



## Propulsion Design With Freeform Fabrication (PDFF)

**Innovation for ceramic materials uses solid freeform rapid prototype manufacturing technology.**

*John H. Glenn Research Center, Cleveland, Ohio*

The nation is challenged to decrease the cost and schedule to develop new space transportation propulsion systems for commercial, scientific, and military purposes. Better design criteria and manufacturing techniques for small thrusters are needed to meet current applications in missile defense, space, and satellite propulsion. The requirements of these systems present size, performance, and environmental demands on these thrusters that have posed significant challenges to the current designers and manufacturers. Designers are limited by manufacturing processes, which are complex, costly, and time consuming, and ultimately limited in their capabilities.

The PDFF innovation vastly extends the design opportunities of rocket engine components and systems by making use of the unique manufacturing freedom of solid freeform rapid prototype manufacturing technology combined with the benefits of ceramic materials. The unique features of PDFF are developing and implementing a design methodology that uses solid freeform fabrication (SFF) techniques to make propulsion components with

significantly improved performance, thermal management, power density, and stability, while reducing development and production costs. PDFF extends the design process envelope beyond conventional constraints by leveraging the key feature of the SFF technique with the capability to form objects with nearly any geometric complexity without the need for elaborate machine setup. The marriage of SFF technology to propulsion components allows an evolution of design practice to harmonize material properties with functional design efficiency.

Reduced density of materials when coupled with the capability to honeycomb structure used in the injector will have significant impact on overall mass reduction. Typical thrusters in use for attitude control have 60–90 percent of its mass in the valve and injector, which is typically made from titanium. The combination of material and structure envisioned for use in an SFF thruster design could reduce thruster weight by a factor of two or more. The thrust-to-weight ratios for such designs can achieve 1,000:1 or more, depending on chamber pressure.

The potential exists for continued development in materials, size, speed, accuracy of SFF techniques, which can lead to speculative developments of PDFF processes such as fabrication of custom human interface devices like masks, chairs, and clothing, and advanced biomedical application to human organ reconstruction.

Other potential applications are: higher fidelity lower cost test fixtures for probes and inspection, disposable thrusters, and ISRU (*in situ* resource utilization) for component production in space or on Lunar and Martian missions, and application for embedding MEMS (microelectromechanical systems) during construction process of form changing aerostructure/dynamic structures.

*This work was done by Daudi Barnes of DMX Engineering, Jim McKinnon of Frontier Engineering, and Richard Priem of Priem Consultants for Glenn Research Center. Further information is contained in a TSP (see page 1).*

*Inquiries concerning rights for the commercial use of this invention should be addressed to NASA Glenn Research Center, Innovative Partnerships Office, Attn: Steven Fedor, Mail Stop 4–8, 21000 Brookpark Road, Cleveland, Ohio 44135. Refer to LEW-18557-1.*

## Economical Fabrication of Thick-Section Ceramic Matrix Composites

**Applications for these composites include combustors, high-temperature filter elements, and process industry parts requiring corrosion resistance.**

*Marshall Space Flight Center, Alabama*

A method was developed for producing thick-section [ $>2$  in. ( $\approx 5$  cm)], continuous fiber-reinforced ceramic matrix composites (CMCs). Ultramet-modified fiber interface coating and melt infiltration processing, developed previously for thin-section components, were used for the fabrication of CMCs that were an order of magnitude greater in thickness [up to 2.5 in. ( $\approx 6.4$  cm)]. Melt process-

ing first involves infiltration of a fiber preform with the desired interface coating, and then with carbon to partially densify the preform. A molten refractory metal is then infiltrated and reacts with the excess carbon to form the carbide matrix without damaging the fiber reinforcement. Infiltration occurs from the inside out as the molten metal fills virtually all the available void space. Densifi-

cation to  $<5$  vol% porosity is a one-step process requiring no intermediate machining steps.

The melt infiltration method requires no external pressure. This prevents over-infiltration of the outer surface plies, which can lead to excessive residual porosity in the center of the part. However, processing of thick-section components required modification of the con-

ventional process conditions, and the means by which the large amount of molten metal is introduced into the fiber preform. Modification of the low-temperature, ultraviolet-enhanced chemical vapor deposition process used to apply interface coatings to the fiber preform was also required to accommodate the high preform thickness.

