Development of New and Innovative Matrix Materials and Application Methods for PMCs, CMCs and C-C Composite Systems

Randy Lee   Jacobs ESTS / ICRC / EM40

Description/Objectives/Approach

- ★ Common polymer thermosets such as epoxies, phenolics, polyimides and cyanate esters have a long history of accomplishments as primary matrix resins in advanced composite structures and assemblies. However, a new generation of matrix candidates, precursors and monomers, both organic and inorganic, are at hand. Many of these are more viable, more affordable and environmentally compatible.
- ★ Some of these classes might include, but are not limited to, synergistic copolymer thermosets, engineered hybrid thermoplastics, high yield multifunctional aromatic monomers, oxide/non-oxide inorganic precursors, organic/inorganic liquid crystal polymers, high temperature elastomers, low observables, semi-flexible glasses and ceramics.
- ★ Process applications and optimizations may involve common fabric impregnation, resin infusion, sol-gel processing, hot melt infusion, in-situ copolymerization, CVD/CVI, and monomer infiltration. Specialized matrix processing may facilitate chemical binding interactions with carbon, glass and organic fiber surfaces. Some operations may offer green technologies and reduced volatile emissions.
- ★ This effort seeks to explore these technologies, exploit their benefits and characterize their feasibility as next generation matrix materials for advanced composites, adhesives and coatings.

Rationale for MSFC Technology Development

- ★ MSFC has the engineering/scientific expertise to lead technical efforts for experimental laboratory processing and developmental polymer synthesis required for small batch processing.
- ★ MSFC possesses extensive composite fabrication capabilites, adhesive mixing and coating application facilities, and a dedicated clean room for prepreg preparation and tailoring with the potential for experimental matrix prepregging operations and evaluations.
- ★ MSFC possesses extensive characterization capabilities for organic and inorganic analysis of novel monomers and polymers.

Value to NASA/Commercial

- ★ Such matrix systems may offer improved thermal and mechanical properties, high T_g, and low CTE (increased resistance to cryogenic microcracking). Others may utilize the benefits of mesogenic side chains, facilitate smart technology or permit *non-autoclave curing processes* and low temperature crosslinking mechanisms which can offer portability. Still others can provide greater toughness, high temperature elasticity, hermeticity, and the ability to transform into a different material when exposed to energy.

Readiness Level

- ★ Building upon extensive published workings and industry accomplishments, several monomer families and potential precursors have already been evaluated to varying degrees, so the learning curve may be minimal for these candidates. Other matrix systems will require further testing and process development to define feasibility requirements.

JACOBS ESTS Group

ICRC A Subsidiary of VSE Corporation

Alternative Polymer Precursors and Innovative Spinning/Processing Methods for Producing Rayon-Like Carbon Fibers

Randy Lee   Jacobs ESTS / ICRC / EM40

Description/Objectives/Approach

- ★ Recent materials and methodologies for producing carbonized rayon fabrics used in composite RSRM nozzles have utilize brands such as NARC, Enka and Avtex via the process of regenerated cellulose. However, environmental concerns associated with caustic processing of such traditional rayons have all but eliminated these sources.
- ★ A number of alternative and potential fiber precursor concepts have gained attention in recent times. Some of these include Lyocel-type cellulose derivatives, polyvinyl alcohol and aromatic nylons. One of the mainstream PAN sources was also evaluated at some point in the past. However, most of these studies had limited funding and thorough investigations into their feasibilties have been inconclusive.
- ★ It is believed that polymers with cyclic structures or those which undergo cyclization during the spinning/precipitation/coagulation processes are required to produce carbon fibers which are acceptible (sp^2-bonded carbon rings facilitate the carbonization process).
- ★ There is also evidence that specific fiber shape morphology features characteristic of classic rayons are required to produce effective composite interlaminar strengths. These attributes must manually be incorporated into alternative precursors which do not develop such features during the normal fiber processing sequence.
- ★ Candidates for such studies might include, but are not limited to, melt-spun phenolic fibers, PBI, PBO, aramids, melt-spun PAN, and renewable or recycled blends of lignin/cellulose, all of which can lead to glassy carbonaceous microstructures with minimal conductivity.
- ★ A variety of fiber processing ideas are at hand. Some of these include, but are not limited to, alternative spinning methods in aprotic solvents, graduating coagulation baths, gradient skin-core formation, co-monomer variations, and post-spin modifications. Other ideas are available. Most of the newer candidates support environmentally compatible processing.

