UHTC COMPOSITES WITH NANOTUBE-REINFORCEMENTS FOR ADVANCED TPS APPLICATIONS

M. Stackpoole[(1)], G. Rom[(2)], J. Whitt[(3)], T. Squire[(4)] and J.O. Arnold[(5)]

[(1)]ELORET Corp., Sunnyvale, CA 94086, USA, Email: mstackpoole@mail.arc.nasa.gov
[(2)]NASA EA Program, M.S. 234-1, Moffett Field, CA 94035, USA,
[(3)]NASA EA Program, M.S. 234-1, Moffett Field, CA 94035, USA
[(4)]NASA Ames Research Center, M.S. 234-1, Moffett Field, CA 94035, USA, Email: Thomas.H.Squire@nasa.gov
[(5)]NACNT/UARC, M.S. 229-3, Moffett Field, CA 94035, USA, Email: jarnold@mail.arc.nasa.gov

ABSTRACT

Ultra high temperature ceramics (UHTCs) are candidates for use on hypersonic entry vehicles with sharp leading edges. While a sharp leading edge geometry improves a vehicle's aerodynamic performance (a high lift/drag ratio and cross range capabilities 2.5 times those of blunt vehicles), it also induces more severe heating during atmospheric entry, and requires materials with a very high temperature capability.

The aerodynamic performance of a sharp vehicle may be of great value for future NASA solar system missions. The execution, for example, of a maneuver like aero-gravity assist, to reduce travel time to distant planets, would require a vehicle with a very high lift/drag ratio, and materials with temperature capabilities similar to those of UHTCs.

While recent work at NASA Ames has demonstrated the promise of these materials, their application to a mission of this kind would require an increase in their high temperature performance (achieved by increasing thermal conductivity). A conceptual study reported at the 2004 Probe Workshop, which used conservative assumptions about the extent to which the high thermal conductivity of carbon nanotubes (on the order of 3000 W/mK in the axial direction) would be carried over into the properties of UHTC materials that contained them, concluded that development of such composite materials would be valuable. Addition of nano-reinforcements to UHTCs offers the possibility of improving not only their thermal conductivity, but also their thermal shock, strength and modulus.

This paper summarizes current work on processing and characterization of ceramic composites with carbon nanotube reinforcements. Initial samples of aligned nanotubes in a refractory matrix have been processed. Preliminary mechanical properties on SiC tapes have demonstrated that partial nanotube alignment is possible through a tape casting approach. Initial microscopy has also been completed, and it confirms that nanotubes survived the composite consolidation process.

BACKGROUND

Aero-Gravity Assist (AGA) is a novel inteplanetary transportation technology concept, which would enable relatively short trip durations and/or the use of smaller launch vehicles for solar system exploration [1]. The maneuver requires a vehicle with a very high lift/drag (L/D) ratio, on the order of 10. An aerodynamic vehicle concept called a waverider, developed in the 1950s, employed a slender shape and sharp leading edges, and it has been proposed that waveriders have the aerodynamic characteristics appropriate for AGA.

Previous studies have indicated significant benefits from AGA [1]. The 1999 baseline mission to Pluto-Kuiper Belts used a 9.5 year trajectory with a large launch vehicle (launch V_∞ = 12.3 km/sec). By comparison, the employment of AGA for a 2013 Earth-Venus-Mars-Pluto mission would allow a launch V_∞ = 7 km/sec, with L/D of 8.0. If the launch V_∞ were raised to 8.0 km/sec, the trip time could be reduced from 9.5 years to 6.0 years. These results are significant, and suggest a strong return on investment from R&D of materials that would enable the employment of waveriders. Both candidate ablating materials and ultra high temperature ceramics (UHTCs) were discussed in the study, which concluded that UHTCs were an enabling technology for AGA, because of their unique combination of mechanical, thermal and chemical properties. However, it was noted that further work was needed to extend UHTC capabilities for this application.

Fig. 1 [1] shows the boundary between ablating and non-ablating UHTCs for typical AGA trajectories for Venus and Mars at an equivalent

Earth altitude. The figure shows that ablation of UHTCs (then available) would occur below altitudes of ~ 260,000 ft (79.2 km) and at speeds of 11 - 12.5 km/sec in Venus' atmosphere and 13.4 - 14.6 km/sec in Mars' atmosphere.

