placed in the tube furnace, wherein it was heated to 1,150 °C and held at this temperature for one hour. The test fixture was then retracted from the furnace (see Figure 1) and allowed to cool to 150 °C. The cooling process took approximately 5 to 6 minutes. Upon reaching 150 °C, the test fixture with the coupon was placed back in the furnace and reheated to 1,150 °C. The entire heating-and-cooling sequence was considered one cycle, and the lifetimes of the coupons were assessed on the basis of the numbers of cycles to failure.

The heat treatment of the NiCoCrAlY bond coats at reduced oxygen partial pressure yielded a significant increase in lifetimes: Coupons heat-treated to 1,750 °F (954 °C) at reduced oxygen partial pressure exhibited more than double the cycle lives of those containing as-sprayed NiCoCrAlY. This considerable increase in life can be attributed to the fact that selective oxidation of the aluminum and chromium in the bond coat yielded a graded interface. The heat treatment of the NiCrAlY bond coats yielded little or no increase in lifetimes.

The failure mechanisms of the coupons containing NiCoCrAlY bond coats differed from those of the coupons containing the NiCrAlY bond coats: The NiCoCrAlY-bond-coated specimens failed by decohesion and/or delamination at the interfaces between the top and bond coats. The NiCrAlY-bond-coated specimens underwent cohesive failure within the bond coats. Evidence of failure by these mechanisms can be seen in the left and the middle part, respectively, of Figure 2.

In an effort to reduce the extent of internal oxidation in the bond coats, platinum and rhodium coats were employed as diffusion barriers. Initially, as-sprayed NiCoCrAlY-bond-coated coupons were coated with platinum to a thickness of 2 µm by physical vapor deposition (PVD). An example of a platinum diffusion barrier can be seen in the right part of Figure 2. The platinum-coated Inconel coupons were heat-treated to 1,800 °F (982 °C), then magnesium aluminate spinel top coats were thermally sprayed over the platinum coats. Rhodium diffusion barriers were applied to the surfaces of NiCoCrAlY-bond-coated coupons by pen electroplating. (Pen electroplating was investigated as a means of forming diffusion barriers because it is easy to perform and does not entail costly capital investment.)

The rhodium diffusion barriers yielded only a marginal increase in the lives of NiCoCrAlY-bond-coated coupons. However, platinum diffusion barriers applied by PVD in conjunction with reduced-oxygen-partial-pressure heat treatment yielded substantial increases in lifetimes. The platinum films were thick enough to constitute oxygen-diffusions barriers that slowed the growth of internal oxides by promoting the formation of alumina-rich scale at the interfaces between the top and bond coats. The best results achieved to date were realized by use of sputtered platinum diffusion barriers in conjunction with heat treatments to 1,800 °F (982 °C) at reduced oxygen partial pressures. This combination yielded a four-fold increase in the fatigue lives of NiCoCrAlY-bond-coated coupons.

This work was done by Otto J. Gregory and Markus A. Downey of the University of Rhode Island, and Steve Wnuk and Vince Wnuk of HPI Inc. for Glenn Research Center.

Inquiries concerning rights for the commercial use of this invention should be addressed to NASA Glenn Research Center, Innovative Partnerships Office, Attn: Steve Fedor, Mail Stop 4–8, 21000 Brookpark Road, Cleveland, Ohio 44135. Refer to LEW-17530-1.

Multifunctional, High-Temperature Nanocomposites

Electrical and thermal conductivities increase with proportions of nanotubes.

Langley Research Center, Hampton, Virginia

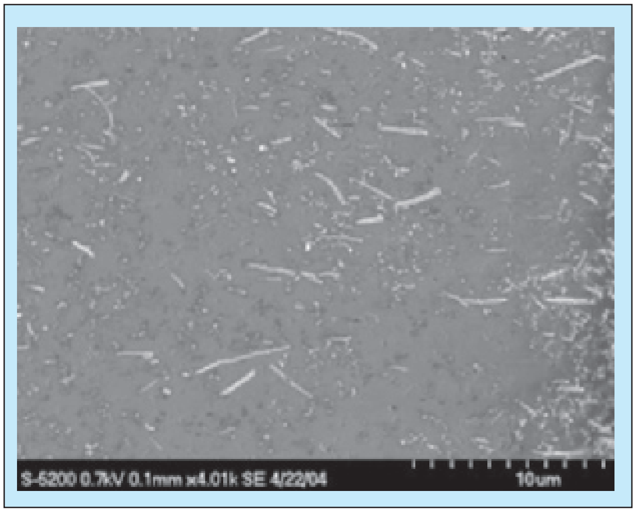
In experiments conducted as part of a continuing effort to incorporate multifunctionality into advanced composite materials, blends of multi-walled carbon nanotubes and a resin denoted "PETI-330" (wherein "PETI" is an abbreviation for "phenylethynyl-terminated imide") were prepared, characterized, and fabricated into moldings. PETI-330 was selected as the matrix resin in these experiments because of its low melt viscosity (<10 poise at a temperature of 280 °C), excellent melt stability (lifetime >2 hours at 280 °C), and high temperature performance (>1,000 hours at 288 °C). The multi-walled carbon nanotubes (MWCNTs), obtained from the University of Kentucky, were selected because of their electrical and thermal conductivity and their small diameters. The purpose of these experiments was to determine the combination of thermal, electrical, and mechanical properties achievable while still maintaining melt processability.

