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Development of New Rocket Engine Liner Materials Based on Copper Alloys with Diamond Particle Additions

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Abstract

Novel copper-diamond materials containing particulate dispersions of diamond within a copper alloy matrix have been produced as next-generation rocket engine combustion chamber liner materials. These Copper-Diamond (Cu-D) composite materials have significantly higher thermal conductivity than conventional liner materials and have the potential to increase the engine performance significantly. Liner fabrication techniques include hot pressing and spark plasma sintering (SPS), which are capable of scale up to full-size production parts. The materials have been evaluated for thermal cycling resistance and ease of manufacturing. The results indicate great promise of these materials and associated economics to replace state-of-the-art combustion chamber liner materials such as GRCop-84 and NARloy-Z. Combustion chamber fabrication processes are also discussed, including SPS and additive manufacturing.

1.0 Introduction

Liquid-fueled rocket engine combustion chamber liners are regeneratively cooled to maintain a high heat flux so that the liner surface temperatures are well below the melting point of the liner. NARloy-Z (Cu-3 wt.% Ag-0.5 wt.% Zr alloy) is the state-of-the-art material used to make the liner in engines such as RS-25 and RS-68. The current trend is to develop copper alloys with higher alloy content (e.g., GRCop-84, which contains 8 at.% Cr and 4 at. % Nb) to improve high temperature capability. However, higher alloying results in a lower thermal conductivity (25% lower than Cu for GRCop-84). To alleviate this problem, it was proposed to use diamond particles in a NARloy-Z matrix. The reported thermal conductivities of diamond vary, but can be 3 to 6 times that of copper (Ref. 1). Addition of 40 vol.% of diamonds (~16 wt.%) could nearly double the thermal conductivity of NARloy-Z based upon a rule of mixtures calculation – a huge benefit. An additional benefit is lower density. NARloy-Z-40%D composite is >25% lighter than NARloy-Z. In the early days of research in this area primary goal was to increase the thermal conductivity of copper by blending diamonds with copper powder and sintering the blended powder at elevated temperatures to produce a fully dense composite. It was targeted to nonstructural applications such as thermal management in electronics applications (Ref. 1). For structural applications in propulsion systems, however, materials with good mechanical properties are needed; thermal conductivity alone is not sufficient. The applications include components in advanced earth-to-orbit propulsion, in-space propulsion, and nuclear thermal propulsion systems. Component examples include combustion chamber liners, injectors and heat exchangers (Ref. 2). Combustion chamber liner is probably the most challenging application and it is the focus of this paper. Benefits of higher thermal conductivity depend on the engine design and appear to be highly significant for the expander cycle engine such as the Next Generation Engine (RL10 –NGE). The first attempt to develop such multifunctional composite material was reported in Ref. 2.

This paper gives an overview of the development of advanced rocket engine liner materials based on copper alloys with diamond particle additions. In the next section (section 2) thermal conductivity of copper-diamond (Cu-D) composite is explained. Contact thermal resistance between diamond particles and copper matrix is discussed in some detail. The effects of diamond particle size and the role of carbides at Cu-D interface are described. Processing techniques are discussed next in section 3. Topics discussed are: mixing techniques for copper powder and diamond particles, consolidation techniques such as hot pressing and Spark Plasma Sintering (SPS) and machining. Section 4 presents and discusses thermal and mechanical properties of Cu-D composites. Section 5 focuses on fabrication techniques to make liquid rocket engine components using Cu-D material and associated challenges and approaches used. The paper concludes with a discussion of advancing the technology readiness level of Cu-D composites for chamber liner applications.

2. Thermal Conductivity of Cu-D Composites

For liquid rocket engine combustion chamber liner applications, copper-based alloys are in use today because they are the most effective low-cost solution for handling extreme heat fluxes in throat locations in regeneratively cooled designs. ‘Pure’ copper has higher thermal conductivity than copper alloys with a value that can exceed 400W/m.K; however, it is of low strength and lacks high-temperature creep resistance. Alloying copper with other elements has been developed for increased high-temperature strength and creep resistance up to service temperatures of 450-550ºC at the expense of some modest loss in thermal conductivity. For instance, the preferred alloys for NASA liquid engine applications are NARloy-Z and GRCop-84, which have estimated thermal conductivities of 320 W/m.K and 300 W/m.K respectively, compared to 360 W/m.K for ‘pure’ copper (consolidated by PM route). The ability of diamond to enhance effective thermal conductivity in Cu-based alloy designs enables lighter weight, higher thermal conductivity and intrinsically strong, creep-resistant liner materials to be developed. Early work on Cu-D composites done at Penn State (Ref.1) is shown if Fig. 1. It is interesting to note that a simple mixture of copper and diamond powders consolidated by FAST (Field Assisted Sintering Technology) did not show any improvement in thermal conductivity. However, significant improvement is observed when there is a carbide forming element such as Zr or Cr in the copper matrix.

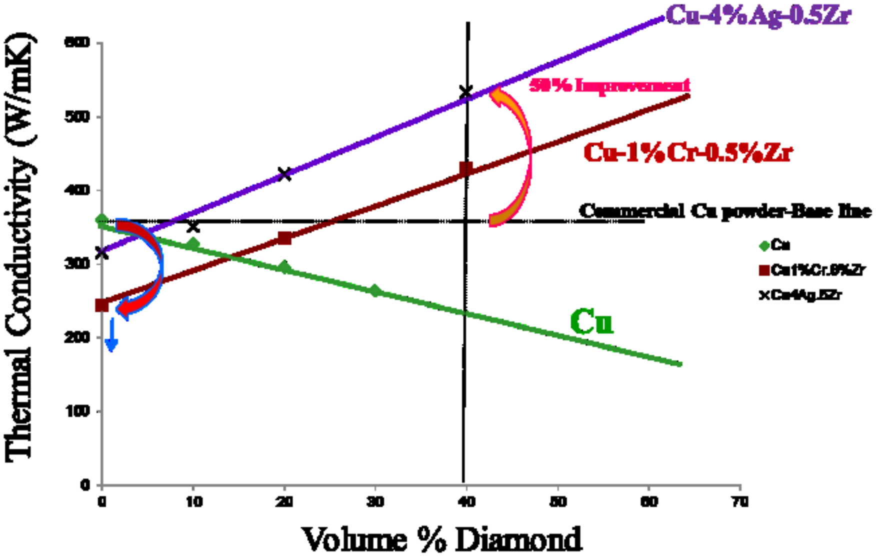


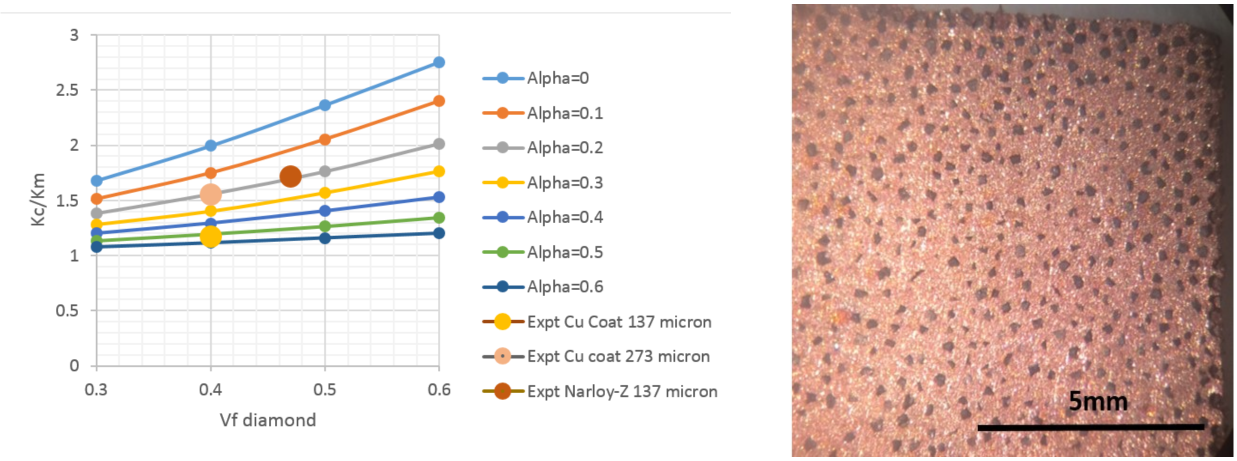
Fig. 1: Thermal conductivity of Cu-D composites (Ref. 1)

