to achieve desired mechanical and thermophysical properties. The contouring parameters were optimized to minimize surface roughness. The core

infill parameters yielded high densities and good strengths and ductilities. A minimum density of 99.2%, and in many cases higher, was achieved by SLM prior to a Hot Isostatic Pressing (HIPing) operation. Full density was easily achieved after HIPing.

Best results with GRCo<sub>p</sub>-42 was obtained using powders that contained the fines (-1250 mesh) as shown in Table 2 [9]. Based on several NASA engine applications, the elongation was one of the driving properties since ductility is important in the thermal cycling of a combustion chamber at high temperature, because the elongation and strength was best with the fines, it was determined that future production powder lots will include the fine particles and limit the maximum diameter of the powder to 45 μm.

Table 2. Mechanical characterization summary of GRCo<sub>p</sub>-42 with various powder sizes.

Powder Source	Size (mesh)	Tensile (MPa)	Yield (MPa)	Elong. (%)
Vendor 1	-325 without fines	265	153	8.7
Vendor 1	-270 without fines	234	137	7.2
Vendor 1	<b>-325 with fines</b>	<b>359</b>	<b>173</b>	<b>32.5</b>
Vendor 2	-325 without fines	342	186	21.3
Vendor 2	<b>-325 with fines</b>	<b>419</b>	<b>218</b>	<b>28.4</b>
Vendor 3	-325 without fines	355	182	25.4

Separate studies were completed on powder re-use and determined it is feasible to mix virgin and used powder so long as the reused powder does not have excessive oxidation. Fully used powder can also achieve desired mechanical properties, but there is about a 2% reduction in ultimate strength and no discernible difference of tensile and elongation properties at room temperature with once-used fully recycle powder.

### 2.3 SLM Process Development

The LCUSP program, initiated in 2014, was established to develop the necessary GRCo<sub>p</sub>-84 AM build parameters, characterize SLM microstructures and mechanical properties, and build and test representative chambers. The SLM, of Laser-Powder Bed Fusion (L-PBF), process uses a layer-by-layer approach, in which the desired component features are created by melting the powder using a laser, as depicted in Fig. 5.

This process for copper alloys has been well described in prior publications for GRCo<sub>p</sub> alloys [Ref 10,11,12]. The behavior of the GRCo<sub>p</sub> material during the SLM process was different than original expected. It appeared that GRCo<sub>p</sub>-84 was easily melted in the process. Most likely, the 14 vol.% Cr<sub>2</sub>Nb phase is responsible for a higher absorption of near-IR laser energy than pure copper and results in easier heating initially. The reflectivity of copper rapidly decreases with

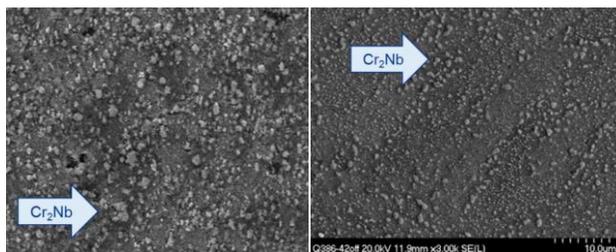
temperature, and the powder should absorb more energy from the laser and heat readily [13].



Fig. 5. SLM fabrication of GRCop-84 chambers.

Parameter and process development for GRCop-84 was conducted on MSFC's Concept Laser M2 with a build volume of 250x250x250mm. The system had proven itself "copper friendly", making GRCop-84 parts. It featured an inert atmosphere glovebox and build chamber for handling the powder and parts, and the 400W infrared laser could readily achieve the high-energy density needed to fully melt the GRCop alloys. However, the machine features are now standard in most machines and further development in EOS machines have demonstrated equivalent results.

Initial Scanning Electron Microscope (SEM) images taken during development of the GRCop-84 revealed some interesting observations (Fig. 6). First, the SLM process did not result in segregation of the Cr<sub>2</sub>Nb precipitates. This is likely due to turbulence in the melt pool mixing the molten Cu and solid Cr<sub>2</sub>Nb particles. Once the laser moves away, the liquid-solid mixture rapidly solidified by the conduction of heat out of the material through the GRCop-84 substrate. This apparently did not allow sufficient time for buoyancy effects to segregate the Cr<sub>2</sub>Nb to the surface of the molten copper. The results was a very uniform distribution of Cr<sub>2</sub>Nb throughout the sample.



(a) As-Extruded (b) SLM  
 Fig. 6. Scanning Electron Microscope Backscatter characterization of GRCop-84 Cr<sub>2</sub>Nb.