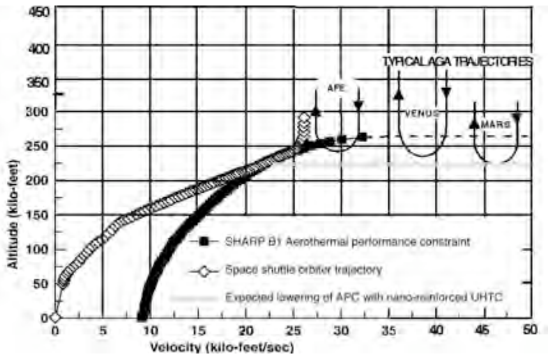

Fig. 1: Desired lowering of APC for Nano-reinforced UHTCs, compared to data on baseline UHTCs taken from [1]

The increased thermal conductivity UHTCs developed in this study for a waverider application would have the effect of bringing the aerothermal performance constraint of the materials to lower altitudes (i.e., increased atmospheric density) through elevating their use temperatures. To demonstrate such an advance would, of course, require extensive materials testing. On the basis of the modeling reported in 2004, however, we believe that the addition of nanotubes to UHTCs may be a viable way to achieve this extension of their capabilities, and take us a step closer to flying AGA at Venus or Mars.

UHTC development at NASA Ames was conducted under the SHARP, SLI and NGLT programs [2]. UHTCs, a family of materials that includes the diborides and carbides of hafnium and zirconium, show promise for use in a number of high temperature structural applications, such as sharp leading edges on Earth- and planetary-entry vehicles. A sharp geometry at the leading edge induces a higher heat flux than a blunt geometry (heat flux at the leading edge is inversely proportional to the square root of the leading edge radius)[3]. A higher heat flux generally means a higher temperature, and the temperature limit of the leading edge material will consequently impact the shape of the leading edge and/or the entry trajectories that a vehicle can fly. For this reason, UHTCs may be an enabling technology for a range of vehicles with sharp geometries, including waveriders. The suitability of the materials for leading edge applications stems from their high melting temperatures (>3000°C), and the fact that useful mechanical and physical properties are retained to high temperatures (~1800°C) [4].

Another attractive feature of UHTCs is their relatively high thermal conductivity, 65 – 135 W/mK [5], which gives them better thermal shock resistance than more insulating materials, and allows heat to be conducted from a high heating area (e.g. the leading edge) to a region of lower heating, where it is re-radiated into the atmosphere.

The potential of UHTCs for sharp leading edge hypersonic re-entry applications was recognized over 30 years ago. The first work was conducted by ManLabs, under contract to the Air Force in the 1960's and 1970's [4]. Their work was an investigation of the oxidation resistance of different UHTC/additive combinations in simulated reentry environments, and it indicated that materials such as HfB_2 and ZrB_2, with SiC additions, provided the best set of compromised properties. The SiC appears to have aided the consolidation of the diborides by preventing exaggerated diboride grain growth, and to have improved the materials' oxidation resistance, especially at intermediate temperatures. Because it does not appear that the SiC significantly effects the materials' strength or toughness, they can be considered monolithic ceramic materials, at least for mechanical property evaluation.

However, the brittle nature of monolithic materials makes them susceptible to tensile stresses. Such stresses are generated within a leading edge segment during entry, and are due to thermal gradients within the material (thermal shock). An increase in thermal conductivity will improve thermal shock performance in these systems.

THERMAL ANALYSIS

Initial thermal/stress analyses were performed on a UHTC (HfB_2 with 20 vol. % SiC) wing leading edge concept, to evaluate the potential benefits of an orthotropic composite with nanotube additions [7]. The model used conservative assumptions about the extent to which the properties of carbon nanotubes would carry over into the resulting composite material. For this analysis, a 2-D coupled thermal/stress model of a wing leading edge, shown in Fig. 2, was used. This model was developed for the 2nd Generation RLV Program at NASA Ames.