Modeling Thermal conductivity of Cu-D composites

Predictions of diamond-filled copper thermal conductivity have been attempted using solutions for the thermal transport problem. A commonly used relation known as the differential effective medium theory, or differential effective medium (DEM) scheme, comes from Bruggeman (Ref. 3) and modified by Hasselman et al (Ref. 4) to allow for interface resistance effects due to finite-size diamond particles. This relation is often used to estimate thermal conductivity for composites containing high volume fractions of thermally conducting particles above 30-35% loading as given below:

$$(1-Vf)^3 = \left[\frac{K_m}{K_{eff}}\right]^{(1+2\alpha)/(1-\alpha)} \left[\frac{K_{eff}-K_p(1-\alpha)}{K_m-K_p(1-\alpha)}\right]^{3/(1-\alpha)} \qquad (1)$$

where Vf is the volume fraction of particles, K_m, K_p, and K_{eff} are the thermal conductivities of the matrix, particle, and composite respectively, and α is a dimensionless parameter depending on interface thermal resistance (ITR) between filler particles and matrix. It is defined as $\alpha = a_k/a$, where a is the particle radius, and a_k is the Kapitza radius ($a_k = R_{int}.K_m$, where R_{int}= ITR). For α=0 the above equation requires perfect heat transfer across the particle-matrix interface. The thermal conductivity predicted vs. actually seen in a study of Cu-D composites by S. Pickard of Global Technology Enterprises (GTE) with well-dispersed diamond particle distributions (Ref. 5) is shown in Fig. 2. The values of thermal conductivity measured in this study for Vf=0.45 diamonds of 137 micron mean particle size (shown by red dot) exceeded 540 W/m.K, or 1.5 times the value for commercially pure Cu. The density of this Cu-D composite is 6.1 g/c.c., which is > 30% lower than for Cu alloys. We see that the best fit for the experimental data is for a value of the theoretical interfacial resistance parameter, corresponding to α = 0.2 in the equation above. This low value of α indicates that low interfacial resistance and high thermal conductivity has been developed through processing. For calculation purposes, thermal conductivity of 'pure' Cu is taken as 360 W/m.K, and thermal conductivity of diamond filler particles is assumed to be 1800 W/m.K, which is typical of mid-quality diamond.



(a) (b)

Fig. 2: (a) Plot of theoretical diamond-copper thermal conductivity (K_c) normalized by matrix conductivity (K_m) for various αvalues. Experimental data points are shown that fit to predictions at some α values; (b) Diamond particle distribution in wet-blended copper-diamond sample containing 40 vol. % of refractory carbide-coated diamond particles. Diamond particle size 275 microns (50/60 mesh). The sample was made using Acumet 500A copper powder of 17 micron particle size using hot pressing (Ref. 5)

S. Pickard has also examined phonon scattering at Cu-D interface (Ref. 6). He observed that presence of finite ITR between the diamond particles and the ‘pure’ Cu matrix arises from multiple sources including phonon scattering from the interface between dissimilar components (dissimilar in acoustic or elastic properties), heat carrier mismatch and weak bonding. Treating phonons according to wave theory, and assuming transverse acoustic waves at normal incidence, the (intensity) reflection coefficient at a boundary between two different elastic materials is given as:

$$R = \left[\frac{Z_1 - Z_2}{Z_1 + Z_2} \right]^2 \qquad (2)$$

where Z is the acoustic impedance, equal to the square root of the product of mass density and elastic modulus. Clearly, minimum reflection, and therefore maximum transmission, occurs when $Z_1 = Z_2$. Reflection, and therefore phonon scattering, increases as ΔZ increases. If we consider both matrix phase (Cu) and dispersed phase (diamond) of the composite to be semi-infinite, we should be able to obtain maximum transmission and therefore highest thermal conductivity by incorporating an intermediate impedance coating (analogous to an impedance-matching transformer in acoustics). In the case of thermal conductivity, the optimum acoustic impedance for a coating material would be:

$$Z_{coat} = \sqrt{Z_1 Z_2} \qquad (3)$$

Table 1 gives the acoustic impedance of several interface materials. Note that the acoustic impedance of refractory carbide ZrC is close to the optimum matching transformer impedance (~423x10^5 kg/ms) for a Cu-diamond interface, indicating potentially good thermal performance of adherent refractory carbide-coated diamond in Cu matrix alloys. In experiments with the Al-diamond system, thermal conductivity is poor without a nanometer thick SiC layer on the diamond, the use of SiC coating layer is also supported by the acoustic model which shows SiC acoustic properties are intermediate to that of Al and Diamond providing good matching at the interface.

Table 1. Acoustic impedance of selected ceramics and metals

	Al	**Cu**	**Diamond**	**SiC**	**ZrC**	**HfC**	**Si**	**Graphite**	**B4C**
k *(W/mK)*	200	360	3000	75	20	22	140	150	30
Z *(10^5 kg/ms)*	136	420	561	310	424	606	199	44	395
CTE (ppm/K)	24	18	3	5.3		5.8	5	6	5.6

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Coatings can be applied by a number of techniques, including chemical vapor deposition (CVD) and natural in situ carbide formation by diffusion. NARloy-Z-D composite is an example of the latter. Coating thickness needs to be optimized based on both wave theory and experiment.

Quantum Chemistry based Modeling of Kapitza Thermal Conductance

Smelyanzkii and Fogel have developed an analytical model of interface thermal resistance using quantum chemistry approach (Ref. 7). They used the term Kapitza thermal conductance instead of ITR. Their model also takes into account phonon interactions at the matrix-particle interface. Their approach focused on the Diamond-Copper matrix interface in NARloy-Z composite, which contains 0.5wt. % Zr. Zr is a known carbide former. The Zr in NARloy-Z matrix migrates and reacts with outermost atomic layers of diamond to form ZrC. Their findings are summarized in Table 2. The D/ZrC/Cu interface is shown to have a contact thermal conductance that is 3.5 times that of the direct D/Cu interface. These findings are of interest in alloy selection and processing approach to developing high thermal conductivity Cu-D composites. They also underscore the importance of controlling diamond-carbide-metal interfaces. Refractory metal carbides appear to be a good choice for improving the thermal conductivity. They also appear to govern the mechanical properties of the Cu-D composites. Cu-D interface voids and defects will adversely affect mechanical properties.

Table 2: Contact thermal conductance for various interfaces

Parameter Interface	Θm, K	σmax, kW/cm.K
D/Cu	310	6.6
D/Zr	250	3.5
D/Ag	221	2.4
D/ZrC	680	70
ZrC/Cu	310	35
D/ZrC/Cu	680/310	23

Notes: Here θ_m – temperature at maximum phonon frequency (kT = h x frequency where k is Boltzmann's constant and h is Planck's constant) – Debye's temperature is used for θ_m as an approximation. (Ref. 7)

3. Processing of Copper-Diamond Composites

This section discusses processing techniques used for making Cu-D parts, including material and process selection. Alloy powder and diamond particle size and distribution are important factors. Diamond particles may require coatings depending on the end application. Processing techniques include mixing, sintering and consolidation by hot pressing and spark plasma sintering. Fabrication techniques are introduced in this section, but discussed in greater detail in section 5.

Powder Selection – Copper & Diamond

Copper powders are readily available commercially either as pure copper, or as alloy powders. Alloy powders include NARloy-Z, Cu-Zr, GRCop-84 and more. Powder selection is based on cost, availability and performance requirements of the end product.

Diamond powders come in different particle sizes, from a few microns to a few hundred microns. As mentioned before larger diamonds have smaller surface to volume ratio and hence tend to give higher thermal conductivity. However, larger diamonds in the matrix make it more difficult to machine using conventional techniques. They also tend to increase surface roughness. Quality of commercially available diamonds varies and have variable thermal conductivity, typically in the range 1500 – 2000 W/mK.

