Fabrication of High Thermal Conductivity NARloy-Z-Diamond Composite Combustion Chamber Liner for Advanced Rocket Engines

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Abstract

NARloy-Z alloy (Cu-3%Ag-0.5%Zr) is a state of the art alloy currently used for fabricating rocket engine combustion chamber liners. Research conducted at NASA-MSFC and Penn State – Applied Research Laboratory has shown that thermal conductivity of NARloy-Z can be increased significantly by adding diamonds to form a composite (NARloy-Z-D). NARloy-Z-D is also lighter than NARloy-Z. These attributes make this advanced composite material an ideal candidate for fabricating combustion chamber liner for an advanced rocket engine. Increased thermal conductivity will directly translate into increased turbopump power and increased chamber pressure for improved thrust and specific impulse. This paper describes the process development for fabricating a subscale high thermal conductivity NARloy-Z-D combustion chamber liner using Field Assisted Sintering Technology (FAST). The FAST process uses a mixture of NARloy-Z and diamond powders which is sintered under pressure at elevated temperatures. Several challenges were encountered, i.e., segregation of diamonds, machining the super hard NARloy-Z-D composite, net shape fabrication and nondestructive examination. The paper describes how these challenges were addressed. Diamonds coated with copper (CuD) appear to give the best results. A near net shape subscale combustion chamber liner is being fabricated by diffusion bonding cylindrical rings of NARloy-Z-CuD using the FAST process.

Introduction

NARloy-Z alloy (Cu-3Ag-0.5Zr) is state of the art alloy used for making the combustion chamber liners for liquid rocket engines such as RS-68 and RS-25. Research conducted at NASA-MSFC (Ref. 1) and Penn State (Ref. 2) has shown that NARloy-Z containing 40vol% diamond (NARloy-Z-40D) has nearly 50% higher thermal conductivity than copper. Furthermore, NARloy-Z-40D is about 24% lighter than NARloy-Z. These attributes make the chamber liner lightweight and thermally efficient and in turn help to improve the performance of the advanced rocket engines. Increased thermal conductivity will directly translate into increased turbopump power and increased chamber pressure for improved thrust and specific impulse.

Prior work on NARloy-Z-D composites used the Field Assisted Sintering Technology (FAST, Ref. 1, 2) for fabricating test coupons. NARloy-Z-D composites containing 10, 20 and 40vol% of high thermal conductivity diamond powder were investigated. Thermal conductivity (TC) data are shown in Figure 1. TC increased with increasing diamond content and showed 50% improvement over pure copper at 40vol% diamond (>500 W/mK). This TC was chosen as target value for this material. It was proposed to fabricate a subscale combustion chamber liner using the FAST technique to increase the technology readiness level (TRL) for this material to TRL 4.