The second observation was that the Cr<sub>2</sub>Nb appears to have been refined in size. The Cr<sub>2</sub>Nb present in the powder particles is actually an agglomeration of finer Cr<sub>2</sub>Nb particles formed in liquid copper during the gas atomization process. It appeared that thermal, and perhaps mechanical forces, acting upon the agglomerations broke them up and formed the finer particles seen in the SLM sample. This is important because basic strengthening mechanisms such as Ashby-Orowan strengthening predict that the strength of a material will be increased as the average diameter of the particles is decreased [14].

The AM process parameters for GRCop-42 were developed on the same MSFC Concept Laser M2 used for the LCUSP program for GRCop-84, and the NASA GRC led materials characterization. In parallel, commercial service vendors were established to develop machine specific parameters and provide GRCop-42 components fabricated on EOS M290 and EOS M400 machines. The GRCop-42 development included the fundamental SLM process parameter development, full characterization and mechanical testing of the AM material. Representative mechanical properties can be seen in Table 3.

Table 3. Summary of SLM GRCop-42 and GRCop-84 mechanical properties.

Material	Source Machine	Tensile (MPa)	Yield (MPa)	Elong (%)
GRCop-84	Extruded	368	197	27
<b>GRCop-84</b>	<b>SLM, M2</b>	<b>390</b>	<b>208</b>	<b>30</b>
GRCop-42	Extruded	354	200	30
<b>GRCop-42</b>	<b>SLM, M2</b>	<b>359</b>	<b>173</b>	<b>32.2</b>
<b>GRCop-42</b>	<b>SLM, M400</b>	<b>355</b>	<b>172</b>	<b>33.6</b>

Two of the concerns during development were that transferring parameters to different machines and scaling would be challenging. Larger build platforms can have different purge and laser focal plane characteristics as well as radically different thermal environments. Similar parameters were used when transferring between systems and scaling to larger volumes. Some adjustments were made on different machines based on the specific laser. Overall, similar processing parameters resulted in similar properties that met requirements. The average tensile curves at room temperature (20°C) for the SLM GRCop-42 built on the MSFC Concept M2 and a vendor's EOS M400 are shown in Fig. 7.

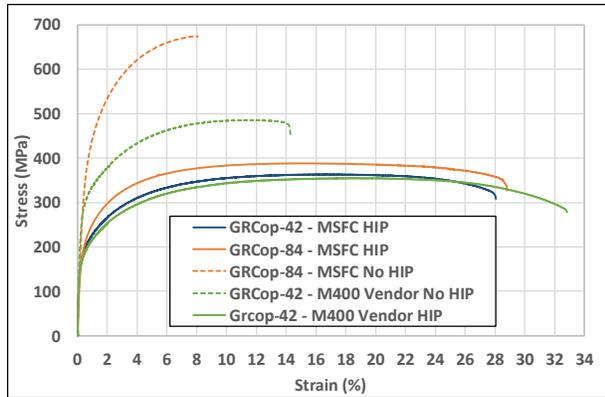


Fig. 7. Stress-Strain curve of SLM GRCop-42/-84 showing HIP and un-HIP conditions

A comparison to SLM GRCop-84 from the MSFC Concept M2 is also shown. The SLM tensile data follows similar trends to the extruded material shown previously. The SLM GRCop-42 samples demonstrated slightly higher elongation compared to the GRCop-42 extruded material. The SLM material in the as-built (non-HIP) condition exhibits high residual stresses and higher strength, but the elongation is greatly reduced [15]. This demonstrates the needs for at least a post-build stress relief heat treatment to achieve good ductility.

Additional mechanical test data was completed at a series of temperatures including elevated temperatures similar to chamber hot wall operating conditions. The datasets show repeatable properties and low scatter. The ultimate tensile strength can be seen in Fig. 8. While the SLM GRCop-84 exhibits an average of 8% higher ultimate strength at 20°C, the SLM GRCop-42 has similar strength above 200°C. This is caused by decrease in the pure Cu matrix strength and its inability to transfer stress to the Cr<sub>2</sub>Nb particles as efficiently at elevated temperatures. The result is the two alloys have similar strengths above 200-400 °C. The strength remains generally superior to competitive alloys in this temperature range, and exposure of the GRCop alloys to these temperatures has minimal impact on the properties.

The 0.2% yield strength as a function of temperature can be seen in Fig. 9. While the SLM GRCop-84 exhibits an average of 14% higher yield strength at 20-400°C, the SLM GRCop-42 has similar strength above 600°C. This is one of the major properties that must be traded to get the higher thermal conductivity offered by GRCop-42.

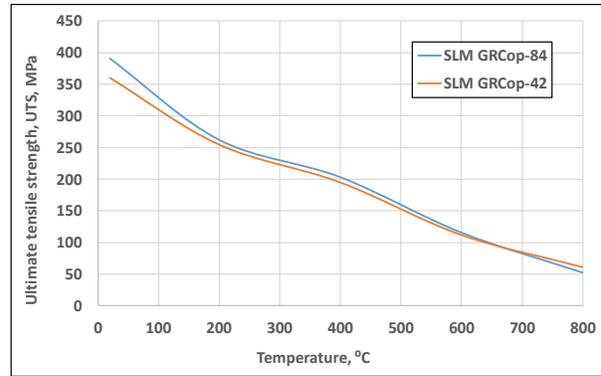


Fig. 8. Ultimate Tensile Strength vs Temperature of SLM GRCop-84/-42.