Value to NASA/Commercial

- ★ It is well documented that flame surface composite nozzle ablators are most effective when certain carbonized rayon fabrics are used as the primary reinforcement. Thus, other NASA centers and commercial STS endeavors stand to benefit immensely from these efforts.
- ★ With the vanishing of domestic classic rayon sources, development of acceptible alternatives is mandatory.

Rationale for MSFC Technology Development

- ★ MSFC has the engineering and scientific expertise to lead development activities for prototype fiber production and may acquire state-of-the-art processing facilities for fiber carbonization and associated processing in the near future.
- ★ MSFC possesses extensive capabilites for process characterization and materials analysis of monomers, polymers, organic and inorganic fiber precursors which may become candidates of interest.

Readiness Level

- ★ While a few private industry entities have experimented with the processing and feasibility requirements of such fiber alternatives, further R&D is necessary to synthesize fibers that are truly rayon-like.
- ★ Some candidates, such as PAN and Lyocel, have notable histories of success for such applications, so shorter learning curves can be expected (with application of the appropriate modifications).

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New and Innovative Methods for Bonding/Joining C-C and CMC Components, and Fabricating C-C/CMC Honeycomb Composite Assemblies

Randy Lee   Jacobs ESTS / ICRC / EM40

Description/Objectives/Approach

★ Secondary bonding in polymer matrix composites (PMCs) has been practiced in the commercial and defense industries for several decades. While some of those applications have provided fairly strong, robust joints, analogous methods for bonding C-C and CMC substrates together are only in their infancy.

★ This effort seeks to develop and mature the materials and practices required to produce strong adhesively bonded joints between bi-material interfaces such as ceramic-ceramic, ceramic-metal, ceramic-graphite and carbon-carbon.

★ These techniques are expected to provide the capabilities to fabricate large, high temperature, structural honeycomb assemblies from monolithic and combined C-C, CMC and metal constituents.

★ A few of the materials and processes which might be examined include, but are definitely not limited to, high yield polymer thermoset bonding agents which cure via free radical crosslinking (nonautoclave curing), preceramic polymer adhesives (existing silane and silazane products already cure through radical mechanisms), nano-metal-catalyzed resins which generate their own sintering temperatures, localized matrix densification of bonding interfaces (proven to produce very strong joints), use of high carbon resins for co-curing and co-pyrolysis of joined interfaces. Many other ideas are available.

Rationale for MSFC Technology Development

★ MSFC currently has the technical know-how and hands-on expertise to oversee, participate in and lead small to large scale development efforts and fabrication operations for both demonstration and production articles.

★ MSFC possesses extensive capabilities for composite fabrication as well as mixing and processing of particulate-based resin slurries and bonding agents. The facility also contains a dedicated clean room for prepreg preparation and tailoring with the potential for experimental matrix prepregging operations and evaluations.

★ MSFC possesses extensive ambient and high temperature characterization capabilities for organic and inorganic analysis of innovative materials and precursors.

Value to NASA/Commercial

★ Development of such techniques will pave the way for advanced structual assemblies and honeycomb-type structures which can offer novel aerospace applications. Well joined cores and face sheets comprised of individually fabricated C-C and CMC components could find some unusually innovative applications aboard future commercial space planes from outer skin strucures to substructure components.

Readiness Level

★ Building upon current technologies, minimal development effort would be required for proof of concept or the production of bonded demonstrator assemblies with moderate joint strengths.

★ Methodologies for producing strong C-C and CMC joints have been under development for many years with limited successes. The technology needs to be refined and matured so joints can be fabricated that are robust and strong enough to replace fasteners.