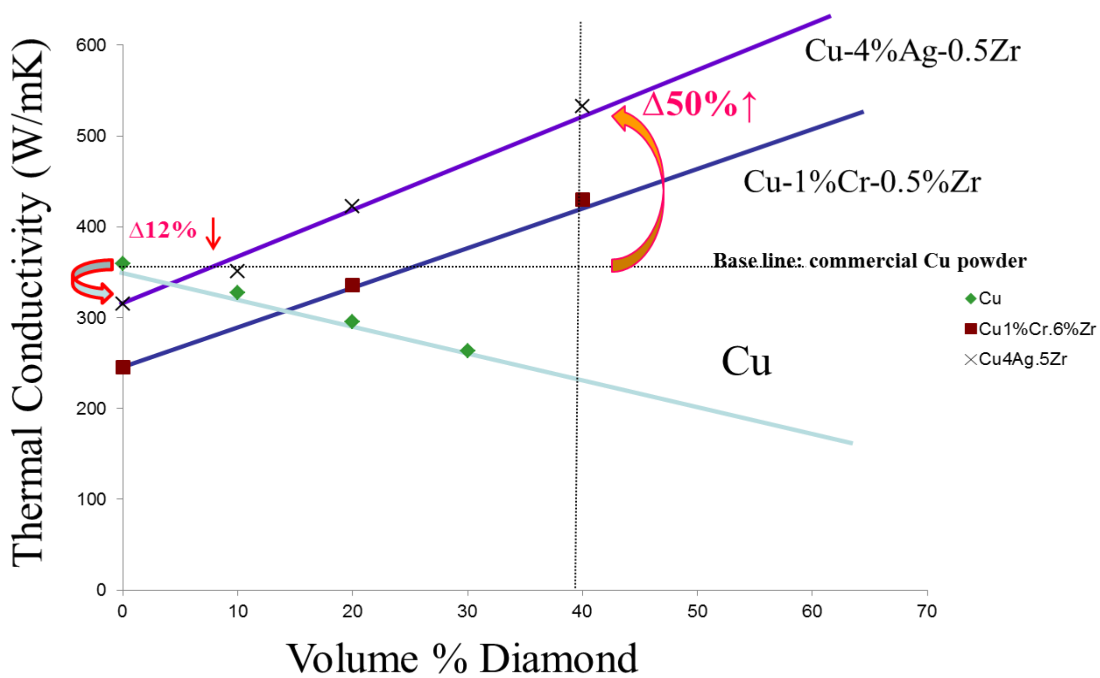


Figure 1: Thermal conductivity enhancement in Cu-Ag-Zr-D (NARloy-Z-D) composite (Ref. 2)

Combustion Chamber Liner Design

An existing subscale chamber liner and chamber assembly are shown in Figure 2 for illustration purposes. The liner is basically a 2.75 in. OD, 2.50 in. ID and 8 in. long cylinder with cooling channels machined on the outside. This subscale combustion chamber liner was designed to fit in an existing hot fire test assembly at Marshall Space Flight Center (MSFC) shown in Figure 3.

B A

Figure 2: Combustion chamber liner (A) and chamber assembly (B)

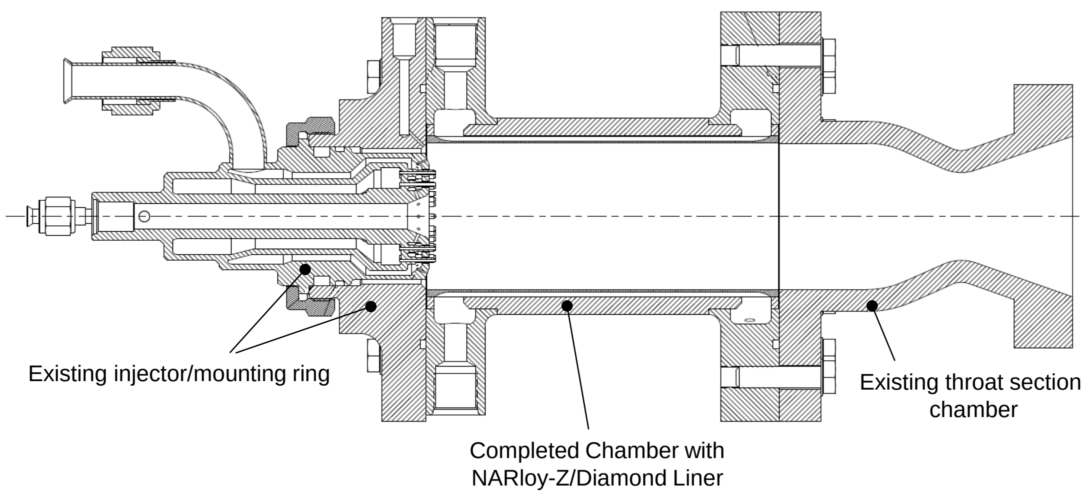
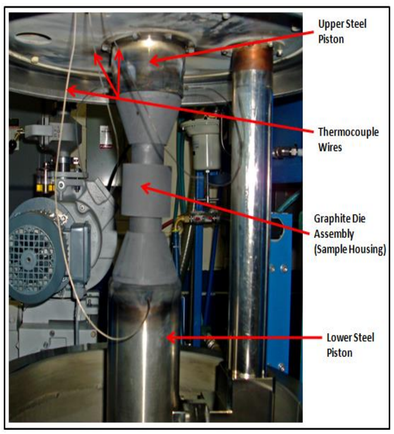


Figure 3: Hot Fire Test assembly schematic

Fabrication Process

Field Assisted Sintering Technology (FAST) is used to make the liner. This is a powder metallurgy technology in which NARloy-Z powder is blended with diamond powder, poured into a mold and sintered under pressure to produce a full density part. Since the chamber liner is a cylinder with relatively thin wall (0.125 in.) the FAST process could make only about an inch tall cylinders. Therefore it was decided to make eight, one inch tall cylindrical rings first, stack them in a mold and diffusion bond them to form the eight inch tall cylindrical liner. Cooling channels will be machined afterwards by a machining vendor.