Coating selection for Diamond

Diamonds can be used either coated or uncoated. If the alloy matrix has a carbide former in it (e.g., Zr, Cr) coating may not be necessary. If there is no carbide former in the matrix coating diamonds with a refractory carbide layer such as MoC, HfC or ZrC will be necessary. Coating process can be chemical vapor deposition (CVD), electrolytic or a combination there of. Carbide coatings generally use CVD process. Metallic coatings (e.g., Cu, Ni) use electrolytic process. Coating adhesion, thickness and coverage must be controlled for best results.

In addition to improving contact thermal conductance carbides improve the mechanical bond between diamond and copper alloy matrix, which is an important consideration in structural composites. Microstructural evidence suggests that free energy of formation (ΔG) of carbides is the main driver for atomic migration to diamond particle interface (Ref. 1). For example, zirconium carbide (ZrC) has a ΔG = -173KJ/mol compared to ΔG of -76 KJ/mol for chromium carbide ($Cr_{23}C_6$). In CuCrZr-D composite ZrC is found to dominate the interface. Furthermore, ZrC at the Cu-D interface appears to form a coherent boundary with copper matrix and helps to improve ductility. Naturally formed carbides tend to have better interfaces than coated carbides although heat treatment can in principle produce a good coherent interface. It should be possible to coat diamond with metallic Zr and form ZrC coating during sintering at elevated temperatures.

Mixing techniques

Powder metallurgy techniques are commonly used to process Cu-D composites. The basic process is simple: copper alloy powder is mixed with diamond particles and sintered in a die under pressure at high temperatures to form a fully dense part. Mixing is done in a blender such as turbula or acoustic mixer. Ball milling can also be used but diamonds can be abrasive. Diamond particles are much lighter than copper powder particles and tend to segregate easily during handling. Dry mixtures made this way tend produce parts with segregated microstructure as shown in Fig. 3. A binder such as isopropyl alcohol is often used during mixing (wet process) to help copper particles to adhere to diamond particles. Wet processing helps to reduce segregation and produce a more uniform microstructure (Fig. 3).

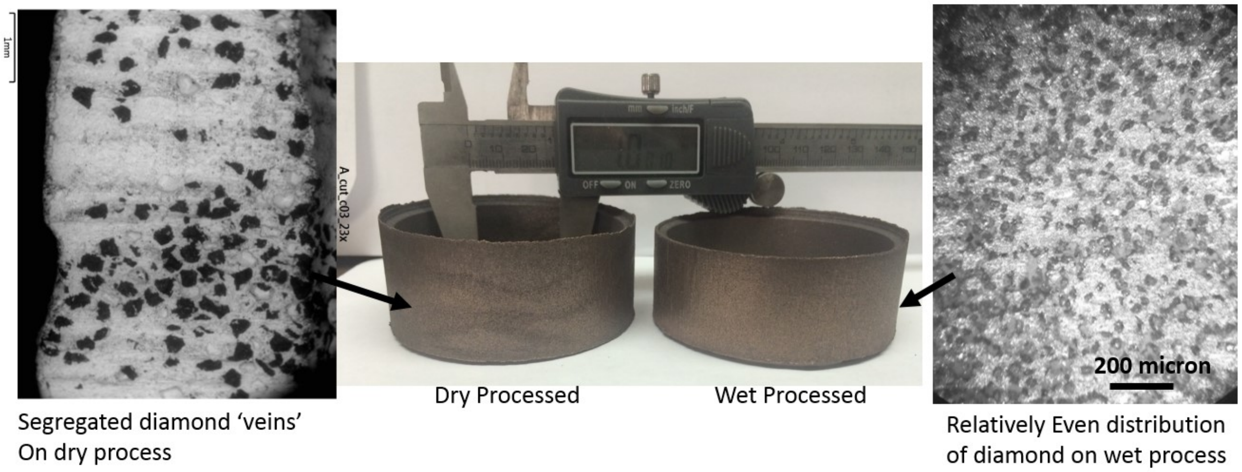


Fig. 3: Appearance of near net shape 2.75” OD x 0.125” wall x 1” tall copper-diamond rings containing Vf=0.4 diamond made by dry powder blending and by a wet process using a paste-like substance comprising the blended powder and isopropyl alchohol. The two types of powder blending were loaded into the dies and consolidated by hot pressing at GTE. The opening of the calipers in the image are 1”. (Ref. 5)

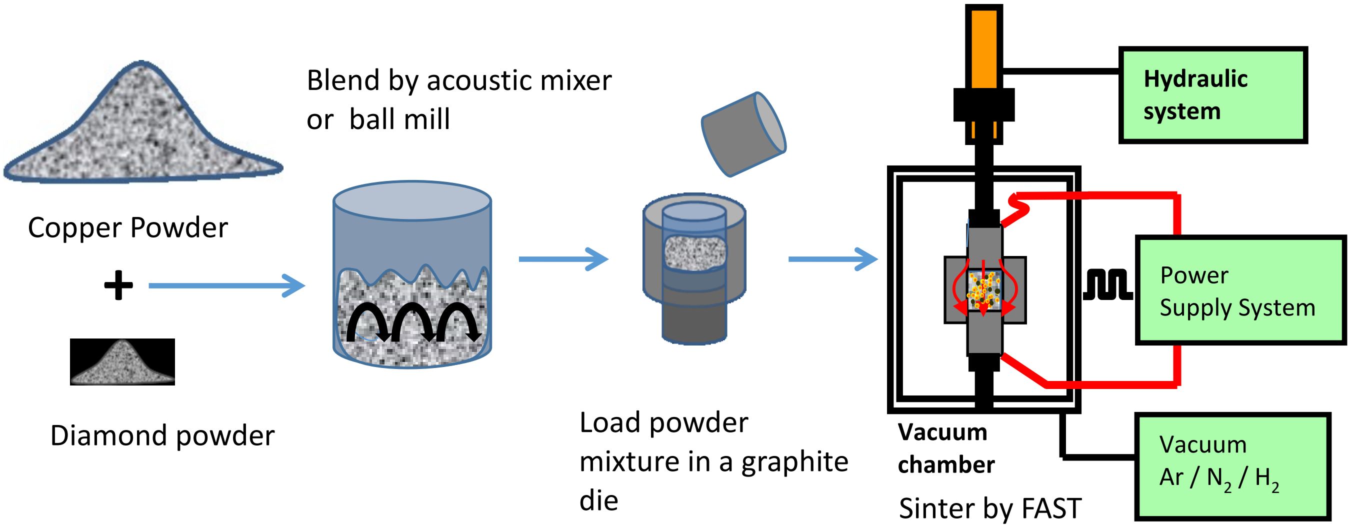


Fig. 4: Sequence of powder mixing and sintering by Field Assisted Sintering Technique (FAST)

Consolidation techniques

Different techniques are available for consolidating Cu-D composites: hot pressing (HP), hot isostatic pressing (HIP), microwave sintering, and spark plasma sintering (SPS, aka field assisted sintering technology (FAST)). SPS and HP appear to be the most commonly used techniques and are descibed below. All techniques aim to make full density parts. Full density (near 100% dense) is required for best properties.

Spark Plasma Sintering (SPS) or Field Assisted Sintering technology (FAST):
This process is shown schematically in Figure 4. Blended powder is poured into a graphite (or some other high temperature material) die and placed in the vacuum chamber of the FAST unit. After pumping down the powder is compresssed to high pressure (of the order of 10,000 psi). Powder is heated in two ways: 1) by heating the die in the furnace and 2) passing a pulsating current through the part being consolidated. Because of dual heating the heating rates are high and sintering occurs in a relatively short time, usually les than an hour. After sintering is complete the furnace is cooled and the die is taken out and the part removed.

Hot Pressing: Blended powder is poured into a graphite (or any aother suitable material) die and placed in a furnace chamber which is evacuated. Pressure is applied and held while the furnace temperature is raised to sintering temperature. Unlike SPS there is no direct current passed through the part. Heat transfer is relatively slow in this method and sintering times are much longer, of the order of hours. After sintering the furnace is cooled and the part is removed from the die. Table 3 below shows a comparison between SPS and HP techniques.