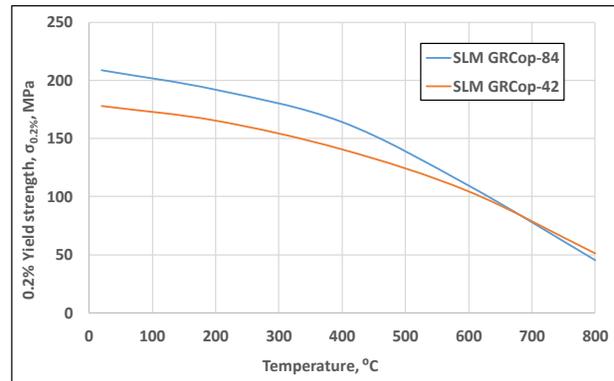


Fig. 9. 0.2% Yield Strength vs Temperature of SLM GRCop-84/-42.

For a given chamber operating pressure, the minimum wall thickness of a liner must be increased to lower the stresses to acceptable levels. How that affects thermal gradients, hot wall temperatures, thermally induced strains and other design considerations must be examined and will require iterations to determine optimal designs in strength limited applications.

The ductility of GRCop-42 is generally superior to that of GRCop-84 at temperatures above 400°C (due to the Cr<sub>2</sub>Nb content of GRCop-84). Both alloys have sufficient ductility for most applications including liners, and will deform large amounts without failure. The elongation is shown in Fig. 10 and the reduction in area is shown in Fig. 11.

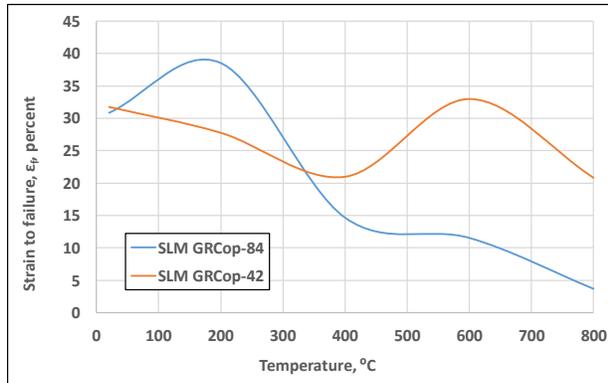


Fig. 10. Elongation vs Temperature of SLM GRCop-84/-42.

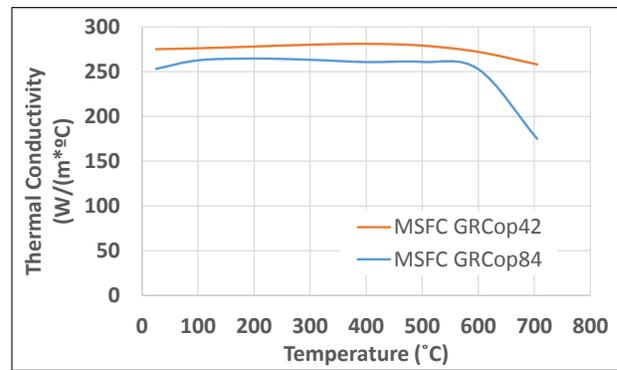


Fig. 12. Thermal Conductivity vs Temperature of SLM GRCop-84/-42.

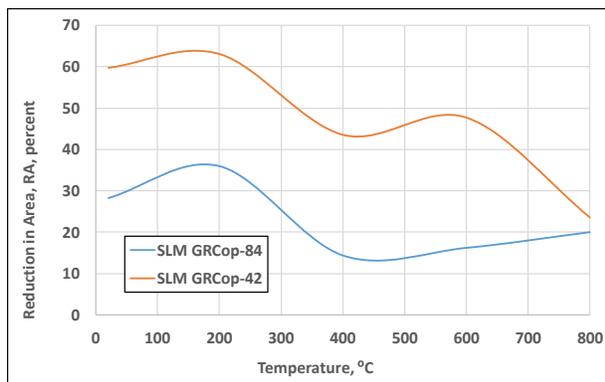


Fig. 11. Reduction in area vs Temperature of SLM GRCop-84/-42.

Thermal conductivity was also measured with the SLM samples and as-expected the GRCop-42 demonstrated a 5-8% higher conductivity than the GRCop-84 (Fig. 12). The observed decrease in the thermal conductivity at the highest temperatures is a result of the excess Cr dissolving into the Cu matrix. Generally, GRCop-84 has more excess Cr, and the effect is greater. If critical, the amount of excess Cr could be reduced, but there might be hydrogen embrittlement issues with hydrogen- and maybe methane-propellant applications.