The mold, core and die were made from graphite initially. NARloy-Z and diamond powder were mixed in acoustic mixer and poured into the mold, placed in the FAST apparatus (Figure 4A) and consolidated to full density at elevated temperatures (Figure 4B). Two plates of NARloy-Z-D were diffusion bonded together using the same FAST parameters and tested for bond strength. In addition, a cylindrical ring was fabricated to demonstrate feasibility.



A

B

Figure 4: FAST system at Penn State Applied Research Laboratory (A); sintering at high temperature (B)

Fabrication Challenges

1. *Machining of NARloy-Z-D Composite*

Diamond is the hardest substance known and NARloy-Z-D composite is not much different. It is too hard to machine by conventional means. Electrical discharge machining (EDM) and water jet cutting/grinding techniques seem to work satisfactorily. Both methods were used for cutting test specimens. Machining of cooling channels proved to be more difficult and required special tooling. Both EDM and water jet techniques were evaluated for grinding channels by different vendors. The results so far indicate that water jet grinding gives better results compared to EDM and is viewed as a preferred method for machining channels.

2. *Net Shape Forming*

Penn State made an evaluation of forming the liner net shape including the cooling channels. This design proved to be difficult to fabricate by FAST. The narrow channels made the graphite mold very weak and susceptible to breakage under processing loads. To alleviate this problem TZM (tungsten-molybdenum) alloy was used for mold and die. A simple hollow cylindrical shape was used for initial trials. The mold and die material worked reasonably well but experienced galling when the mold and die surfaces rubbed against each other. Galling produced rough surfaces in the part and also damaged the molds. To solve this problem mold-die clearances were increased slightly and a dry film lubricant (graphite foil) was used to eliminate galling. This procedure could not be used on grooved molds since the grooves were too narrow for this technique to work. On detailed examination it was concluded that net shape forming with integral channels was extremely difficult to achieve without significant development work. Therefore it was decided to go with a simpler, near net shape liner, i.e., a straight cylinder of appropriate thickness and height, by diffusion bonding cylindrical rings. The cylinder height was limited to about one inch to ensure 100% density. Therefore eight cylinders were processed separately and then stacked in a TZM mold and diffusion bonded together to form the liner.

3. *Segregation of Diamonds in NARloy-Z-D composite*

An acoustic mixer was used to blend NARloy-Z and diamond powders. It produced what appeared to a homogeneous mixture, which was then poured into the mold and consolidated. Early results showed that this mixture tended to segregate badly during pouring and consolidation (Figure 5). Segregated areas showed only diamond particles and very little NARloy-Z. This segregation lowered both mechanical and thermal properties significantly and must be avoided. To alleviate the problem acoustic mixing was combined with a rotational mixing process (called ‘turbula’) to improve homogeneity but the mixture still segregated in the mold. Diamond powder is so slick that segregation is very easy. Tendency for segregation was so high that even blending with an organic binder did not help. The binder did not adhere to the diamond surface. Therefore it was concluded that it was necessary to pre-coat diamond powder with a metal coating for better mixing with NARloy-Z powder. The coating should also help to improve bonding during sintering. At the same time the coating should form a thermally conducting metal carbide layer on diamond particles.

It was decided to try titanium (Ti) coated diamonds since it was readily available as a commercial product supplied by Sandvik Hyperion of Worthington, Ohio. Ti is also a carbide former and TiC layer is reported to have low contact thermal resistance. The coated powder was mixed with NARloy-Z powder. The mixture was much more homogeneous than straight diamonds. It was poured into mold and sintered using FAST. The resulting microstructure was very good (Figure 6A). Thermal conductivity was measured and found to be significantly lower, however (Table 2), suggesting that titanium acted as an insulator. Possible reasons are 1) the surface oxide layer did not dissolve in the matrix and prevented the diamond from contributing to the thermal conductivity; 2) the sintering temperature was probably too low to form TiC and might be a contributing factor to lower TC. It became clear, however, that the diamonds have to be coated with a more thermally conductive metal coating to reduce/eliminate segregation. The metal coating should also help to produce a better bond between copper and diamond during sintering. Titanium coating did not work and it appeared that copper coated diamond might meet these requirements and was pursued further.