JACOBS ESTS Group

ICRC A Subsidiary of VSE Corporation

New and Innovative Methods for Producing Elastomeric Fiber/Fabric-Reinforced Composites for Elevated Temperature Applications

Randy Lee   Jacobs ESTS / ICRC / EM40

Description/Objectives/Approach

- ★ Flexible composite materials with strong ablative and insulative properties can be of great benefit as TPS components in motor components and STS hardware. Elastomers and rubbers generally have low high temperature resistance, so novel polymers and hybrids must be considered. Optimal properties are acheived when the appropriate fibers and reinforcements are incorporated into the material.
- ★ This proposal seeks to identify, develop or synthesize novel elastomers and semi-elastomeric formulations and the methods for matrix introduction into advanced composites, adhesives and coatings.
- ★ Homopolymers of the more common elastomers are mediocre for elevated temperature applications (PU, NBR, SBR, EPDM, etc.). Polyurethanes (isocyanate-crosslinked polyols) are only good to about 200°F (after post-curing, ~300°). Polyurea elastomers (isocyanate-crosslinked polyamines) are good to about 300°-350°F (up to ~400°-450° if post-cured). Siloxanes (silicones) can withstand 400°-500°) and can be uniquely formulated to transform into ceramics upon pyrolysis. The fluoroelastomers have T_gs as high as 600°-650°.
- ★ Flexible aramids, polyimides, benzimidazoles and benzoxazoles (PBI and PBO) can also be synthesized (all main chain mesogenic liquid crystals). However, blended hybrids and copolymers may offer the best route. Systems such as phenolic/NBR and epoxy/PU have some history for providing semi-elasticity in advanced composite systems.
- ★ Special copolymers of elastomeric main chains with mesogenic side groups could offer a unique form of high temperature flexibility. One example might be strategic incorporation of aramid/imide/PBI-type side chains onto siloxane main chains, or mesogenic polymers may simply be blended with the appropriate elastomers. PBI/PBO-like polymers or side groups would offer the capability to form thermosetting crosslinkings within the structure, increasing temperature resistance even higher. Other configurations are possible

Value to NASA/Commercial

- ★ Such matrix systems could offer improved performance capabilities for heterogeneous material systems in terms of high temperature flexibility and thermal stability.
- ★ Availability of such materials would be of enormous benefit to many current and future NASA programs and commercial endeavors requiring semi-elastomeric composites, adhesives and coatings for thermal applications.

Rationale for MSFC Technology Development

- ★ MSFC has the engineering/scientific expertise to the lead technical efforts for experimental laboratory processing and developmental polymer synthesis for small batch processing.
- ★ MSFC possesses extensive capabilites for composite fabrication, adhesive and polymer mixing and experimental matrix prepregging..
- ★ MSFC possesses extensive characterization capabilities for organic and inorganic analysis of innovative monomers and polymers.

Readiness Level

- ★ Building upon extensive published workings and industry accomplishments, several monomer families and potential precursors have already been evaluated to varying degrees, so the learning curve may be minimal for these candidates. Other polymer synthesis routes and matrix formulations will require further testing and process development to define feasibility requirements.

JACOBS ESTS Group

ICRC A Subsidiary of VSE Corporation

New and Innovative Methods for Fabricating Oxidation-Resistant C-C Composites for Nozzle Throats, Exit Cones, Leading Edges and TPS Structures

