Technology Focus: Composites and Coatings

Rapid Fabrication of Carbide Matrix/Carbon Fiber Composites

Melt infiltration offers advantages over chemical vapor infiltration.

Marshall Space Flight Center, Alabama

Composites of zirconium carbide matrix material reinforced with carbon fibers can be fabricated relatively rapidly in a process that includes a melt infiltration step. Heretofore, these and other ceramic matrix composites have been made in a chemical vapor infiltration (CVI) process that takes months. The finished products of the CVI process are highly porous and cannot withstand temperatures above 3,000 °F ($\approx$1,600 °C). In contrast, the melt-infiltration-based process takes only a few days, and the composite products are more nearly fully dense and have withstood temperatures as high as 4,350 °F ($\approx$2,400 °C) in a highly oxidizing thrust chamber environment. Moreover, because the melt-infiltration-based process takes much less time, the finished products are expected to cost much less.

Fabrication begins with the preparation of a carbon fiber preform that, typically, is of the size and shape of a part to be fabricated. By use of low-temperature ultraviolet-enhanced chemical vapor deposition, the carbon fibers in the preform are coated with one or more interfacial material(s), which could include oxides. The interfacial material helps to protect the fibers against chemical attack during the remainder of the fabrication process and against oxidation during subsequent use; it also enables slippage between the fibers and the matrix material, thereby helping to deflect cracks and distribute loads. Once the fibers have been coated with the interfacial material, the fiber preform is further infiltrated with a controlled amount of additional carbon, which serves as a reactant for the formation of the carbide matrix material.

The next step is melt infiltration. The preform is exposed to molten zirconium, which wicks into the preform, drawn by capillary action. The molten metal fills most of the interstices of the preform and reacts with the added carbon to form the zirconium carbide matrix material. The zirconium does not react with the underlying fibers because they are protected by the interfacial material(s). The success of the melt-infiltration step depends on interface material selection and uniform coating of the fibers, infiltration with the correct amount of carbon, and careful control of temperature and rate of heating.

This work was done by Brian E. Williams and Robert E. Benander of Ultramet for Marshall Space Flight Center. Further information is contained in a TSP (see page 1).
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Coating Thermoelectric Devices To Suppress Sublimation

Thermoelectric materials are covered with adherent, chemically stable metal outer layers.

*NASA's Jet Propulsion Laboratory, Pasadena, California*

A technique for suppressing sublimation of key elements from skutterudite compounds in advanced thermoelectric devices has been demonstrated. The essence of the technique is to cover what would otherwise be the exposed skutterudite surface of such a device with a thin, continuous film of a chemically and physically compatible metal. Although similar to other sublimation-suppression techniques, this technique has been specifically tailored for application to skutterudite antimonides.

The primary cause of deterioration of most thermoelectric materials is thermal decomposition or sublimation—one or more elements sublime from the hot side of a thermoelectric couple, changing the stoichiometry of the device. Examples of elements that sublime from their respective thermoelectric materials are Ge from SiGe, Te from Pb/Te, and now Sb from skutterudite antimonides. The skutterudite antimonides of primary interest are $CoSb_3$ [electron-donor (n) type] and $CeFe_{3-x}Co_xSb_{12}$ [electron-acceptor (p) type]. When these compounds are subjected to typical operating conditions [temperature of 700 °C and pressure $<10^{-5}$ torr (0.0013 Pa)], Sb sublimes from their surfaces, with the result that Sb depletion layers form and advance toward their interiors. As the depletion layer advances in a given device, the change in stoichiometry diminishes the thermal-to-electric conversion efficiency of the device.