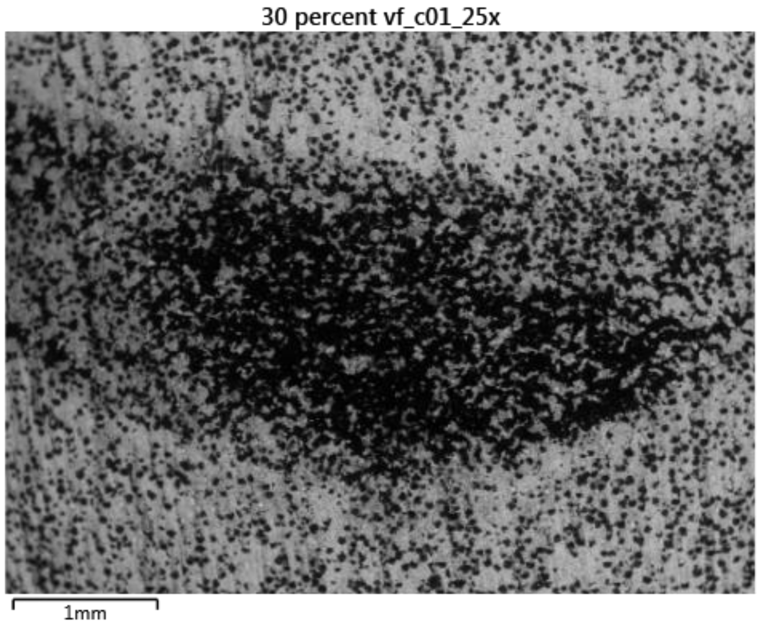


Figure 5: SEM Micrograph of Diamond segregation (dark area) observed in NARloy-Z-30%D Composite

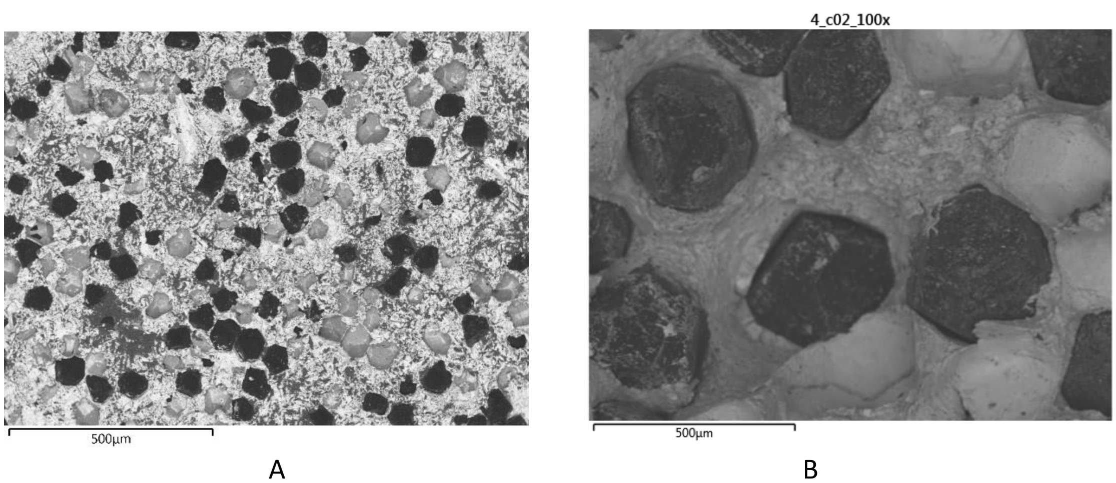


Figure 6: SEM fractograph of NARloy-Z-Ti coated diamond composite (A) and NARloy-Z-Cu coated diamond composite (B). Note: coating has come off in the dark looking diamonds in both cases.