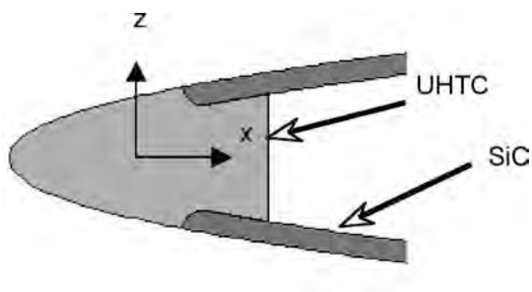

Fig. 2: Representation of a sharp leading edge

To evaluate the performance of a carbon nanotube/ UHTC sharp leading edge, two cases were considered. The first (nominal) case considered a baseline UHTC system (HfB_2/SiC), using its established thermal conductivity and assuming it to be isotropic. The second case considered a UHTC matrix with aligned nanoreinforcements in the x-direction (Fig. 2). The model conservatively assumed that the thermal conductivity in the x-direction doubled for the nano/UHTC material, a much lower increase than would be expected for the volume fraction range of nanotubes added. The thermal conductivity in the z-direction was assumed not to change from that of the baseline UHTC material. In both cases, it was assumed that there is no change in the isotropic mechanical properties of the UHTC.

Key results from this model are highlighted in Figs. 3 and 4. Fig. 3 shows a temperature history comparison at three locations on the UHTC wing leading edge, for the baseline UHTC and the system with double the thermal conductivity in the x-direction. A significant decrease in stagnation point temperature is observed in the higher thermal conductivity system over the baseline UHTC system. It is also worth noting that a slight but acceptable rise in temperature is observed at the windward and leeward attachment points for the system with higher thermal conductivity in the x-direction. Fig. 4 displays the maximum principal stress history in the middle of the UHTC wing leading edge. A significant decrease in tensile stress is observed for the system with higher thermal conductivity in the x-direction, indicating a material more resistant to thermal shock than the nominal UHTC material.

This preliminary analysis indicates considerable benefits may be had from an orthotropic carbon nanotube reinforced UHTC composite. More complete model details and results are presented in Ref. [7].

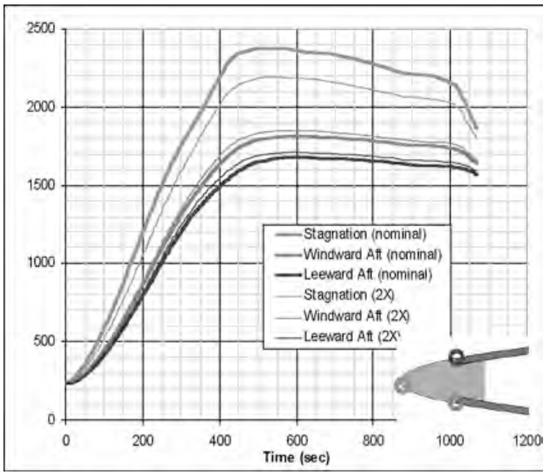

Fig. 3. Temperature history comparison at three locations on the UHTC wing leading edge model

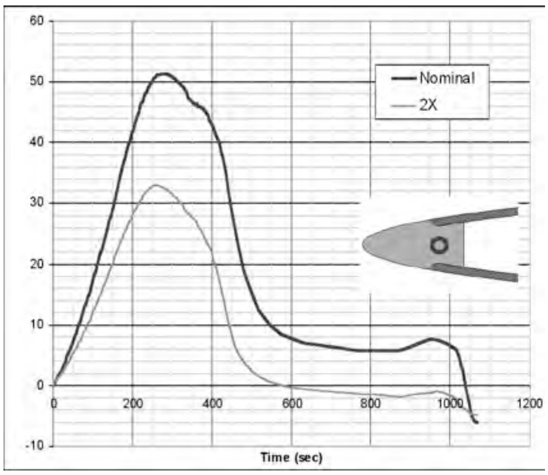

Fig. 4. Principal tensile stress in the UHTC leading edge versus time.

NANO-REINFORCED SiC COMPOSITES

Initial composite samples of an SiC matrix with nanotube reinforcements were processed, to verify that a tape-casting approach could achieve partial alignment of nanotubes. The relatively strong van der Waals forces of nanotubes, which make them inclined to agglomerate, can give rise to processing challenges and make it difficult to achieve uniform dispersions. Further challenges are introduced when an orientation-controlled structure is desired.