The problem, then, is to prevent sublimation, or at least reduce it to an acceptably low level. In preparation for an experiment on suppression of sublimation, a specimen of $CoSb_3$ was tightly wrapped in a foil of niobium, which was selected for its chemical stability. In the experiment, the wrapped specimen was heated to a temperature of 700 °C in a vacuum of residual pressure $<10^{-5}$ torr (0.0013 Pa), then cooled and sectioned. Examination of the sectioned specimen revealed that no depletion layer had formed, indicating the niobium foil prevented sublimation of antimony at 700 °C. This was a considerable improvement, considering that uncoated $CoSb_3$ had been found to decompose to form the lowest antimonide at the surface at only 600 °C. Evidently, because the mean free path of Sb at the given temperature and pressure was of the order of tens of centimeters, any barrier closer than tens of centimeters (as was the niobium foil) would have suppressed transport of Sb vapor, thereby suppressing sublimation of Sb.
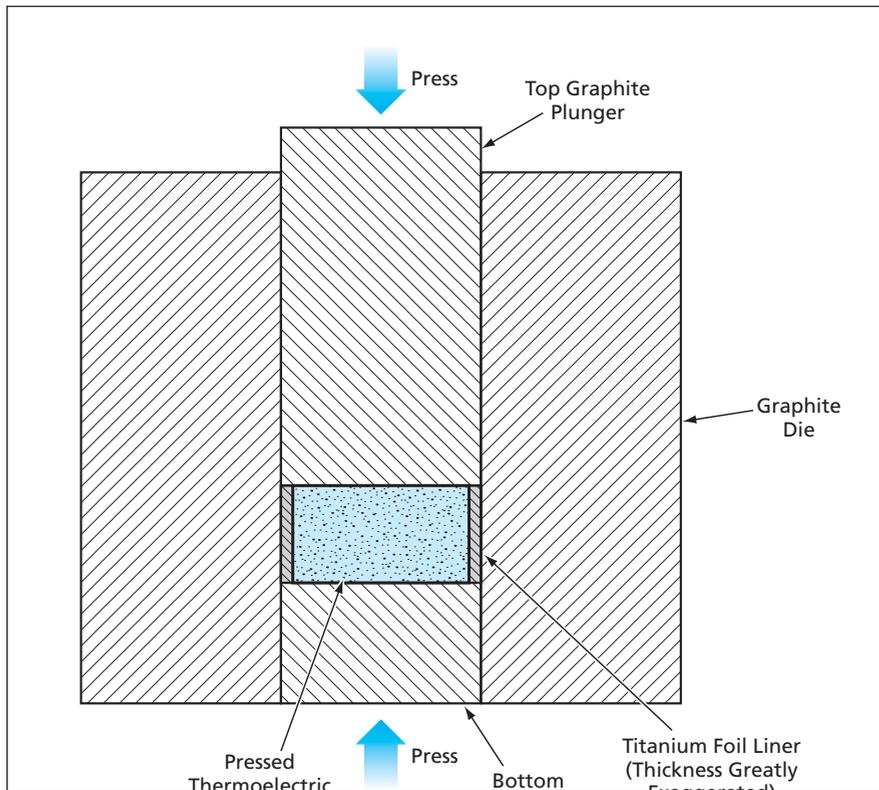
In a **Powder-Metallurgy Process** used to fabricate a segment of a thermoelectric device, the particles of thermoelectric material are sintered by heat and pressure, which is also exploited to bond the sintered mass to the outer layer of titanium foil.

then further processed. The combination of high temperature and pressure in the die acts to promote bonding between particles, and as such, is ideal as a means of adding an adherent sublimation-suppressing outer layer. Hence, the process is modified by simply lining the inner wall of the die with a foil of the barrier material before filling the die with the thermoelectric powder (see figure).

In preparation for further experiments, the modified process was used to fabricate specimens of n- and p-type skutterudites covered with adherent 25-μm-thick foils of titanium. In the experiments, these specimens were heated in a vacuum under the same conditions as in the experiments described above, then sectioned and examined. Like the niobium foils in those experiments, the titanium foil outer layers in these experiments were found to have suppressed sublimation of Sb.

Guided by the aforementioned experiments, a powder-metallurgy process for fabricating skutterudite was modified to provide for covering the outer surfaces of the segments with titanium foils. In the unmodified process, the thermoelectric material, in powder form, is hot-pressed in a graphite die, then removed,

⬢ Ultrahigh-Temperature Ceramics
Materials are being developed to withstand temperatures above 1,650 °C.

Ames Research Center, Moffett Field, California

Ultrahigh temperature ceramics (UHTCs) are a class of materials that include the diborides of metals such as hafnium and zirconium. The materials are of interest to NASA for their potential utility as sharp leading edges for hypersonic vehicles. Such an application requires that the materials be capable of operating at temperatures, often in excess of 2,000 °C. UHTCs are highly refractory and have high thermal conductivity, an advantage for this application. UHTCs are potentially applicable for other high-temperature processing applications, such as crucibles for molten-metal processing and high-temperature electrodes.

UHTCs were first studied in the 1960's by the U.S. Air Force. NASA's Ames Research Center concentrated on developing materials in the HfB_2/SiC

family for a leading-edge application. The work focused on developing a process to make uniform monolithic (2-phase) materials, and on the testing and design of these materials. Figure 1 shows arc-jet models made from UHTC materials fabricated at Ames. Figure 2 shows a cone being tested in the arc-jet. Other variations of these materials being investigated elsewhere include zirconium–based materials and fiber-reinforced composites.

Current UHTC work at Ames covers four broad topics: monoliths, coatings, composites, and processing. The goals include improving the fracture toughness, thermal conductivity and oxidation resistance of monolithic UHTCs and developing oxidation-resistant UHTC coatings for thermal-protection-system sub-

strates through novel coating methods.

Figure 1. **Examples of UHTC Components** are shown that have been tested in the NASA Ames Arc Jet facility to evaluate the materials response in a simulated reentry environment. The cone and wedge models are representative of the scale and geometries anticipated for use on UHTC sharp leading-edge vehicles.