While not shown in the details of this paper, prior publications demonstrated details on the surface finish of the GRCop materials [9,10,23]. There is additional development being completed to further improve surface finish.

The GRCop-42 and GRCop-84 process parameter development yielded the desired initial values for density, mechanical and thermophysical properties, and surface finishes. Additional improvements are being still made as experience is gained, but successful printing, mechanical testing, and hot-fire testing to be described later in the paper have been successfully achieved. The GRCop-42 process parameters resulted in an improved processing time compared to the GRCop-84, with an approximately 20% reduction in build time. MSFC and GRC, along with industry partners, have demonstrated that both are readily printable alloys that can be additively manufactured into fully dense components with consistent properties.

The powder supply chain improved with more vendors capable of meeting the powder specifications with GRCop-42 compared to GRCop-84. The ability to meet the GRCop-42 chemistry and vendor competition also reduced powder pricing, making the overall process more economically attractive.

#### 2.4 Post-Processing Considerations for Chambers

Successful development of SLM chambers placed considerable emphasis on the post-processing after initial build and removal from the build box. Based on experience, much of the overall fabrication time is post-processing of the parts to ensure full part integrity and removal of all loose powder prior to HIPing. Post-processing of combustion chambers presents additional challenges for AM due to the complexity of the small internal features. The post-processing considerations include: powder removal and verification of clear channels, build plate removal, HIP, machining, welding, inspections, and flow testing. A generic flow diagram is shown in Fig. 13. A more detailed process discussion was presented in [10]. It should be noted that additional operations are required when the bimetallic combustion chambers are fabricated using a structural jacket.

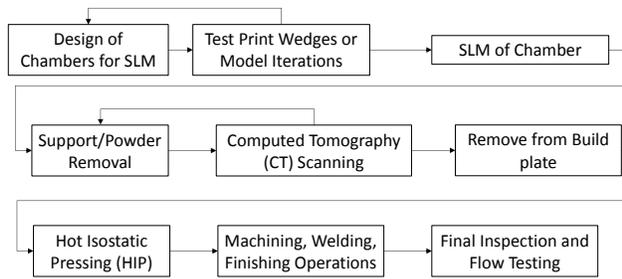


Fig. 13. General SLM additive process for chambers.

Powder removal is a critical step and several chambers have been scrapped due to inability to fully remove powder after an AM build. Trapped powder can be caused by a variety of mechanisms, including residual moisture, design features, excessive local heating during the build, build failures (short feed, deformation from residual stresses, re-coater arm impacts), oxidation, and surface finish. Various techniques are used for powder removal including manual removal, vacuum and compressed air, shaker tables, and rotational and variable frequency machines. It should be noted that analysis or proper precautions may be needed for the powder removal process as fatigue loads could be introduced that could affect part integrity.

The most common technique to verify powder removal is computed tomography (CT) scanning. This allows confirmation of successful powder removal. An example of a CT scan on a GRCo alloy combustion chamber can be seen in Fig. 14; it is evident which channels are clear and which channels are still packed with powder. Any fluids should be avoided until full powder removal can be verified.

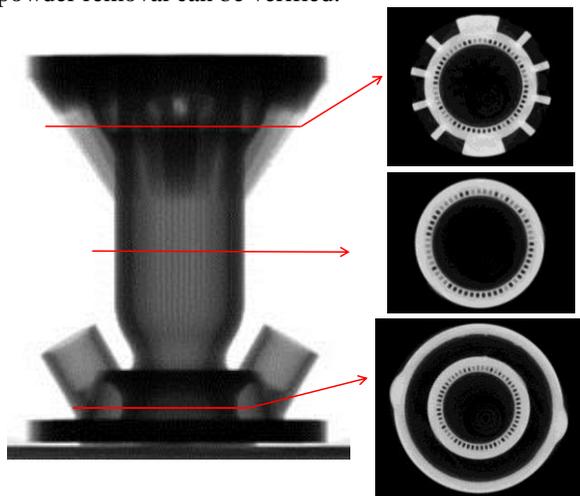


Fig. 14. Computer Tomography (CT) post-processing of chamber showing clogged and cleared channels.

Once powder removal was verified for the chamber, it was removed from the build plate. This was typically accomplished with electro discharge machining (EDM), although a band saw has also been used. The choice of

cutting technique will depend on requirements and available material included in the build between the part and the build plate. HIPing was used to both reduce residual stresses and close any remaining porosity to bring the GRCo to full density. Complete closure of the pores is critical to prevent blistering when using high pressure hydrogen as a fuel.