Table 3: Comparison of SPS and HP Consolidation for NARloy-Z-D composite

SPS consolidation conditions	HP consolidation
20 mins at 950C, 8 Ksi Pressure, fast heating (>500C/min) and furnace cooling	1 hr hold at 980C, slow heating, 3C/minute (in 700-980C range),3 hr cool down to 300C, 6 Ksi pressure

Machining

Diamond is the hardest material known and presents challenges for machining. Even diamond coated tools tend to wear quickly. Electrical discharge machining works well and has been used successfully to machine test specimens. Waterjet cutting is another method that works and has been used to make channels in NARloy-Z-D composite. From a machining perspective net shape manufacturing techniques discussed below are attractive and should be pursued where possible.

Additive Manufacturing

Additive manufacturing is a general term that defines a layer-by-layer fabrication method to form three-dimensional shapes as opposed to machining and joining multiple parts. Several types of additive manufacturing have evolved over the last decade and are being advanced for combustion devices component fabrication. This process has been used successfully to make combustion chambers out of GRCop-84 at Marshall Space Flight Center and looks promising for making chamber liners out of Cu-D composites. This approach is discussed further in section 5.

4. Properties of Copper-Diamond Composites

This section presents and discusses properties of Cu-D composites, including physical, mechanical and thermal properties that are important in design and fabrication of combustion chamber liners for advanced liquid rocket engines.

Tensile properties

Tensile properties of NARloy-Z-D composites tested at MSFC are shown in Table 4. Test specimens were EDM machined from a slab 0.25 inch thick. As expected ductility is low, especially for uncoated diamonds. NARloy-Z-CuD (copper coated diamond) gave the best tensile elongation at 2-3%. The tensile strength numbers are good and acceptable for chamber liner applications. In general the properties were highly variable, which is attributed to variable diamond segregation in the microstructure. Coated diamonds gave more consistent properties.

A few elevated temperature tests were also conducted. The tensile strength was 11 ksi for NARloy-Z-40D, at 935ºF. Tensile strength at 1000ºF appears to be a little lower for NARloy-Z-CuD probably because of dilution effect of copper in the coating.

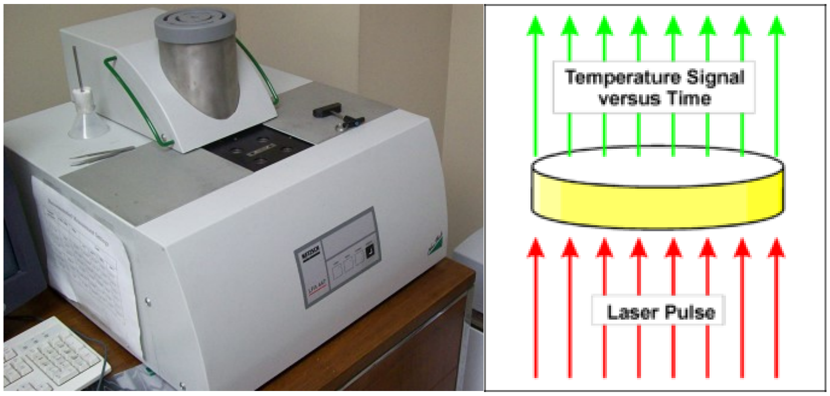
NARloy-Z-D was diffusion bonded with and without an interlayer of NARloy-Z powder. Bond strength was better for joints made with NARloy-Z inter layer at 11 ksi.

Table 4: Tensile properties of NARloy-Z-D composites (Ref. 8)

Sample type	Composition	Test temperature, Environment	YS, ksi	UTS, ksi	Elongation, %
NARloy-Z	Base line	75ºF, air	18	45	33
NARloy-Z-30D	30 vol% diamond	75ºF, air	19	19	<1
NARloy-Z-40D	40 vol% diamond	75ºF, air	18-20	18-24	<1
NARloy-Z-40D	40 vol% diamonds	935ºF, GN2	11	11	<1
NARloy-Z-30(Ti-D)	30 vol% Ti-coated diamond	75ºF, air	12	12-13	<1
NARloy-Z-30 (Cu-MoC-D)	30 vol% diamonds, Cu-MoC coated	70ºF, air	18	23	2-3
NARloy-Z-30 (Cu-MoC-D)	28 vol% MoC coated, copper over coated diamonds (from GTE)	1000ºF, 250 psi He	5-6	5-7	2-3
NARloy-Z-40D diffusion bonded using FAST	40 vol.% Diamond; (NARloy-Z used as bonding aid)	70ºF, air	10	11	<1

Thermal Conductivity

Thermal conductivity (TC) measurements of NARloy-Z-CuD composites were made by Dr. Aaron Rape of Momentive, Inc. using a laser flash method. He used Netzsch Nanoflash LFA447 apparatus (Figure 5).



A B

Fig. 5: Netzsch Nanoflash LFA447 thermal diffusivity measuring apparatus (A); schematic of laser flash method of measuring thermal diffusivity (B)

Thermal diffusivity is measured directly and thermal conductivity is calculated using the following relationships:

$$\text{Thermal diffusivity, } \alpha = 0.1388 \frac{d^2}{t_{1/2}} \tag{4}$$

where d = sample thickness, $t_{1/2}$ = time to half maximum temperature.

$$\text{Thermal conductivity, } K = \alpha c_p \rho \tag{5}$$

where c_p = specific heat and ρ = density.

Results are shown in Table 5 from the work done at GTE (Ref. 6). The following specific heat values are assumed: c_p (diamond)=0.560J/k.g, c_p (copper)=0.385 J/k.g, c_p (NARloy-Z)= 0.370J/k.g). c_p values for the composite are estimated by rule-of-mixtures calculations using the specific heat of the diamond and the metal matrix components multiplied by the weight fraction present.

It is clear from the this table that powder blend gave variable thermal conductivity, which is attributed to variable diamond segregation. Electroplated powders appear to give consistently better results because of better microstructure.

Table 5. Thermal conductivity data for Cu-diamond samples with both ‘pure’ Cu and NARloy-Z matrixes measured at RT (Ref. 6)

Diamond Size (micron)	Coating Type	Sample thick. mm	Vf % dia., (Grade)	Matrix	Density, ρ g/cm3	Specific heat, c_p (j/k.g)	Diff. α cm2/sec	Calc. k (W/m.K)	Consol. method
137	RC	1.55	45, (M3)	Cu	6.50	0.426	1.58	438	EP,sps
137	RC	1.37	40, (M1)	Cu	6.78	0.420	1.48	421	PB,hp
192.5	RC	1.49	55, (M3)	Cu	5.98	0.442	1.91	505	EP,sps
273.5	RC	1.58	55, (M3)	Cu	5.98	0.442	2.12	562	EP,sps
273.5	RC	2.74	40(M3)	Cu	6.78	0.420	1.98	563	PB,hp
137	none	1.919	25.2,(M3)	NARloy-Z	7.7*	0.396	1.41	431	PB,sps
137	none	2.848	30.4,(M3)	NARloy-Z	7.41*	0.401	1.61	477	PB,sps
137	none	2.722	47, (M3)	NARloy-Z	6.47*	0.421	2.03	553	PB,sps
137	RC	2.848	51,(M1)	NARloy-Z	6.23*	0.429	1.38	369	PB,sps
137	RC	1.50	40,(M1)	NARloy-Z	6.79	0.413	1.15	322	PB,hp
192.5	none	1.257	40,(M3)	NARloy-Z	6.79	0.413	1.80	505	PB,hp

Notes: EP=electroplated, PB= powder blend, *=measured density, hp=hot press, sps=spark plasma sinter.