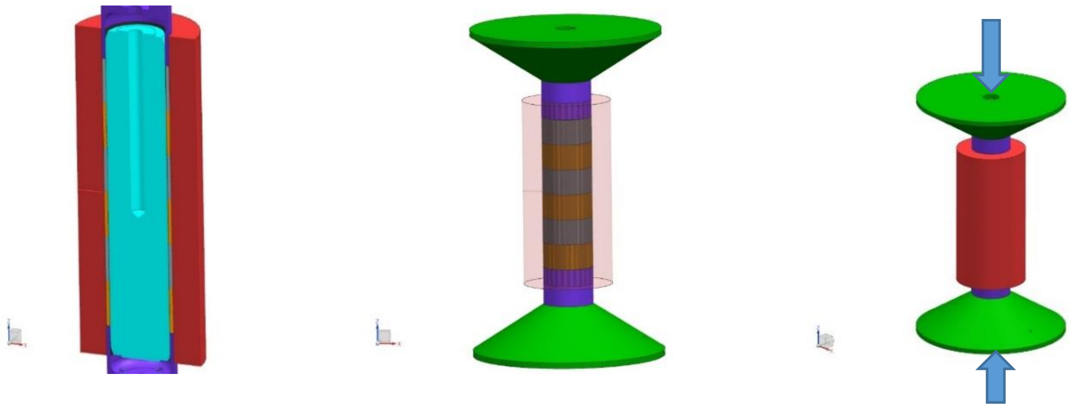
4. Copper Coated Diamonds

Although copper coating was ideal from sintering and thermal conductivity points of view it is not a carbide former and Cu-D interface has a very high contact thermal resistance (Ref. 1). So the copper coating alone will not be sufficient; a low contact thermal resistance metal carbide layer between copper and diamonds is required. A company called Global Technology Enterprises (GTE) located in Bozeman, Montana, made diamonds coated with metal carbides that offered high contact thermal conductivity. They have developed a chemical vapor reaction technique for coating diamonds with refractory metal carbides and provided us with a sample of their molybdenum carbide (MoC) coated diamonds for this research. MoC serves as a high contact thermal conductivity layer between diamond and copper. Mixing trials showed that straight MoC-coated diamonds did not mix well with NARloy-Z, an over coat of copper was required. Sion Pickard of GTE was able to over coat the MoC-coated diamonds with copper using an electroplating process. He provided a sample of Cu-MoC-D (CuD for short) powder for trial purposes. In the first trial, a combustion chamber liner ring was fabricated from a mixture of NARloy-Z and 28vol% CuD powder at Penn State using FAST (Figure 7). Test specimens were cut from this ring for evaluating thermal and mechanical properties. Both thermal and mechanical properties were acceptable (see Tables 1 & 2) and a decision was made to proceed with this powder mixture for making the liner. A higher volume % of CuD in the 35-40% range was selected to improve thermal conductivity to meet the goal of >500 W/mK for the liner.

Figure 7: Combustion chamber liner ring (2.5” ID., 2.75” OD, 1.0” long) made from NARloy-Z-CuD composite made at Penn State using FAST

5. *Diffusion bonding of NARloy-Z-CuD rings*

The combustion chamber liner is made by diffusion bonding eight NARloy-Z-CuD rings as shown schematically in Figure 8. Early trials showed that bond strength was improved by using a thin layer of NARloy-Z powder in between rings. At the time of writing this paper Penn State has successfully completed a trial run of NARloy-Z liner by diffusion bonding eight NARloy-Z rings (Figure 9). The same technique will be used for diffusion bonding NARloy-Z-CuD rings to make the liner.