Following HIP, traditional operations can be completed such as machining of interfaces, welding operations, porting, and any finishing operations. Generally speaking, GRCo alloys can be easily machined with carbide tooling and respond similar to other high-strength copper alloys. It is also at this phase of the process that a bimetallic jacket would be applied if necessary using a secondary directed energy deposition (DED) AM process. Following all operations, the chambers completed final dimensional inspections and flow testing.

### 3. AM Bimetallic Jacket Development

In some high pressure and large scale chamber configurations, a structural jacket is necessary to handle radial and axial loads. An optimized design makes use of higher-strength to density material, typically a nickel based superalloy, providing a higher strength to weight ratio [16,17]. A secondary AM process is used to apply the structural jacket. Several processes have been evaluated for the jacket including:

1. Blown Powder DED
2. Electron Beam DED
3. Laser Wire DED
4. Arc-based DED
5. Coldspray

Each of these have advantages and disadvantages that have been discussed in prior papers [Ref 18,19,20]. At MSFC, development has been focused on the blown powder DED and electron beam DED. The blown powder DED fabrication technique uses a coaxial nozzle with a central laser source and powder injected (or blown) into the laser focus creating a melt pool and material deposition. The powder is accelerated, or blown, into the melt pool using an inert carrier gas to allow for minimal or reduced oxidation in the high temperature deposition/weld. This DED head system, with integrated focus optics and blown powder nozzle(s), is attached to a robot or gantry system that controls a toolpath defined by the CAD model. NASA has demonstrated the blown powder DED technology using Inconel 625 on both standard and hybrid (integrated machining) DED systems [21].

NASA also demonstrated the use of a bimetallic jacket through the EBF<sup>3</sup> at LaRC under the LCUSP program. Under LCUSP, a GRCo-84 SLM liner was fabricated in 2-pieces and an Inconel 625 jacket was applied. The EBF<sup>3</sup> uses a wire-fed electron beam energy

deposition approach and applied the Inconel 625 structural jacket on the length of the chamber including the manifold preparations. The manifolds were then traditionally welded using Electron Beam (EB) welding. An example of the LCUSP 35K-lb<sub>f</sub> thrust chamber can be seen in Fig. 15.

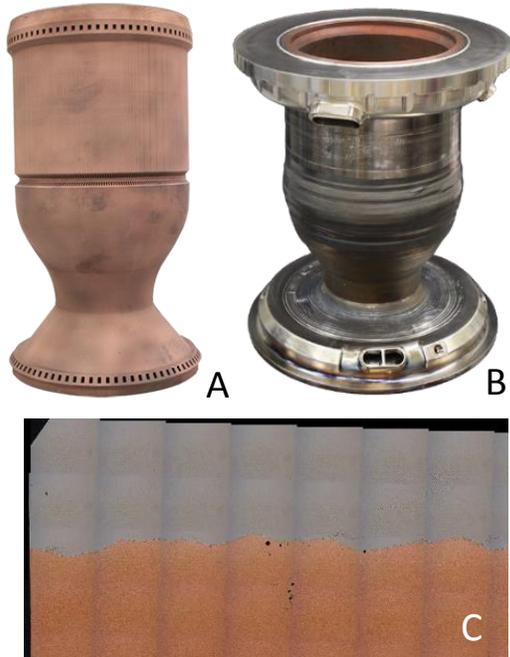


Fig. 15. Bimetallic LCUSP Chamber Development  
a) SLM 2-piece GRCop-84 liner, b) Chamber with EBF<sup>3</sup> Inconel 625 structural jacket, c) Mixing of Inconel 625 with GRCop-84 liner.

Several lessons were learned during the bimetallic development, including deposition toolpath strategy, proper diffusion and mixing of the Inconel 625 and GRCop base alloy, and shrinkage of the throat and overall length. In some development chambers, nearly 10% shrinkage was observed. The EBF<sup>3</sup> used the highest heat input with the electron energy source, but required high heat to achieve good penetration of the Inconel 625 into the copper [22]. The blown powder did provide some reduction in heat with less distortion, but chambers still experienced 3-9% shrinkage.

#### 4. Chamber Hot-fire Testing Results

NASA has fabricated and tested over 20 different SLM GRCop-alloy, channel-cooled, combustion chambers since 2016. Chambers have all been constructed using the previously described AM technology, with some units incorporating the bimetallic AM jacket. The thrust chambers tested ranged operated with Pc's from 200 to over 1,400 psia in a variety of propellants and mixture ratios, producing 1,000 to 35,000 lb<sub>f</sub> thrust. The propellants demonstrated in this testing

included LOX/LH<sub>2</sub>, LOX/GH<sub>2</sub>, LOX/RP-1, and LOX/LCH<sub>4</sub>, and all hot-fire testing was conducted at MSFC Test Stands 115 and 116. These chambers were typically regeneratively-cooled with fuel; in addition, some chambers were cooled with water to characterize heat flux performance. MSFC has accumulated over 385 starts and 20,000 seconds on various AM GRCop-alloy and AM bimetallic chambers. The design of AM GRCop-alloy chambers has been discussed in prior literature [10,11,23]. From experience, the two main adjustments to the design process for AM SLM regenerative cooling chambers reside in accounting for the minimum feature size that can be reliably built using SLM and the resultant surface finish [23]. There are also complex geometric features, such as channel geometry and flowpaths that could not be manufactured with traditional techniques.