The thick-section CMC processing developed in this work proved to be invaluable for component development, fabrication, and testing in two comple-

mentary efforts. In a project for the Army, involving SiC/SiC blisk development, nominally 0.8 in. thick  $\times$  8 in. diameter ( $\approx$ 2 cm thick  $\times$  20 cm diameter) components were successfully infiltrated. Blisk hubs were machined using diamond-embedded cutting tools and successfully spin-tested. Good ply uniformity and extremely low residual porosity (<2 percent) were achieved, the latter being far lower than that achieved with SiC matrix composites fabricated via CVI or PIP. The pyrolytic

carbon/zirconium nitride interface coating optimized in this work for use on carbon fibers was incorporated in the SiC/SiC composites and yielded a >41 ksi ( $\approx$ 283 MPa) flexural strength.

*This work was done by Jason Babcock, Gautham Ramachandran, Brian Williams, and Robert Benander of Ultramet for Marshall Space Flight Center. For more information, contact Sammy Nabors, MSFC Commercialization Assistance Lead, at sammy.a.nabors@nasa.gov. Refer to MFS-32736-1.*

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## Process for Making a Noble Metal on Tin Oxide Catalyst

**This method produces an efficient, room-temperature catalyst for recombining carbon monoxide and oxygen products.**

*Langley Research Center, Hampton, Virginia*

To produce a noble metal-on-metal oxide catalyst on an inert, high-surface-area support material (that functions as a catalyst at approximately room temperature using chloride-free reagents), for use in a carbon dioxide laser, requires two steps: First, a commercially available, inert, high-surface-area support material (silica spheres) is coated with a thin layer of metal oxide, a monolayer equivalent. Very beneficial results have been obtained using nitric acid as an oxidizing agent because it leaves no residue. It is also helpful if the spheres are first de-aerated by boiling in water to allow the entire surface to be coated. A metal, such as tin, is then dissolved in the oxidizing agent/support material mixture to yield, in the case of tin, metastannic acid. Although tin has proven especially beneficial for use in a closed-cycle CO<sub>2</sub> laser, in general any metal with two valence states, such as most transition metals and antimony, may be used. The metastannic acid will be adsorbed onto the high-surface-area spheres, coating them. Any excess oxidizing agent is then evaporated, and the resulting metastan-

nic acid-coated spheres are dried and calcined, whereby the metastannic acid becomes tin(IV) oxide.

The second step is accomplished by preparing an aqueous mixture of the tin(IV) oxide-coated spheres, and a soluble, chloride-free salt of at least one catalyst metal. The catalyst metal may be selected from the group consisting of platinum, palladium, ruthenium, gold, and rhodium, or other platinum group metals. Extremely beneficial results have been obtained using chloride-free salts of platinum, palladium, or a combination thereof, such as tetraammineplatinum (II) hydroxide ([Pt(NH<sub>3</sub>)<sub>4</sub>](OH)<sub>2</sub>), or tetraamminepalladium nitrate ([Pd(NH<sub>3</sub>)<sub>4</sub>](NO<sub>3</sub>)<sub>2</sub>).

It is also beneficial if the coated spheres are first de-aerated by boiling. The platinum salt will be adsorbed onto the coated spheres. A chloride-free reducing agent is then added to the aqueous mixture whereby the catalyst metal is deposited on the tin(IV) oxide-coated spheres. Any reducing agent that decomposes to volatile products and water upon reaction or drying may be used.

Formic acid, hydroxylamine (NH<sub>2</sub>OH), hydrazine (N<sub>2</sub>H<sub>4</sub>), and ascorbic acid are particularly advantageous. After the metal has been deposited on the tin(IV) oxide-coated spheres, the solution is evaporated to dryness, whereby the desired noble metal-on-metal oxide catalyst is obtained.

This innovative process results in a more uniform application than other methods. Similarly, the method of forming and applying a precious metal to either tin oxide, or an inert substrate, is a one-step process and occurs at a lower temperature than that commonly used by other processes. This invention is inherently clean because excess reagents, such as nitric acid and formic acid, as well as unwanted products, such as nitrates and formates, all decompose and are removed from the system by simple evaporation without the necessity for separating them by filtration or washing.

*This work was done by Patricia Davis and Irvin Miller of Langley Research Center and Billy Upchurch of Science and Technology Corporation. Further information is contained in a TSP (see page 1). LAR-13741-1*