Additional points worth noting:

1) Larger diamond particle sizes result in higher thermal conductivity, which is most simply related to increased surface area-to-volume ratio as particles get smaller (interfacial thermal resistance increases).
2) Using diamond with no pre-coating produces highest conductivity values in the NARloy-Z matrix, whereas for a ‘pure’ Cu matrix, refractory carbide pre coating returns the highest reliable conductivity values. Use of no coating for ‘pure’ Cu-diamond composites results in highly variable and unreliable conductivity.
3) Hot pressing (HP) and SPS for carbide-coated diamond in ‘pure’ Cu appear to show similar thermal conductivity values for both consolidation approaches.
4) HP and SPS for uncoated diamond in NARloy-Z matrix indicate that SPS values may be slightly higher for the NARloy-Z matrix.
5) There is no difference in thermal conductivity of samples made using elecroplated Cu or made by powder blending.

Density

One important benefit of Cu-D composite is the lower density relative to copper and its alloys. As mentioned earlier 40 vol% of diamond in NARloy-Z can lower the density by nearly 30%. The combination of lower density and higher thermal conductivity will result in significantly lower mass for the combustion chamber liner. Actual weight savings will depend on the engine design. Table 5 gives the range of densities obtained in the GTE study.

Thermal Cycling Behavior

Thermal expansion coefficients (CTE) of diamond and copper are very different. Diamond has a lower CTE than copper and its alloys and this is a potential source of thermal stresses during heating and cooling. Any thermal cycle could potentially result in debonding at the Cu-D interface and loss of thermal conductivity (TC) and mechanical strength. Aaron Rape et al (Ref. 9) have studied this problem and reported the results for NARloy-Z-D composites. The CTE results are shown in Fig. 6.

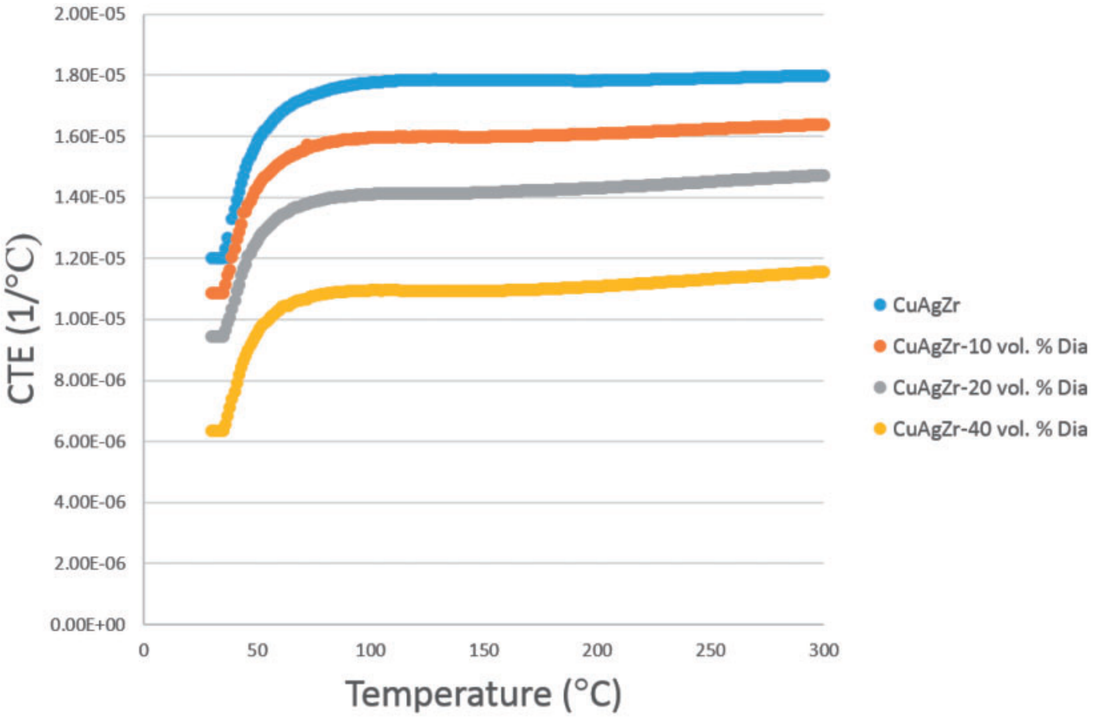


Fig. 6: Coefficient of thermal expansion for CuAgZr–diamond composite system showing the reduction of CTE with increasing diamond content.

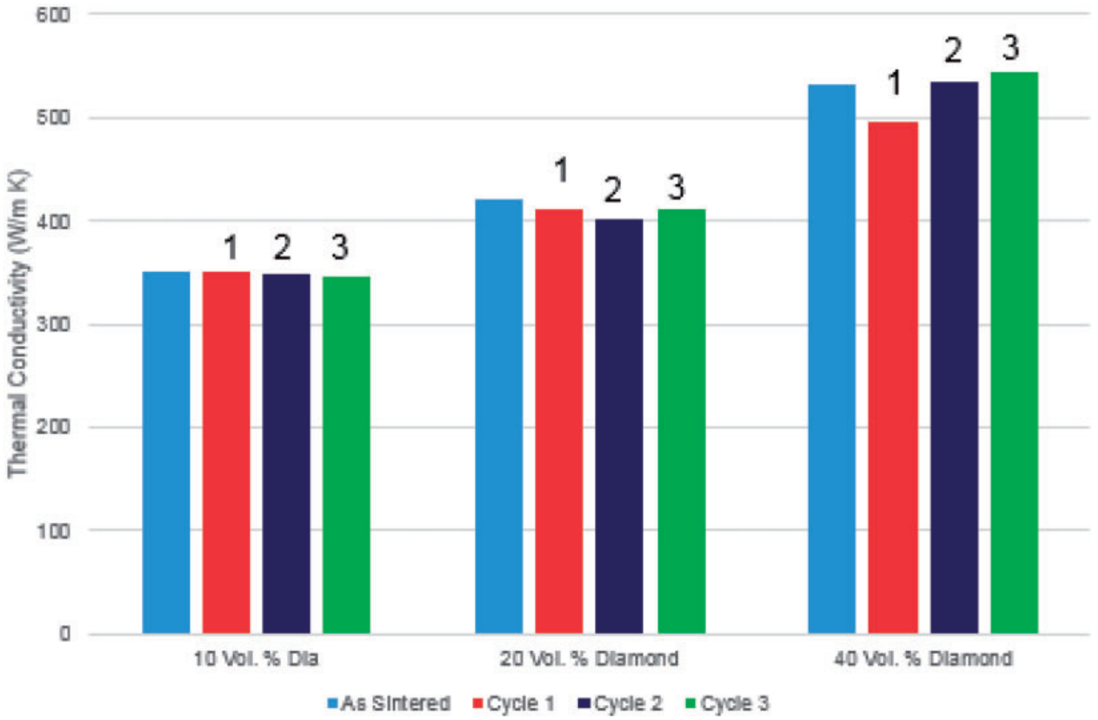


Fig. 7: Thermal conductivity results of CuAgZr–diamond samples after being exposed to thermal cycles (Ref. 9)

Thermal conductivity as a function of number of thermal cycles is presented in Fig. 7. In this figure, Cycle 1: -55-125°C, Cycle 2: - 55-155°C and Cycle 3: -55-200°C. These temperatures are typical for heat sink applications. The material did not suffer a loss of thermal conductivity due to the thermal cycles suggesting that no debond occurred between diamond and copper. This result is encouraging and indicative of good bond strength between ZrC and NARloy-Z matrix. Thermal cycles in a combustion chamber liner in a rocket engine will be more extreme: lower limit temperatures which may approach the temperature of liquid hydrogen (-253˚C), or liquid methane (-162˚C) fuels used with LOX oxidiser. Liquid nitrogen cooling (LN) to -192˚C is often used to simulate low-temperature cooling of the combustion chamber liner. At the high temperature end of operation the chamber liner, temperature may exceed 500˚C. GTE has studied the thermal cycling behavior of Cu-D composites in some detail (Ref. 6).