The initial SLM GRCop-84 chambers that completed hot-fire tested used LOX/LCH<sub>4</sub> at 4000 lb<sub>f</sub> thrust-class. A throat section was successfully regen-cooled with liquid methane during its testing in 2016 and further allowed thermal models to be developed to characterize two-phase flow, which occurred during the subcritical coolant's phase change. This chamber design went through a few design iterations to further optimize performance and weight. A series of modified methane cooled chambers later demonstrated active throttling, as shown in Fig. 16, with full regen-cooling with an as-built surface of the coolant channels. Smaller methane cooled chambers for 1,000 lb<sub>f</sub> thrust were also developed and successfully tested with active throttling capabilities. To date, a total of 8 designs of GRCop methane chambers have been tested accumulating over 2,600 seconds and 72 starts. These chambers were developed for technology development in NASA's lunar lander programs and provided critical performance data of methane cooling.

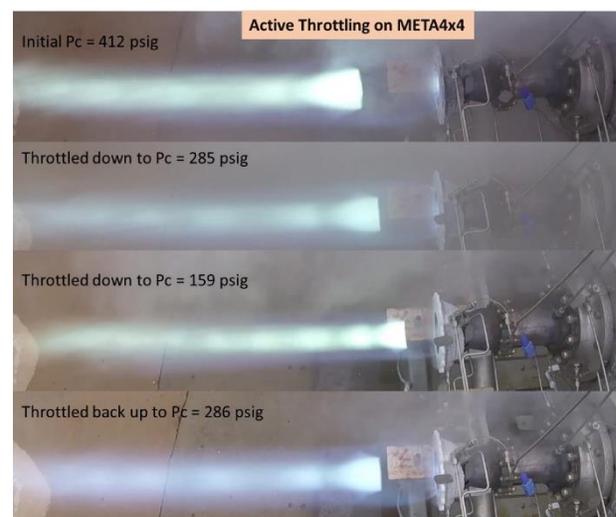


Fig. 16. Throttling of Methane-cooled SLM GRCop-84 supporting lunar lander engines.

Several of the 1,200-2,400 lb<sub>f</sub> thrust chambers units served as workhorse hardware to hot-fire test a variety of new SLM injectors, along with channel-cooled nozzle designs and carbon-composite nozzle extensions [24]. These chambers included SLM GRCop-84 and later GRCop-42 liners. Test conditions, including Pc's, MR's, and coolant flow rates, were varied to challenge the SLM-fabricated chambers. Fig. 17 shows one of the tests with a Carbon-Carbon (C-C) nozzle. As part of this testing, chambers fabricated on different machines and with slightly different build parameters were evaluated. Some liners from industry partners were fabricated with 50% reduction in surface roughness (indicated by profilometer and optical measurements) that resulted in a more than 20% reduction in coolant pressure drop.

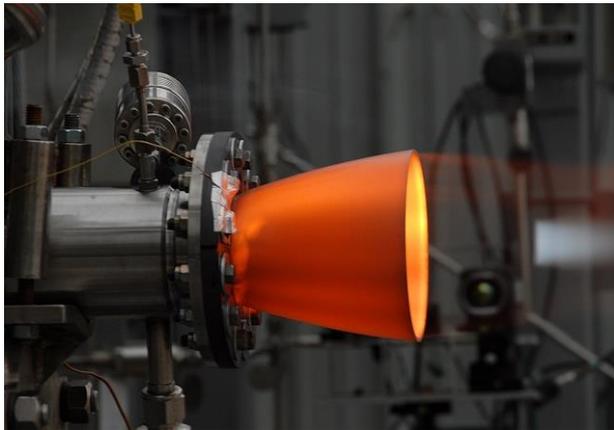


Fig. 17. Hot-fire testing of 1.2K LOX/GH<sub>2</sub> SLM GRCop-84 liner with C-C nozzle.

A high duty cycle test series was completed on 2,100 lb<sub>f</sub> thrust SLM GRCop-42 chambers to demonstrate performance and durability of the hardware. This LOX/GH<sub>2</sub> thruster was tested in early 2019 using a water-cooled liner. It was exposed to long duration tests (180 seconds) and multiple cycle tests [25, 26]. A total of 188 tests were completed on the two GRCop-42 liners, accumulating a combined 8,030 seconds of test time. The conditions included Pc's up to 1,224 psig and MR's up to 8.0. The high MR testing was completed at the end of the series to fully demonstrate chamber liner durability. The first GRCop-42 liner completed 168 tests and a total of 7,400 seconds (Fig. 18).