Randy Lee   Jacobs ESTS / ICRC / EM40

Description/Objectives/Approach

- With moderating costs and expanding opportunities for applications, next generation carbon-carbon (NCC) materials should capitalize on lessons learned from descendent technologies. For C-C platforms offering greater thermostructural capabilities, improved ablative properties (or reuseabily), lower thermal conductivity and reduced density, the choice of reinforcements, matrices and manufacturing approaches become critical.
- While there are an abundance of materials and processing approaches which have been employed in the C-C field, this effort will focus on improving the current state-of-the-art for 2-D NCC based on non-pitch reinforcements (amorphous PAN, rayon and alternative fibrous precursors) and glassy carbonaceous matrix fractions derived from innovative monomers and polymers, along with other specialized constituents designed to incorporate advanced capabilites.
- In synergistic combination, these types of constituents provide an excellent balance of high strength, low density, high ablative resistance, reuse-ability options, low conductivity, high thermal shock resistance, versatile manufacturing options, lower manufacturing costs, and a proven track record for both small and large structures.
- Some of the M&P technologies which might be examined include, but are definitely not limited to, hybrid fiber tows, novel fiber processing methods, alternative weaving configurations, multi-functional monomers with high char yields (> 80%), in-situ polymerization, non-autoclave curing mechanisms, a host of techniques to improve interlaminar mechanical properties (covered under a different proposal), CVC gradient conversion techniques for matrix deposition and oxidation protection, doping and strategic incorporation of specialized nano-constituents and the carbides and borides of certain rare earth/lanthanide metals (Zr, Hf, Ta and W) into the matrix and/or outer composite layers to provide hyper-oxidation protection. An extensive list of additional ideas and innovations are available.

Value to NASA/Commercial

- Improved versions of C-C are of great interest throughout NASA as well as commercial and private industry. Reuseable nozzles, leading edges, skin structures and substructural components derived from NCC would provide substantial benefits to risk and safety factors.
- Historically, C-C has often been the material of choice for many programs, and NCC is expected to expand the options available for future launch vehicles, commercial space planes and STS platforms.

Rationale for MSFC Technology Development

- MSFC currently has the techical know-how and hands-on expertise to oversee, participate in and lead small to large scale development efforts and fabrication operations for both demonstration and production NCC articles.
- MSFC possesses extensive composite manufacturing capabilites and testing facilities for high temperature material characterization.
- MSFC may acquire state-of-the-art processing capabilities for processing small scale C-C articles in the near future.

Readiness Level

- Building upon current methodologies and technology levels for C-C, minimal development efforts are expected to provide proof of concept and demonstrator test articles for many of these techniques. Other ideas may require further development and optimization.

JACOBS
ESTS Group

ICRC
A Subsidiary of VSE Corporation

New and Innovative Manufacturing Approaches for Producing Full Scale C-C, C-C/SiC and Ceramic Matrix Composite Aerospace Structures

Randy Lee   Jacobs ESTS / ICRC / EM40

Description/Objectives/Approach

Technology development effort to determine process feasibility and optimization parameters for both large structures and small components requiring high ablative properties (or reusability) and oxidation protection. Such articles might include, but are not limited to, small motor components, large nozzle throat rings, nose caps and leading edge panels. A multitude of ideas, materials and processes are viable.

★ **Reinforcement Structures**: Near net shaped 3-D preform architectures and 2-D laminates with enhanced *z*-reinforcements (covered under another proposal) derived from carbonized PAN, pitch, rayon or other carbon fiber precursors, SiC, Nextel and hybrid fiber tows.

★ **Matrix Materials**: Carbon precursors include, but are not limited to, high char yield polymers such as phenolic and styrenic thermosets, pitch mesophases, pyrolitic carbon and CVD. Many other monomers, polymers, organic and inorganic precursors are viable. SiC precursors include, but are not limited to, preceramic monomers and polymers, phenolics, silanes, siloxanes and CVC precursors. Other organic/inorganic polymers and precursors are available.

Various C/SiC application methods are viable including, but not limited to, liquid impregnation, gaseous infiltration, in-situ polymerization, carbonization and ceramicization, CVD, CVI and CVC. Carbon and SiC microstructures can be tailored as amorphous, glassy or crystalline depending on end use requirements. Matrix materials may also be formulated to provide oxidation protection.

★ **Coating Options** (if required): Techniques that infiltrate perpheral substrate layers and porosity provide the best adhesion and mitigation of substrate-to-coating property differentials. Numerous ideas are viable including, but not limited to, CVI, CVC, gaseous, solid state cementation, mass diffusion and plasma conversion, all of which provide unsurpassable substrate-to-coating adhesion with vastly reduced spalling and debonding propensity. Other ideas are available.

Value to NASA/Commercial

★ Improved versions of C-C and C-C/SiC are of great interest throughout NASA as well as the commercial and private industries and the US military. Potential reuseable motor, nozzle and leading edge components derived from improved C-C and/or C-C/SiC would provide substantial benefits to risk and safety factors.