To simulate high temperature cycling, a relatively thin (1-3 mm thickness) thermal conductivity sample of the 'pure' Cu matrix Cu-diamond composite was heated in air to 450˚C in a resistance furnace and rapidly cooled by quickly removing the heated part from the furnace and placing it directly onto a 1"-thick aluminum cold plate at ambient temperature. Immediately afterward, the thermal conductivity of the sample was remeasured by laser flash. Table 6 shows the effect of a single cycle high-temperature excursion on the thermal conductivity of a 'pure' Cu matrix sample containing Vf=40% diamond, 274 micron size diamond, (full designation 274,M3.HP,PB). It can be seen that the thermal conductivity apparently increases slightly after the high-temperature thermal cycle (increase from 563 to 582 W/m.K), which may indicate measurement error rather than an actual change in conductivity.

To simulate low-temperature cycling under service conditions using LN, the thin thermal conductivity samples were plunged into LN and allowed to equilibriate at low temperature before being removed and allowed to equilibriate at room temperature prior to remeasurement of thermal conductivity. This constituted one low-temperature thermal cycle (from RT to -192˚C and back to RT). On 1 and 3 low-temperature thermal cycles of the 'pure' Cu matrix sample (that was previously subjected to the initial high-temperature cycle in Table 6), the thermal conductivity dropped slightly by 3% of its starting value as shown in Table 7. Also shown in the table is the change in thermal conductivity after one low-temperature cycle for a 'pure' Cu matrix sample containing smaller size diamond made using lower quality M1 diamond, which shows a larger drop in thermal conductivity of 8.7% suggesting a possible debond at Cu-D interface.

Table 6. Changes in thermal conductivity on high-temperature cycling of "pure" Cu matrix Cu-D sample

Description	Vf% D in 'Pure' Cu	Starting K (W/m.K)	K after 1 cycle 450^{o}C, fast cool	% decrease in K
274 micron size diamond, 'pure' Cu matrix (274,M3.HP,PB).	40	563	582	(-) 3.5

Table 7. Changes in thermal conductivity on low-temperature cycling of "pure" Cu matrix Cu-diamond samples

Description	Starting K (W/m.K)	K after 1 cycle quench LN	K after 3 cycles	% decrease in K after one cycle
274 micron size diamond, 'pure' Cu matrix (274,M3.HP,PB).	563	557	545	3
137 micron size diamond 'pure'Cu matrix (137,M1,HP, PB)	420	384	NA	8.7

Data for effect of one low-temperature thermal cycle on samples of Cu-diamond with NARloy-Z matrix alloy containing various volume loadings of diamond are shown in Table 8. Fig. 8 shows the thermal cycling effects on thermal conductivity over five cycles for four different diamond contents in NARloy-Z matrix. Overall there is no significant change in thermal conductivity after multiple cycles, confirming the good bond strength of Cu-D interface in NARloy-Z matrix. Slightly larger drops in conductivity are seen with use of lower-grade M1 diamond that has been coated with refractory carbide for both matrix alloys.

Table 8. Changes in thermal conductivity, K, after low-temperature thermal cycling of NARloy-Z-Diamond composites.

Description	Vf% D in NARloy-Z	Starting K (W/m.k)	K after 1 cycle quench LN	% decrease in K
#1) 137 micron diamond, no coating (137, M3, SP, PB)	25.2	430.9	424.7	1.4
#2) 137 micron diamond, no coating (137, M3, SP, PB)	30.4	477.1	467.3	2
#3) 137 micron diamond, no coating (137, M3, SP, PB)	47.2	550	536.2	2.5
#4) 137 micron diamond, <u>Refractory carbide coating</u> (137, M3, SP, PB)	51.5	369	350	5.1

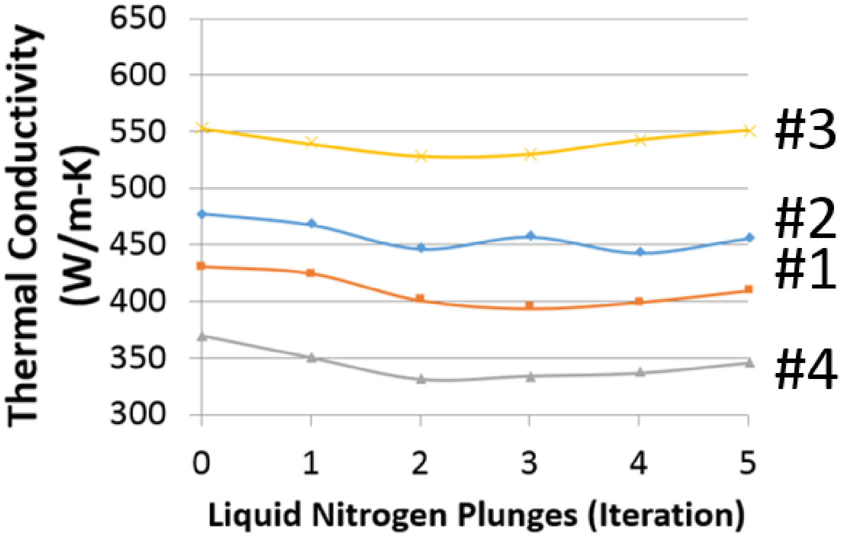


Fig. 8: Trends in thermal conductivity loss over 5 LN quench cycles in NARloy-Z-D composite.

5. Fabricating Copper-Diamond (Cu-D) Combustion Chamber Liners

This section covers the manufacturing aspects of combustion chamber liner using Cu-D composite material. It was clear from the beginning that powder metallurgy (PM) techniques will have to be used since diamond works best in particle (powder) form. PM techniques include hot pressing (HP), hot isostatic pressing (HIP), spark plasma sintering (SPS) - aka field assisted sintering technique (FAST). These techniques have been used successfully to prepare test coupons for both thermal conductivity and mechanical properties testing. Graphite dies are commonly used for processing the powder because of ease of machining and cost. Graphite is a refractory material, capable of withstanding high compressive loads used during sintering. Sintering occurs at elevated temperatures, close to the melting point of copper. Refractory metal alloys such as TZM Molybdenum are also used for dies if higher temperature and pressure capabilities are required. Selection of fabrication method depends on a number of variables, including part size and shape, and the materials to be used.

It should be noted that green density of starting Cu-D powder mixture is typically 30%-40% less than full density. When the powder is poured into the die and compressed there is a relative motion between the die and the plunger causing friction between the die and the plunger. To reduce friction a thin graphite film is often used as a lubricant (especially in metal dies) prior to loading the powder. Graphite dies offer a low friction surface and additional lubrication may not be necessary.

Fabricating full scale parts can be challenging. If the part shape is simple, such as a plate or right cylinder, the die will be simple. Complex shapes present challenges. For example the chamber liner has cooling channels that are normally machined. However, machining Cu-D parts is difficult and it is better to build grooves into the die such that the liner will have channels built in. However the channels are generally quite narrow, 1 to 2 mm. Experience has shown that dies with narrow grooves do not consolidate the powder very well; they are hard to lubricate and tend to bond with the plunger at sintering temperature under high applied pressure. Under these circumstances the cooling channels will have to be machined.

Fabrication of NARloy-Z-D Combustion Chamber Liner using Spark Plasma Sintering (SPS)

A subscale NARloy-Z-D chamber liner was fabricated successfully using SPS technique in Penn State (Ref. 8, 10). Eight rings of NARloy-Z-D were first made (Fig. 9) using SPS. The rings were machined to remove the burs and smoothen the surfaces to be joined. They were stacked as shown schematically in Fig. 10A, and assembled (Fig. 10B). The assembly was placed in the SPS vacuum chamber for diffusion bonding. The chamber is evacuated and bonding pressure applied. An electric current is passed through the stack at the same time. Fig. 11 shows Cu, NARloy-Z and NARloy-Z-30%D liners made by this technique.