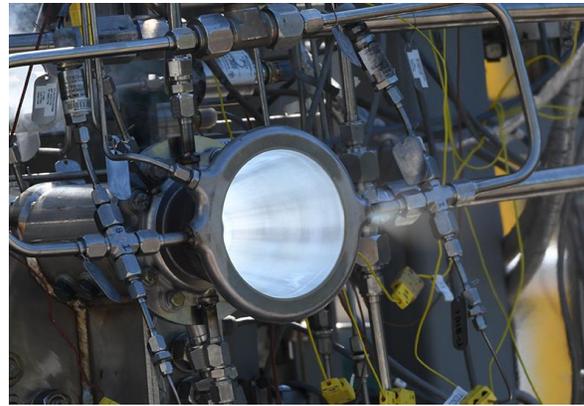


Fig. 18. High Duty Cycle Testing on AM GRCop-42

Sustained peak wall temperatures were demonstrated up to 727°C (1,340 °F) on the SLM GRCop-42 liners. Results showed the resilience of the material at these elevated wall temperatures with consistent performance throughout the test series. The hot-fire testing demonstrated aggressive conditions with high Pc/MR and subsequent heat loads. The chambers were run aggressively to promote the environment for potential blanching, but none was observed in the liners. The liner surface remained smooth and showed good oxidation resistance.

NASA completed the full development and hot-fire testing under the LCUSP program for a bimetallic AM GRCop-84 chamber at 35,000 lb<sub>f</sub> thrust. Testing demonstrated the key AM technologies: GRCop-84 SLM and EBF<sup>3</sup> Inconel 625 jacket, in a relevant environment, testing the AM LCUSP chamber and the one piece AM cooled nozzle to 100% of design conditions.

The LCUSP test program was conducted at Test Stand 116 from October 2017 through March 2018. Both an AM bimetallic full length chamber (Unit 3.0) and a shortened chamber (Unit 2.2) were tested in the program. Fig. 19 shows one unit installed for testing. The copper-Inconel joint performed well, indicated by the successful hot-fire test campaign at 100% power level (1,400 psia and MR=6.2) including the cryogenic shock during startup. Testing provided excellent data on articles manufactured with these technologies and even successfully demonstrated a unique chamber repair made after blocked cooling passages were discovered after initial testing.

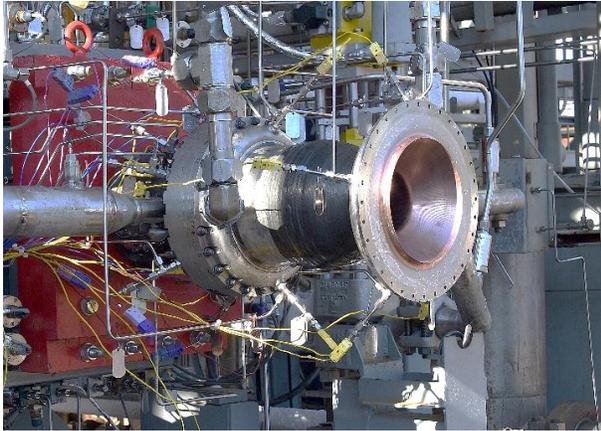


Fig. 19. LCUSP Bimetallic AM chamber installed in the test stand. Fig 1 shows LCUSP chamber during hot-fire.

An additional hot-fire test series was completed on subscale bimetallic chambers using LOX/RP-1 at 2,100 lbf thrust with development partner Virgin Orbit. These chambers demonstrated a bimetallic jacket using the blown powder DED process. This was developed on a hybrid blown powder DED/subtractive machine [21].

NASA also completed initial feasibility testing in late 2018 with a lightweight chamber design. For this unit, the structural layer on the chamber was created with a composite overwrap (of carbon fiber) to reduce weight by 30%, compared to the same size chamber with a superalloy structural jacket. Fig. 20 shows this unit being hot-fire tested. These chambers are part of the Rapid Analysis and Manufacturing Propulsion (RAMPT) program where a series of larger thrust and more aggressive composite overwrap environments will be tested. The initial testing with the GRCop-84 liners demonstrated a series of aggressive wall temperature conditions, with temperatures exceeding 93°C (200°F) on the composite joint.