★ Improved versions of C-C and C-C/SiC are expected to expand the options available for future launch vehicles, commercial space planes and next generation STS platforms.

Rationale for MSFC Technology Development

★ MSFC currently has the techical know-how and hands-on expertise to oversee, participate in and lead full scale development efforts and fabrication operations for demonstration and production articles.

★ MSFC possesses various processing capabilites and extensive testing facilities for high temperature characterization and materials analysis.

★ MSFC may acquire state-of-the-art processing capabilities for processing and densification of small scale C-C and C-C/SiC articles in the near future.

Readiness Level

★ Building upon current methodologies and technology levels for C-C and C-C/SiC, minimal development efforts are expected to provide proof of concept and demonstrator test articles for many of these techniques. Other ideas may require further development and optimization.

JACOBS
ESTS Group

ICRC
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New and Innovative Methods for Fabricating Lightweight C-C/Cement Bimatrix Composites for Nozzles, Leading Edges and TPS Structures

Randy Lee   Jacobs ESTS / ICRC / EM40

Description/Objectives/Approach

- Lightweight composite reinforced concrete structures comprised of chopped fibers, innovative polymers, functional admixtures and cement matrices have gained prominence in recent times. In addition to forming lightweight civil engineering structures, some of these systems have demonstrated their versatility in other fields as ultra-lightweight heat shields and bouyant water vessels.
- Based on Ca-Al silicate formulations and/or renewable fly ash (or coal ash), these unique material systems offer the properties of ultra-lightweight room temperature-cured ceramics with corresponding high temperature properties, high compressive strength, high toughness, low ablation rate (re-useability), high thermal insulation, easy and versatile manufacturability, autoclave and non-autoclave curing options, controllable open cell interconnecting porosity networks and water-based processing with no greenhouse gas production.
- When properly combined with and incorporated into porous carbon fiber-reinforced, / phenolic resin-densified C-C substrates, some very unique TPS structures can be formed. Much of the synergy is based on complimentary interactions between cement hydration reactions and the phenolic condensation crosslinking process to form the bi-matrix. Many other co-matrix polymers and admixtures are viable.
- This endeavor seeks to develop, optimize and refine the specific materials and manufacturing requirements for producing small and large scale lightweight TPS articles from such formulations.

Rationale for MSFC Technology Development

- MSFC currently has the engineering know-how and hands-on expertise to oversee, participate in and lead small to large scale development efforts and fabrication operations for both demonstration and production articles.
- MSFC possesses various processing capabilites and extensive testing facilities for high temperature characterization and materials analysis.
- MSFC may acquire state-of-the-art processing capabilities for processing and densification of small scale C-C and CMC articles in the near future.

Value to NASA/Commercial

- Compared to traditional ablatives, CMC materials based on C-C/Cement could offer long duration firing cycles and potential reusability for nozzles and leading edges with improved risk and safety factors for future programs.

Readiness Level

- Building upon current methodologies and technology levels for C-C and CMCs, moderate development efforts would be required for proof of concept or the successful production of demonstrator test articles incorporating cement bimatrix binders into C-C composites.

JACOBS ESTS Group

ICRC A Subsidiary of VSE Corporation

Advanced Methods for Creating Gradient Conversion Interphases in Mixed Materials for Enhanced Binding and Phase Integration

Randy Lee   Jacobs ESTS / ICRC / EM40

Description/Objectives/Approach

- ★ Graded bi and tri materials can offer enormous improvements over systems where secondary materials are simply deposited or bonded onto the first. When mass diffusion occurs on one or both sides of the interface, the two phases become fused together to create an interphase region or graded boundry zone where the two materials blend together. These systems defy the limitations of ordinary adhesion.
- ★ There are already several instances throughout the ceramics, composites and coatings industries which utilize such concepts for intimately joining materials or forming barriers for insulation and energy/mass transfer processes. The two most prominent attributes of graduating interphases in solid bimaterials are microstructural (physical) and compositional (chemical) gradients. Other properties follow.
- ★ This proposal seeks to explore, develop and optimize the most appropriate material candidates and processing requirements for producing effective multi-phase graded materials in nonmetallic, metallic and mixed constituent systems in which enhanced and unique properties are required during the formation of advanced coatings, secondary bonds and composite matrices.
- ★ To edify the concept, a few proven examples include, but are not limited to, chemical vapor conversion (CVC), plasma-assisted CVC and CVI, surface passivation, thermo and electromigration, reactive diffusion and infiltration, solid state cementation and sintering.