Fig. 9: Combustion chamber liner ring (2.5" i.d., 2.75" o.d., 1.0" long) made from NARloy-Z-Cu-30vol.%D composite using SPS technique at Penn State (Ref. 10)

A B

Fig. 10: Fabrication of liner by stacking eight rings (A) and diffusion bonding by SPS (B)

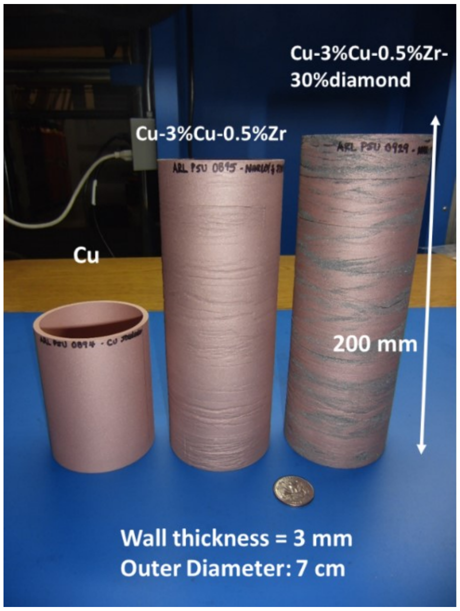


Fig. 11: Subscale combustion chamber liners made by diffusion bonding several rings using FAST (SPS) (Ref. 10)

Fig. 12: Combustion chamber liner (with cooling channels) and test assembly

The next step will be to machine channels in the liner, which is then clad it with a structural jacket. Traditional method is to electroplate nickel on copper liner. Fig. 12 shows a machined liner and the test assembly built in the traditional way with a structural jacket and manifolds.

Fabrication of Combustion Chamber Liner Using Additive Manufacturing Techniques

Additive Manufacturing (AM) is an emerging technology for fabricating liquid rocket engine components in general and combustion chambers in particular. Potential benefits are reduced cost and schedule. Several AM techniques are available (Ref. 11-13):

- Powder Bed based: Selective Laser Melting (SLM), Direct Metal Laser Sintering (DMLS), Electron Beam Melting
- Directed Energy Deposition: Blown Powder Deposition, Laser Wire Cladding, Arc-based Wire Deposition

A schematic of Direct Metal Laser Sintering (DMLS) process is shown in Fig. 13. The part is made by sintering one layer at a time by traversing a laser beam on a powder bed, which is then lowered and fresh powder is added after each traverse until the part is built.

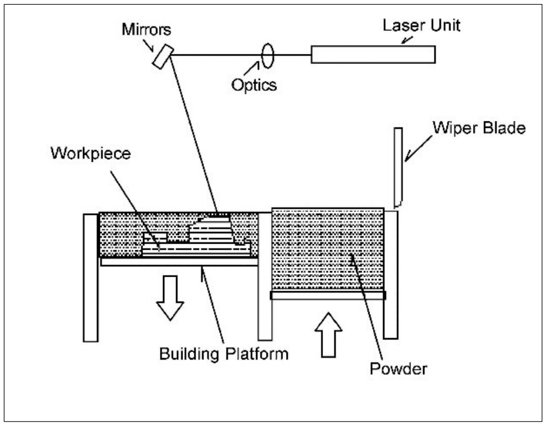


Figure 13: Direct Metal Laser Sintering (DMLS) Process schematic

Numerous combustion chambers have been designed, developed and tested at Marshall Space Flight Center (Ref. 11-13) and the technology is maturing rapidly. Liner materials used are GRCop-84 and commercially available Cu-Zr alloys. Selective Laser Melting (SLM) and Direct Metal Laser Sintering (DMLS) technologies appear to be sufficiently mature for fabricating the chamber liner. Fig. 14 is a photograph of GRCop-84 chamber halves fabricated using the SLM method.

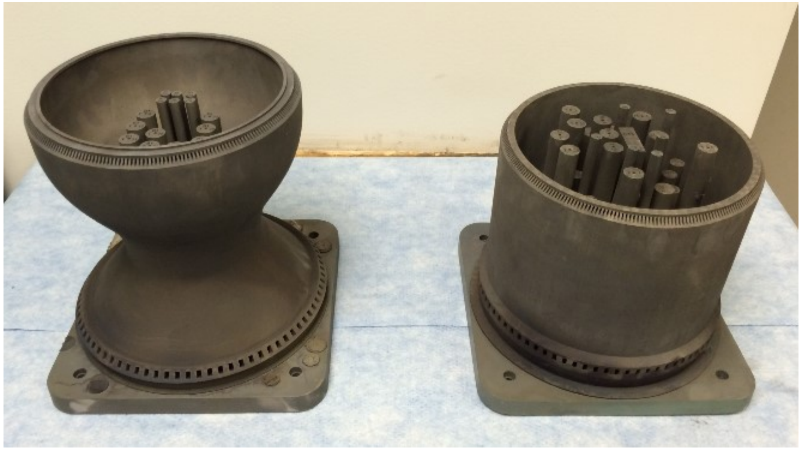


Fig. 14: Two chamber halves (on build plate with material samples) built with GRCop-84 using SLM (Ref. 11, 12)

Bimetallic Chamber Development

Combustion chambers are typically made from two kinds of materials: high thermal conductivity copper alloy for the inner liner and high strength nickel base alloy for the outer structural jacket. The bimetallic cladded combustion chamber builds upon the development work for propulsion additive manufacturing technology. In one example (Ref. 11) the bimetallic chamber was designed to be fabricated in three major processes: 1) One-piece 3D-printed copper alloy liner and closeouts, 2) Cladding of a structural jacket creating a bimetallic joint and 3) Welding of the coolant inlet and outlet manifolds. The one-piece copper liner was designed to be additively manufactured with GRCop-84 powder using SLM.

Several techniques are available for bimetallic development, including:
1. Wire-fed Laser Deposition
2. Blown Powder Laser Deposition (Direct Metal Deposition or Directed Energy Deposition)
3. Pulsed-Arc MIG Deposition
4. Hotwire Hybrid Laser-Arc Cladding
5. Electron Beam Freeform Fabrication (EBF^3)

Details of these processes may be found in the literature (Ref. 11-13). In all cases it is important to have good bond strength between the liner and the structural jacket.

A generic process flow is shown in Fig. 15 for SLM method using GRCop-84. The process for making Cu-D liners is expected to be very similar.

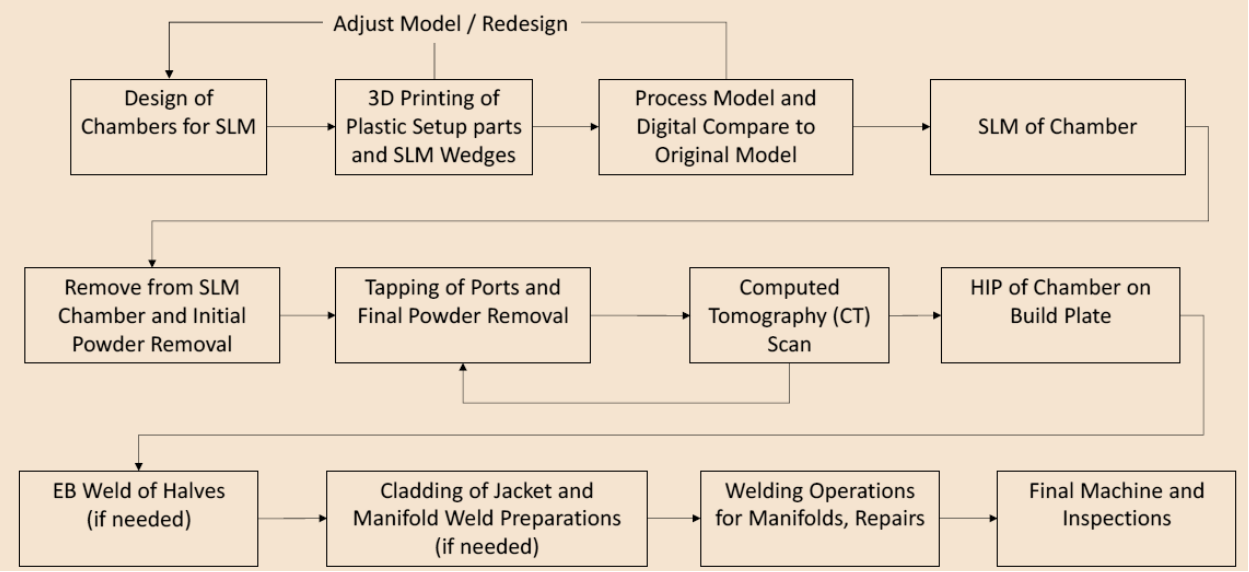


Fig. 15: Generic process flow for Design and Fabrication of SLM GRCop-84 chambers (Ref. 11)

Fabrication of Cu-D Composite Liner by Additive Manufacturing

It is clear from the above discussion that Cu-D composite powder should behave similar to GRCop-84 powder which has been used successfully in a number of combustion chamber designs. It is obvious that powder quality and uniformity is of essence. Mixture of diamond particles and copper alloy powder will tend to segregate and is not recommended. Coated diamond particles should be used in place of copper alloy powder. Powder particle size is also important but at this time we do not know the best combination of diamond particle size, refractory metal carbide coating thickness, and copper plating thickness. This problem has been addressed by GTE (Ref. 6). They have looked at diamond quality and the Cu-D interfaces in detail. The goal is to produce coated diamond powder which has the best combination of high thermal conductivity, and good Cu-D interface bond strength. Quality of diamonds can vary as shown in Fig. 16. Higher quality diamonds give higher thermal conductivity but cost more. Diamond selection depends on the end product property requirements in terms of thermal conductivity and tensile strength.