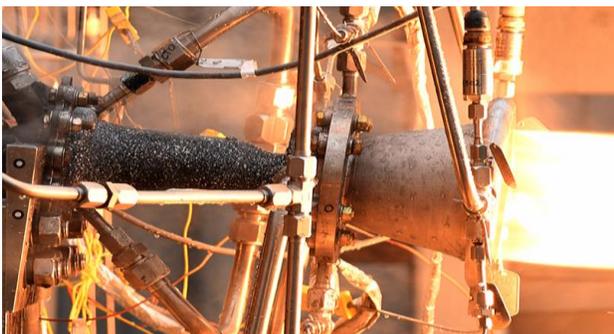


Fig. 20. Composite overwrap SLM GRCop-84 liner hot-fire testing under RAMPT program.

NASA is continuing to advance the SLM GRCop-42 and GRCop-84 development in a GE Concept Laser M2, EOS M290, and EOS M400 SLM machines. The latter EOS M400 provides a larger build volume to

accommodate larger combustion chambers for upper-stage and boost class engine applications, as shown in Fig. 21. In addition to internal NASA development work, several vendors are providing GRCop-42 and GRCop-84 as a commercial printing service. Initial material properties from these vendors are included in this paper and updated results will be distributed in future publications.



Fig. 21. Large-scale SLM GRCop-42 chambers fabricated (Diameters ~15" and Heights ~14").

The SLM development work supports NASA projects including Engine Advanced Manufacturing for MSFC's Liquid Engines Office (LEO), the RAMPT project, Lunar Lander applications, Nuclear Thermal Propulsion, and NASA's Space Technology Mission Directorate (STMD) Announcement for Collaborative Opportunity (ACO) program with commercial space partners. Several of these projects are making use of the current scale and evaluating the larger scale. NASA will complete hardware fabrication and hot-fire testing of the larger GRCop-42 chambers in early 2020. Investments are being made by NASA in the material characterization and property database to further enable the technology readiness and process maturity. Test samples from the existing scale build platforms (M2, and M290) and the EOS M400 will complete a series of mechanical and thermophysical property testing to develop a design database for the SLM GRCop-42 and GRCop-84. This data is being tested continuously and will be made available to industry partners and general industry.

## 5. Conclusions

NASA has completed development using AM for process development, material characterization, property databases, and hardware fabrication of GRCop-42 and GRCop-84 thrust chambers. General lessons learned and comparisons of the AM SLM GRCop-84 and GRCop-42 alloys were determined:

- 1) GRCop-alloys are readily printable using SLM,
- 2) Full density can be achieved with consistent properties across several SLM/L-PBF machines,

- 3) SLM GRCop-42 offers 5-8% higher conductivity over SLM GRCop-84,
- 4) SLM GRCop-42 offers higher ductility over SLM GRCop-84,
- 5) GRCop-84 offers higher ultimate and yield strength over SLM GRCop-42,
- 6) SLM GRCop-42 showed 20% reduction in processing time compared to SLM GRCop-84,
- 7) GRCop-84 and GRCop-42 showed resistance to oxidation during aggressive test environments and high sustained wall temperatures,
- 8) GRCop-84 and GRCop-42 demonstrated resistance to blanching during high duty cycle hot-fire testing with high Pc and MR.

NASA has fabricated and tested over 20 different AM GRCop-alloy channel-cooled combustion chambers since 2016. GRCop-alloy and AM bimetallic chambers tested at NASA have accumulated over 385 starts and 20,000 seconds. The test conditions ranged from 200 to over 1,400 psia in a variety of propellants and mixture ratios, producing 1,000 to 35,000 lb<sub>f</sub> thrust. The propellants demonstrated in this testing included LOX/LH2, LOX/GH2, LOX/RP-1, and LOX/LCH4. Most chambers were regeneratively-cooled using the fuel, while water coolant was used in specific tests to characterize heat flux environments.

High duty cycle testing was demonstrated on a SLM GRCop-42 liner, accumulating over 168 starts and 7,400 seconds. No signs of blanching or degradation were observed, and the liner remained in excellent condition. Sustained peak wall temperatures were demonstrated above 727 °C on SLM GRCop-42 liners at MR greater than 8 for LOX/H2. Similar temperatures were also demonstrated during testing on SLM GRCop-84 chambers. All hardware performed well and the data showed the resilience of the material at these elevated wall temperatures with consistent performance throughout test series. Several developmental hot-fire test series demonstrated aggressive conditions with high Pc, MR and subsequent heat loads. The chambers were run aggressively to promote the environment for potential blanching, but none was observed in the liners.

NASA is continuing to advance the technology for AM GRCop-84 and GRCop-42 combustion chambers. Several U.S. vendors have and are being established to provide these designs as a commercial printing service and NASA is using vendor-supplied chambers as part of development testing under various programs. NASA recently demonstrated large-scale SLM of a GRCop-42 chamber in an EOS M400 and achieved properties consistent with the Concept Laser M2 material. Several large-scale chambers have been fabricated and will be tested in the future. Mechanical and thermophysical property testing of the SLM GRCop-84 and GRCop-42 is being completed to develop a design database and

disseminate data to industry partners and general industry.

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