Rationale for MSFC Technology Development

- ★ MSFC currently has the engineering know-how and hands-on expertise to oversee, participate in and lead small to large scale development efforts and fabrication operations for both demonstration and production articles.
- ★ MSFC possesses extensive composite fabrication capabilites, adhesive mixing, bonding and coating application facilities, and a dedicated clean room for prepreg preparation and tailoring with the potential for experimental matrix prepregging operations and evaluations.
- ★ MSFC possesses extensive characterization capabilities for organic and inorganic analysis of innovative monomers and polymers.

Value to NASA/Commercial

- ★ Various programs throughout NASA stand to benefit immensely from methods that lead to vastly improved adhesion and joining of mixed material interfaces and coating systems; improved protection of matrix materials from oxidation and space environments; and mitigation of differential CTEs, thermal conductivites and thermal shock in advanced composite structures, bonded joints and coating interfaces.

Readiness Level

- ★ Building upon current methodologies and technology levels, many concepts require minimal to moderate development efforts for proof of concept or the production of demonstrator test articles. Others would require more extensive development and optimization.

JACOBS ESTS Group

ICRC A Subsidiary of VSE Corporation

Methods for Improving Interlaminar Mechanical Properties in Carbon Fiber-Reinforced PMCs, CMCs and C-C Composite Systems

Randy Lee   Jacobs ESTS / ICRC / EM40

Description/Objectives/Approach

★ Attempts to enhanced interlaminar tension and interlaminar shear (ILT/ILS) strengths in 2-D composites have been on-going for decades. This study seeks to exploit, improve and optimize such technologies and to innovate new and alternative approaches for increased ILT/ILS, particularly in PAN-based composite systems.

★ Improvements in matrix-to-fiber (chemical) bonding may include, but are not limited to, alternative matrix precusors, novel infiltration and prepregging methods, modified fiber processing to control the specific reactivities and density of fiber surface functional groups and matrix coupling mechanisms. Other techniques are available.

★ Enhancements in mechanical bonding and interlocking may provide the greatest benefits, especially for high temperature composites where chemical bonding becomes less relevant. A few techniques might be, but are not limited to, incorporation of *z* reinforcements without degrading in-plane strengths including stitching, punching, weaving and strategic implantation of barbed needles, nanotubes, pins, spikes, magnetic and toggle activated micro-fasteners.

★ Other approaches would involve advanced fiber and tow processing techniques such as those which incorporate enhanced fiber shape morhology features (crimps, crenulations, nodules, spikes), use of staple fibers bundled in effective S/Z twisting patterns, and more appropriate hybrid tows or blended yarns to enhance intemingling of fabric layers. Many other ideas are available.

Rationale for MSFC Technology Development

★ MSFC currently has the engineering skills and hands-on expertise to oversee, participate in and lead small to large scale development efforts and fabrication operations for both demonstration and production articles with improved ILT/ILS properties.

★ MSFC possesses extensive capabilities for 2-D composite fabrication, post-processing and machining. The facility also contains a dedicated clean room for prepreg preparation and tailoring with the potential for experimental matrix prepregging operations and evaluations.

★ MSFC possesses extensive ambient and high temperature characterization capabilities for chemical, physical and mechanical analysis of advanced composite materials.

Value to NASA/Commercial

★ Current 2-D composite systems often have a tendency to delaminate when subjected to abnormal thermal gradients or mechanical loads. Improvements in ILT/ILS, without having to use exotic 3-D preforms, would provide enormous benefits throughout NASA, the US military and the aerospace industrial community.