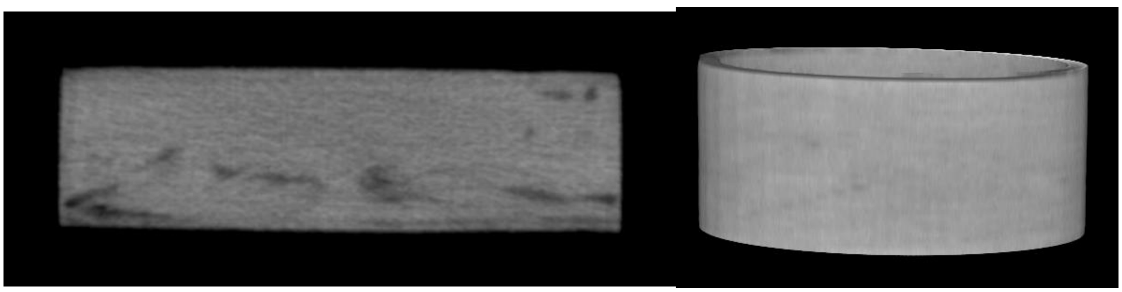
A B C

Figure 8: Fabrication of Combustion Chamber Liner by Diffusion Bonding Multiple Rings – shown schematically. Eight rings stacked inside TZM mold for joining (A), translucent model with multi-colors showing the rings (B), diffusion bonding by FAST (C).

Figure 9: NARloy-Z chamber liner fabricated by FAST. Note: This picture was taken after the part was taken out of the mold. The TZM mold parts attached to the liner on both ends will be separated. The dark areas are graphite foil used as lubricant and will be cleaned out.

6. Nondestructive Examination of NARloy-Z-D Composite

The segregation issues described above first surfaced when cutting the test specimens. Segregated areas were observed on the cut specimens that was visible to the naked eye. Examination under microscope showed areas of heavy segregation (Figure 5). It became clear that a reliable nondestructive technique was needed to assure the homogeneity of the liner that must be free from gross internal defects. Computed Tomography (CT) technique was used on a solid block of NARloy-Z-D and a liner ring, both made by FAST process. The CT technique worked satisfactorily in revealing badly segregated volumes (Figure 10). Now it serves as a standard technique for verifying soundness of NARloy-Z-D parts.



A B

Figure 10: Computed Tomography (CT) images of NARloy-Z-40%D composite plate (A) and ring (B) showing segregation of diamonds. Diamond segregation (indicated by dark areas) is more severe in A than in B

Properties of NARloy-Z-Diamond Composites

1. Tensile properties

Tensile properties of NARloy-Z-D composites tested so far are shown in Table 1. As expected ductility is low, especially for uncoated diamonds. NARloy-Z-CuD gave the best tensile elongation. The tensile strength numbers are good and acceptable for chamber liner applications. In general the properties were highly variable in because of segregation. Coated diamonds gave more consistent properties. Overall NARloy-Z-CuD was the best of all and was selected for making the liner.

Elevated temperature tests were also conducted. The tensile strength was 11 ksi for NARloy-Z-40D, at 935^{o}F. Tensile strength at 1000^{o}F appears to be a little lower for NARloy-Z-CuD but sufficient for proceeding with chamber fabrication.

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 -- 11 ksi (Table 1), which is high enough to proceed with liner fabrication.

Table 1: Tensile properties of various NARloy-Z-D composites

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

2. *Microstructure*

NARloy-Z-CuD Microstructure was examined in both optical and scanning electron microscopes (SEM). Metallography samples could not be prepared because material hardness was too high. However fractured surfaces of tensile specimens were examined in the scanning electron microscope. The results are shown in Figures 6B. This is as typical microstructures and shows fairly uniform distribution of diamonds in NARloy-Z matrix. Elemental analysis verified the presence of metal carbides (both MoC and ZrC) at NARloy-Z – diamond interface.

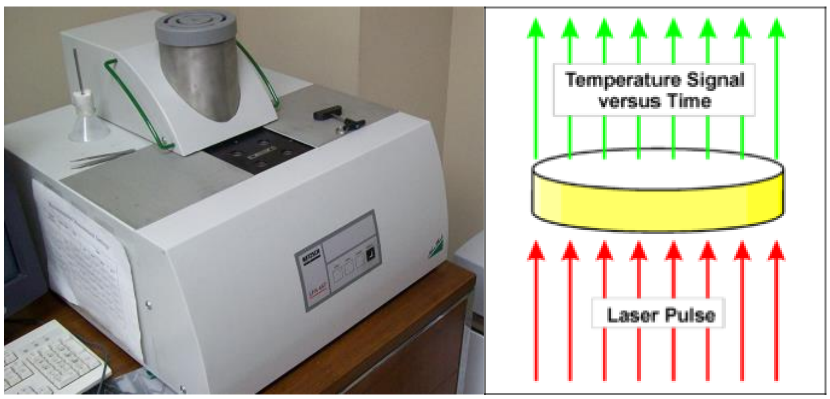
3. *Thermal Conductivity (TC)*

Thermal conductivity measurements NARloy-Z-D composite were made by Dr. Enrique Jackson/MSFC using an optical flash method (Ref. 3). Thermal conductivity (TC) measurements of NARloy-Z-Ti-D and 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 11). In both cases thermal diffusivity is measured directly and TC is calculated. Dr. Rape calculated TC using the following relationships:

Thermal diffusivity, α = $0.1388\,\frac{d^2}{t_{1/2}}$ where α = thermal diffusivity, d = sample thickness, $t_{1/2}$ = time to half maximum temperature.

Thermal conductivity, k = $\alpha c_p \rho$ where c_p = specific heat and ρ = density.

Results are shown in Table 2.



A B

Figure 11: Netzsch Nanoflash LFA447 thermal diffusivity measuring apparatus (A); schematic of laser flash method of measuring thermal diffusivity (B)

Table 2: Thermal conductivity of NARloy-Z-D composite materials

Sample chemistry	**Thermal conductivity (W/m-K)**	**Temperature, °K**	**Comments**
NARloy-Z	320	300	Base line (Ref. 2)
NARloy-Z-30%D	337	380	Diamond segregation observed (Ref. 3)
NARloy-Z-40%D	344	380	Diamond segregation observed (Ref. 3)
NARloy-30%TiD	176	300	Ti lowers TC
NARloy-Z-28%CuD	462	300	Results acceptable; 35-40% CuD recommended

Segregation of diamonds in NARloy-Z matrix is the likely cause of lower TC in samples made with uncoated diamonds. Use of Ti-coated diamonds did not help with TC, possibly due to an insulating layer of TiO_2 which is always present on the surface. Relatively low sintering temperatures during FAST did not promote TiC formation on the surface of diamonds. NARloy-Z-CuD composite gave the best TC results. Diamond content of the actual liner was increased to 35-40vol% CuD to obtain a TC of >500 W/m-K.

Fabrication of Combustion Chamber Liner

The chamber liner is fabricated at Penn State - Applied Research Laboratory. At the time of writing this paper Penn State has made eight rings each of pure copper, straight NARloy-Z (without diamonds) and NARloy-Z-CuD with 35-40-% CuD. Two trial runs of diffusion bonding rings have been completed. The first trial run was made with pure copper rings to test their 250 ton FAST machine used to do diffusion bonding to check out the TZM molds. The second run was made with straight NARloy-Z rings without the diamonds to establish the correct sintering parameters to be used for the real liner to be made with NARloy-Z-CuD rings. A stack of 3 NARloy-Z rings is shown in Figure 12. There are blemishes in the rings such as excess material (e.g., burs) which were removed before diffusion bonding. The rings were finish machined to clean up any surface blemishes. Eight of these NARloy-Z rings were stacked and diffusion bonded successfully (Figure 9). Eight rings of NARloy-Z-CuD have been made (Figure 13) and they are ready for diffusion bonding to form the chamber liner. It is planned to produce the first chamber liner in December 2015.

Figure 12: Stack of three NARloy-Z rings. Each ring is made separately by FAST

Figure 13: NARloy-Z-CuD rings made by FAST, ready for diffusion bonding

Follow-on work

After the chamber liner is fabricated, it is planned to machine cooling channels in the liner using water jet grinding process. A liner with channels is shown in Figure 2A. Following that the liner will be electroplated with nickel to close out the channels. Coolant manifolds will be fabricated and integrated with the hot fire test assembly shown in Figure 2B and Figure 3. The chamber will be hot fire tested at MSFC Test Stand 115 to assess performance.

Summary

High thermal conductivity NARloy-Z-Diamond composite combustion chamber liner rings were fabricated using a powder metallurgy technique in which NARloy-Z powder was mixed with high thermal conductivity copper coated diamond powder (CuD), poured into a TZM mold and consolidated at elevated temperatures and pressures using Field Assisted Sintering Technology (FAST). This breakthrough technology development presented several challenges, which are described in this paper. The liner will be fabricated by diffusion bonding eight rings of NARloy-Z-CuD in the FAST apparatus.

References

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