Two routes are employed to process a nanotube/ SiC composite: a powder processing route, where the nanotubes are directly added to SiC powder, and a preceramic polymer route, where the nanotubes are dispersed in a preceramic polymer (AHPCS), which will pyrolize to form a nanocrystalline SiC. The main advantage of the preceramic polymer route over powder processing is that it does not require processing aids.

Carbon nanotubes were obtained from Nanolabs Inc. (95% purity, diameter of 20-50 nm and lengths of 1-5 microns and 5-20 microns). The preceramic polymer was obtained form Starfire Chemicals (AHPCS). SiC was obtained from Ibiden (0.3 μm average particle size). Nanosperse, a commercially available dispersant from Nanolabs Inc., was used to assist dispersion in all cases. All SiC-derived systems were hot-pressed in Argon at 40 MPa, at temperatures less than 2000°C. Detailed processing information is excluded from this paper.

For both systems, slurries were prepared (nanotube vol. fraction < 5%) and degassed. Tapes were cast with a doctor blade assembly and allowed to dry. Disks were punched from the tapes and stacked, with care taken to preserve the axial orientation of the systems. Samples were characterized to determine density, open porosity, and Young's modulus (by a pulse echo method). The fracture toughness of the samples was estimated by an indentation method (using a Shimadzu HSV-30 hardness tester) according to Eq 1:

$$K_c = \alpha \left(\frac{E}{H}\right)^{\frac{1}{2}} \left(\frac{\rho}{c^{\frac{2}{3}}}\right) \qquad (1)$$

where α is an empirical constant (0.040), c is the radial crack length taken from corners of indent, E is Young's modulus, and H is Vickers hardness.

Directional properties were observed for both SiC systems, indicating nanotube allignment. Modulus data for the SiC powder/nanotube starting materials, obtained parallel and perpendicular to fiber allignment, is summarized in Table 1. The modulus of the SiC without nanotubes is approximately 290 GPa. The modulus obtained for the nanotube-reinforced SiC in the direction perpendicular to the reinforcements is 436 GPa, while the modulus obtained parallel to the reinforcements is ~ 600 GPa.

Fig. 5 demonstrates that samples containing aligned nanotubes show marked improvements in toughness, in the direction perpendicular to the aligned nanotubes, over the matrix material alone. Toughness in the direction parallel to the nanotube alignment has similar values to the material processed without nanotubes (4.94MPam$^{1/2}$).

Table 1: Summary of modulus data for SiC/nanotube composites processed from powder routes

System	E(GPa)
SiC (no additions)	290
Nano/SiC perpendicular to alignment direction	436
Nano/SiC parallel to alignment direction	602

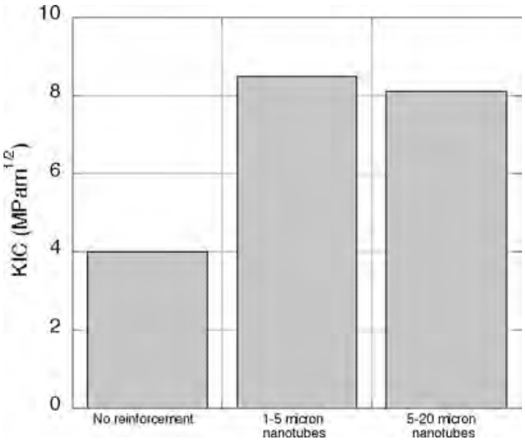

Fig 5: Indentation toughness tested perpendicular to nanotube alignment direction (composites processed from preceramic route)

Fracture surfaces of consolidated nanotube/SiC composites, for samples processed both from powder and preceramic polymer routes, were examined by SEM. Nanotubes were located on the fracture surfaces after firing, an indication that the nanotubes survived the consolidation process. Fig 6 is a typical fracture surface micrograph for the system processed from a preceramic polymer route.