Readiness Level

★ Building upon current methodologies and technology levels, many concepts require minimal to moderate development efforts for proof of concept or the production of demonstrator test articles. Others would require more extensive development and optimization.

JACOBS ESTS Group

ICRC A Subsidiary of VSE Corporation

Alternative Methods for Increasing Ablation Resistance and Decreasing Thermal Conductivity in Carbon Fiber-Reinforced Composites

Randy Lee   Jacobs ESTS / ICRC / EM40

Description/Objectives/Approach

★ While many composite systems can tolerate or may actually benefit from increased thermal conductivities, ablative materials utilized in motor nozzles and vehicle leading edges must possess substantial insulative characteristics. Continuous carbon fibers and fabrics are frequently used in ablative composites, but these reinforcements facilitate undesireable conductivity effects which must be mitigated.

★ Low temperature-processed carbon fibers are often chosen as the route to address thermal conductivity issues in such ablatives. However, for high temperature applications, green fibers can lead to other anomalies and performance issues. There are alternative techniques which may be viable for such mitigation. This study seeks to identify and/or develop effective methods to enhance thermal resistivity in contin-uous carbon fiber reinforced ablator composites.

★ In porous nonmetallics, thermal conductivity is a *bulk* property, especially in heterogeneous composite materials. Thus, mitigation should be addressed using methods that perturb, disrupt or otherwise block thermal energy transfer through the bulk composite.

★ A few techniques might include, but are not limited to, (a) elimination of any existing constituents which are conductive and expendable (such as carbon black fillers in current CCP materials), (b) incorporation of insulative particulate fillers including Al_2O_3, SiO_2 and/or SiC, (c) binder modification with lightweight cement additives (chopped fiber and polymer-modified Ca-Al-B silicates), (d) specialized porosity control techniques (an interconnecting open pore network provides the greatest insulation), (e) use of staple fibers of specified aspect ratio (in lieu of continuous tow) bundled in the appropriate S/Z twisting patterns, (f) hybrid tows or blended yarns in which current rayons are intermingled with SiC or Nextel fibers, (g) modified stabilization treatments during the fiber carbonization process to control fiber porosity and skin-core composition. Other ideas are available.

Value to NASA/Commercial

★ Improvements in ablative and resistivity properties for nozzle and leading edge structures would be of enormous benefit to many current and future NASA programs as well as commercial and US military endeavors.

Rationale for MSFC Technology Development

★ MSFC has the engineering know-how and hands-on expertise to oversee, participate in and lead small to large scale develop-ment efforts and fabrication operations for both demonstration and production articles.

★ MSFC possesses extensive capabilities for composite fabrication as well as mixing and processing of particulate-based resin slurries and bonding agents. The facility also contains a dedicated clean room for prepreg preparation and tailoring with the potential for experimental matrix prepregging operations and evaluations.

★ MSFC possesses extensive ambient and high temperature characterization capabilities for organic and inorganic analysis of innovative materials and precursors.

Readiness Level

★ Building upon published workings and industry accomplishments, several techniques providing ablation/resistivity improvements have already been evaluated to varying degrees. Other approaches will require further development to define feasibility requirements.

JACOBS ESTS Group

ICRC A Subsidiary of VSE Corporation

Manufacturing Development of C-C/Phenolic Bimatrix Ablative Composites for Nozzle Throats, Exit Cones, Leading Edges and TPS Structures

Randy Lee Jacobs ESTS / ICRC / EM40

Description/Objectives/Approach

- ★ Current carbon cloth phenolic (CCP) ablative structures can be greatly improved by reductions in the rates of ablation, erosion and char formation. These processes are almost completely dependent on the level of phenolic (virgin) matrix comprising the composite.
- ★ C-C structures fabricated from carbonized phenolic matrices are well proven to exhibit excellent thermal stability, particularly in terms of thermal shock, low CTE, conductivity and . . . ablative erosion.
- ★ Phenolic polymer matrices form glassy carbons upon pyrolytic conversion. This unique form of amorphous carbon is the principal factor behind the thermal performance of phenolic-based C-C.
- ★ It has already been proven that ordinary CCP material can be converted into porous C-C, processed to a specified level of densification (phenolic resin impregnation/pyrolysis) and then tailored to form a unique carbonized phenolic / virgin phenolic C-C/Ph bimatrix composite offering far superior char and erosion performance over current CCP virgin ablatives (and PICA materials as well).
- ★ The objective of this effort is to develop, fabricate and optimize small and large scale C-C/Ph composite articles representative of flame surface ablators and re-entry leading edges to demostrate performance attributes for future vehicle and commercial applications.