The coating process is shown schematically in Fig. 17. Fig. 18a shows coated diamond particles. Fig. 18b shows the microstructure showing uniform distribution of diamonds, which should give uniform properties to the liner. This powder is well suited for fabricating the liner using AM. GTE used a thin layer of nickel over the carbide coating to improve bonding with the copper layer. Nickel has much lower the thermal conductivity than copper and it does not form carbide. Ideally the coating material should be a carbide former and at the same time alloy with copper to form a high strength interface that does not crack during thermal cycling. Thermal conductivity data suggests that zirconium (Zr) is a carbide former that gives a low thermal resistance interface with diamond and also provides a good bond with copper matrix at the same time. Quality of coatings does matter and the coating process (both CVD and electroplating) must be controlled for best results.

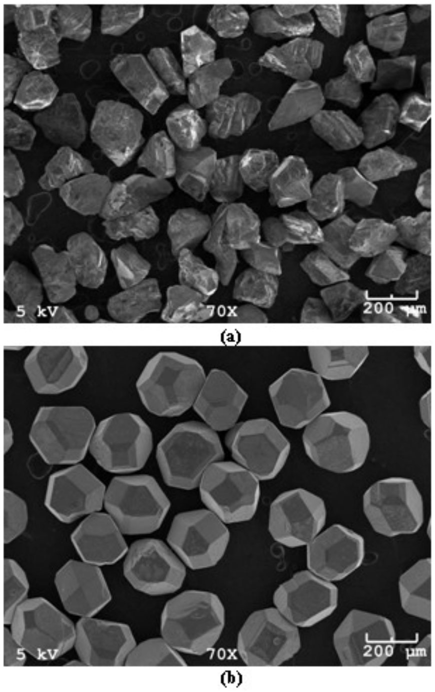


Fig. 16: Two types of synthetic diamond grit used in the experiments: (a) low cost M170/80 mesh diamond powder (6 cents/ct.), which have angular appearance due to mechanical crushing during manufacture; (b) intermediate grade M3 diamond powder (22 cents/ct.) with well-defined cubo-octahedral shape.

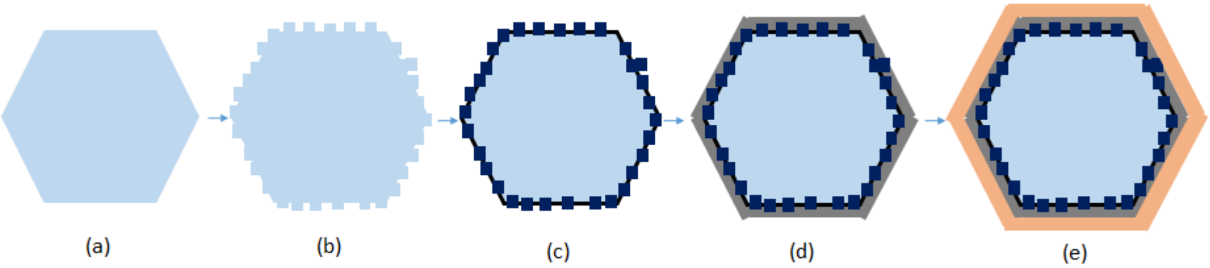
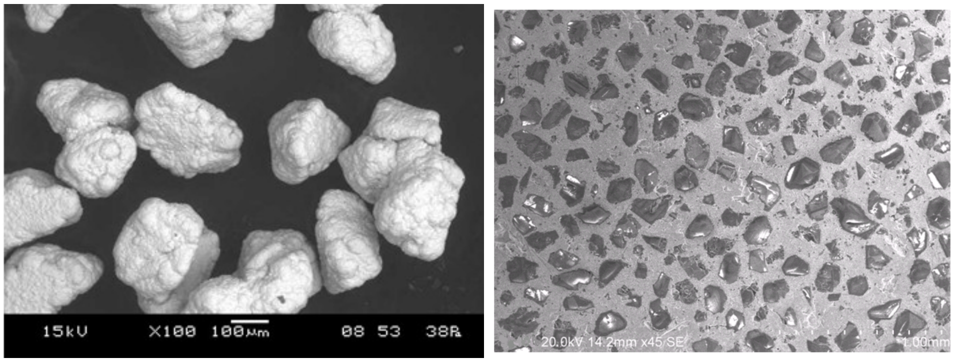


Fig. 17: Stages in current GTE high thermal conductivity copper-diamond powder development: (a) starting diamond with smooth facets; (b) oxidative on corrosive treatment to roughen diamond surface to increase reactivity; (c) application of continuous layer of reactive metal carbide; (d) overcoat of refractory metal to provide a graded interface for thermal cycling resistance; (e) optional overcoat of electroless copper, followed by electrodeposition of thicker copper.



a b

Fig.18: Advantage of using Cu-coated diamond powder: (a) shows appearance of Cu-coated diamond grains, (b) shows very uniform diamond distribution in the SPS-consolidated composite (50/60 diamond mesh size, Vf=55% diamond), no powder mixing/blending required.

As stated earlier, SLM appears to be a good process for making Cu-D composite liners. Blown Powder Deposition method also appears attractive but requires further development. Coated diamond powders should be developed further to identify the best combination of coatings. Judging from the past work it appears that diamond particle size should be optimized. Based on results so far it appears that particle size between 60 and 120 micron may work the best. The first coating used currently is a refractory metal carbide (MoC or HfC) but ZrC might work even better since metallic Zr is known to form a good bond with copper. It may be best to coat diamonds with Zr metal and overcoat with copper. During sintering Zr will react with diamond to form ZrC and also dissolve in copper to form a Cu-Zr matrix which has excellent mechanical properties. Since the basic techniques are already developed for SLM it is not a huge step to make the Cu-D composite liner starting from the current technology readiness level. The authors envision the following sequence of steps:

1. Make coated powder – D-RFC-Cu where RFC is refractory metal carbide, e.g., ZrC, MoC.
2. Make coupons to characterize the material – quality check
3. Test properties - mechanical, thermal, physical
4. Trial runs of AM (SLM) with a model part (e.g., subscale liner) to optimize process parameters
5. Design full scale chamber liner and fabricate a demonstrator chamber which can be hot fire tested

AM techniques developed for GRCop-84 will be applicable to Cu-D composite. Only difference is the powder.

6. Summary

This paper gives an overview of the high thermal conductivity copper alloys that contain diamond particles in the matrix, referred to as Cu-D composites. Diamond particles have much higher thermal conductivity than copper and they do improve the thermal conductivity of the composite significantly. In this paper thermal, physical and mechanical properties of Cu-D composites are presented and discussed. Processing techniques and microstructure are described. Fabrication techniques for Cu-D chamber liner are discussed. The Cu-D composite materials look very promising for fabricating high thermal conductivity combustion chamber liners for advanced rocket engines. They can be clad with high strength nickel-based structural jacket materials using the same technologies currently used for GRCop-84. Coated Cu-D powders can be readily used for making liners using additive manufacturing techniques such as selective laser melting (SLM) and blown powder deposition.

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