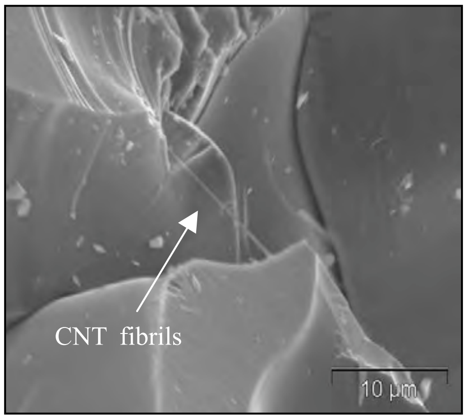

Fig. 6: Fracture surface of post-fired nanotube/SiC composite (processed from a preceramic polymer route)

Initial work on SiC composites with nanotube additions demonstrates a tape casting approach can be used to achieve alignment. This approach, in which the nanotubes survive the consolidation step, merits further pursuit.

UHTC COMPOSITES WITH NANOTUBE ADDITIVES

Tape-casting was also the approach chosen to achieve preferred alignment for the UHTC systems. Many factors have to be considered during casting and all have to be precisely controlled to achieve a "perfect" final product. For example, all the particles have to be approximately the same mass, to prevent settling and separation of the individual phases. Segregation will lead to inhomogeneous materials with different shrinkage rates during drying. This will result in cracked or curled tapes. In addition to the general processing challenges associated with tape-casting, UHTCs, as multi-component systems, present some special challenges. For such systems, both the density and particle size of the constituents need to be considered.

For the UHTC systems, our initial efforts have focused on optimizing these parameters. The aim has been to achieve systems where the additives are compatible with all components of the UHTC system, and to optimize particle size for different components, since a significant density variation is observed in these systems. To date, we have achieved green UHTC tapes that are workable, without phase settling or casting issues. Many formulations to determine suitable binders, dispersants, plasticizers and solvents were evaluated. We have prepared castable slurries of HfB_2/SiC, HfC/SiC and ZrB_2/SiC with nanotube reinforcements, and have a working formulation for each. An example of a typical tape for an HfC/SiC/nanotube system is included in Fig. 7. The attainable tape thicknesses range from ~0.22mm to ~0.5mm for these systems.

SUMMARY AND FUTURE WORK

Initial thermal/stress analysis has indicated that an orthotropic carbon-nanotube-reinforced UHTC composite may offer considerable benefits. The model used conservative property estimates to derive these results. On the basis of this encouraging analysis, samples composed of a SiC matrix and carbon nanotubes have been processed, to determine whether tape casting can effectively achieve the preferred alignment of the nanotubes. All samples were consolidated via hot-pressing. Initial modulus and toughness data for this system indicate that achieving an orthotropic system is possible. SEM confirmed that the nanotubes survived the consolidation step in the SiC composite system. We have also developed a working formulation to tape-cast select UHTC compositions.

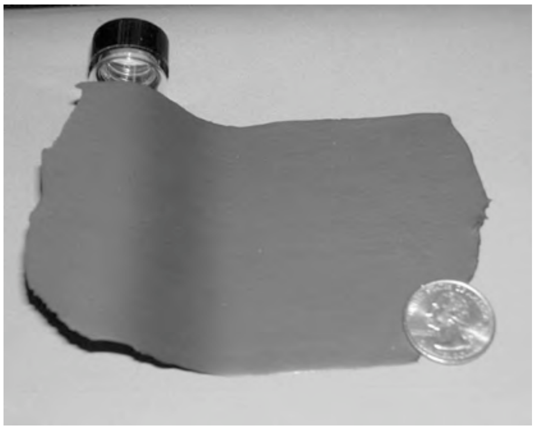

Figure 7: Example of a HfC/SiC/nanotube tape

The next phase of this work will focus on consolidation of stacked nanotube-reinforced UHTC tapes by hot-pressing and Spark Plasma Sintering (SPS), to yield aligned composites with directional properties. A more refined microstructure is expected in samples processed by SPS than in samples processed by traditional hot-pressing, and may yield superior mechanical properties. Select property measurements to demonstrate the effectiveness of alignment will be followed by microstructural evaluation. The final goal is to complete an arc jet evaluation of these aligned nano-reinforced UHTC systems and make a comparison to baseline UHTC compositions. This work will provide a basis for long-term projects on understanding the processing and properties of these new materials.

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