The PETI-330/MWCNT mixtures were prepared at concentrations ranging from 3 to 25 weight-percent of MWCNTs by dry mixing of the constituents in a ball mill using zirconia beads. The resulting powders were characterized for degree of mixing and thermal and rheological properties. The neat resin was found to have melt viscosity between 5 and 10 poise. At 280 °C and a fixed strain rate, the viscosity was found to increase with time. At this temperature, the phenylethynyl groups do not readily react and so no significant curing of the resin occurred. For MWCNT-filled samples, melt viscosity was reasonably steady at 280 °C and was greater in samples containing greater proportions of MWCNTs. The melt viscosity for 20 weight-percent of MWCNTs was found to be ≈28,000 poise, which is lower than the initial estimated allowable maximum value of 60,000 poise for injection molding. Hence, MWCNT loadings of as much as 20 percent were deemed to be suitable compositions for scale-up.

High-resolution scanning electron microscopy (HRSEM) showed the MWCNTs to be well dispersed in the polymer matrices, while high-resolution transmission electron microscopy shows splits in the walls of the MWCNTs but no catastrophic breakage of tubes. To further assess processing characteristics prior to scale-up, samples containing 10, 15, and 20 weight-percent of MWCNTs were processed through a laboratory melting extruder. HRSEM of the extruded fibers shows significant alignment of MWCNTs in the flow direction (see figure). For the samples containing 20 weight-percent of MWCNTs, difficulties were encountered during feeding, and the temperature of a rotor in the extruder rose to 245 °C because of buildup of frictional heat; this indicates that materials of this type having MWCNT concentrations ≥20 weight- percent may not be melt-processable.

On the basis of the results from the foregoing characterizations, samples containing 10, 15, and 20 weight-percent of MWCNTs were scaled up to masses of ≈300 g and used to make specimens having dimensions of 10.2 by 15.2 by 0.32 cm. These specimens were molded by (1) injecting the mixtures, at temperatures between 260 and 280 °C, into a tool made of the low-thermal-expansion alloy Invar® and then (2) curing for 1 hour at 371°C. The tool was designed to impart shear during the injection process in an attempt to achieve some alignment of the MWCNTs in the flow direction.

Qualitatively, the moldings from the 10 and 15 weight-percent samples appeared to be good. The moldings were subsequently characterized with respect to thermal, mechanical, and electrical properties. However, as expected from the results of the extrusion experiments, the 20 weight-percent sample could not be injected because of its higher viscosity.



MWCNTs Were Substantially Aligned along the flow direction after extrusion, as shown in this high-resolution scanning electron micrograph.

The hardness value of each molded PETI-330/MWCNT specimen was found to be lower than that of the neat resin in the sense that an indenter was found to penetrate to a greater depth or an enhanced plastic deformation of the material was observed. The neat resin specimen was found to be electrically insulating. For the other specimens, the electrical resistivity was found to decrease with increasing concentration of MWCNTs, ranging from 8.86×10^3 Ω/cm for the 10 weight-percent sample to 5.13×10^3 Ω/cm for the 15 weight-percent sample. The thermal conductivities were found to increase with the proportion of MWCNTs, ranging from 0.219 W/(m·K) for the neat resin specimen to 0.577 W/(m·K) for the 10 weight-percent specimen and 0.777 W/(m·K) for the 15 weight-percent specimen. This trend in thermal conductivity suggests that nanotubes form networks in the polymer matrices that conduct heat, but not to the extent expected based on the high thermal conductivity of the MWCNTs.

Upon machining of the specimens to prepare them for mechanical tests, voids were observed. Unfortunately, these voids made the samples unsuitable for determination of mechanical properties. Notwithstanding the present lack of data on mechanical properties, the electrical and thermal properties and processing characteristics of these materials offer significant potential for applications in which multifunctionality may be required.

This work was done by John W. Connell, Joseph G. Smith, Emilie J. Siochi, and Dennis C. Working of Langley Research Center; Jim M. Criss of M&P Technologies; Kent A. Watson and Donavon M. Delozier of the National Institute of Aerospace; and Sayata Ghose of the National Research Council. Further information is contained in a TSP (see page 1).
LAR-17082-1

Multilayer Impregnated Fibrous Thermal Insulation Tiles

Temperature rises are limited by transpiration cooling.

Ames Research Center, Moffett Field, California

The term “secondary polymer layered impregnated tile” (“SPLIT”) denotes a type of ablative composite-material thermal-insulation tiles having engineered, spatially non-uniform compositions. The term “secondary” refers to the fact that each tile contains at least two polymer layers wherein endothermic reactions absorb considerable amounts of heat, thereby helping to prevent overheating of an underlying structure. These tiles were invented to afford lighter-weight alternatives to the reusable thermal-insulation materials heretofore variously used or considered for use in protecting the space shuttles and other spacecraft from intense atmospheric-entry heating. Tiles of this type could also be useful on Earth as relatively lightweight components of fire-retardant structures.

The SPLIT concept admits to so many different combinations of constituent materials, spatial distributions of the materials, and fabrication processes, that it is not possible to even list, much less summarize or describe all of them. Instead, a representative example must serve to illustrate the main principles. The starting material for fabricating a typical SPLIT is a porous substrate, having a void volume fraction of about 90 percent, that comprises a rigid tile or fabric made from any of a large variety of carbon fibers and/or ceramics fibers. The fiber composition can be the same throughout the thickness or can be graded: for example, it can differ among front, middle, and rear layers.

The front layer, which is the one to be exposed directly to intense heating, is typically impregnated with a thermosetting resin (e.g., a phenolic or a silicone). This layer becomes the first line of defense against intense heating: a large amount of heat is absorbed in the pyrolysis of the front polymer layer and is dissipated to the environment through a combination of outflow of the pyrolysis gas, and thermal radiation from the char layer formed in the pyrolysis. The outflow of the pyrolysis gas also provides further protection against heating by blocking the inflow of hot ambient gas.

The middle layer (if any) is typically not impregnated. The back layer is the one to be placed in contact or proximity to the structure to be protected. The back layer is initially impregnated with a thermoplastic polymer (the secondary