Rationale for MSFC Technology Development

- ★ MSFC currently has the engineering know-how and hands-on expertise to oversee, participate in and lead small to large scale development efforts and fabrication operations for both demonstration and production articles.
- ★ MSFC possesses various processing capabilites and extensive testing facilities for high temperature characterization and materials analysis.
- ★ MSFC may acquire state-of-the-art processing capabilities for processing and densification of small scale C-C/Ph articles in the near future.

Value to NASA/Commercial

- ★ Compared to traditional CCP platforms, C-C/Ph materials will facilitate long duration firing cycles and potential reusability with descent/ascent capabilities.
- ★ Use of C-C/Ph in typical CCP applications, such as single mission burn nozzles and re-entry vehicles, is expected to provide enormous improvements in risk and safety factors for future programs.

Readiness Level

- ★ Building upon current methodologies and technology levels for C-C and CCP, minimal development effort would be required for proof of concept or the production of demonstrator test articles.

JACOBS ESTS Group

ICRC A Subsidiary of VSE Corporation

Methods for Manufacturing Improved Carbon Cloth Phenolic (CCP) Ablatives for Nozzle Throats, Exit Cones, Leading Edges and TPS Structures

Randy Lee   Jacobs ESTS / ICRC / EM40

Description of Issues and Problems

★ Current methodologies for producing ablative CCP composite RSRM nozzle components utilize low-fired carbonized rayon fabric layers embedded in a phenolic matrix cured to a single 17 hour molding profile (ramps plus holds) with a 6 hour hold at a maximum temp of 315°F. Similar cure cycles are employed for other phenolic ablatives and insulators comprised of glass and silica reinforcements through-out the current STS platform and Ares I concept.

★ Near-catastrophic events such as delaminations, ply lifting phenomena, and anomalous microcracking have become major concerns in many of these phenolic systems. Such events have been known to occur when cured articles are simply heated up during processing or during burn testing. Obviously, for high performance ablator/insulator systems, this is wholly unacceptable.

★ In CCP systems based on both NARC and Enka reinforcements, production of a viscous liquid tar substance during heated testing has been discovered and repeatedly confirmed. The presence and migration of this tar material has been inferred as a possible factor during the initiation and/or propagation of composite defects such as out-of-plane microcracking and interlaminar ply lifting.

★ Such defects are believed to be a result of a combination of multiple factors, some of which may include (a) phenolic matrices that are inadequately cured, leading to closed pores with trapped volatiles which rupture the matrix and degrade fiber-to-matrix adhesion during early heating stages (prior to pyrolysis), (b) tars generated along constituent interfaces within the composite during mid-to-late heating stages which facilitate pore blockage and fiber-to-matrix debonding, and (c) low fired rayon fabric reinforcements (< ~ 2300°-2600°F) which begin to consolidate and release volatiles during the higher heating stages leading to gross fiber-to-matrix debonding.

Objectives and Approach

★ There is clear evidence that char residues are present on the surfaces of low-fired rayon fibers which are deposited from tars released during the fiber precarbonization stage (these could be formed from lignin and hemicellulosic fractions). During high fired carbonizations (> ~ 3500°-3800°F) such residues vanish due to volatilization.

★ It is also known that improperly (and incompletely) cured phenolic resins can produce viscous liquids or tars during thermal degradation that are comprised of high molecular weight thermoplastic exudates from the solidified (crosslinked) polymer body. Both of these tar sources may exhibit limited mesogenic effects (cohesiveness) which harden into a semi-carbonaceous crust upon cooling.

★ There are curing approaches which are known to alleviate these effects, providing phenolic matrices that are fully crosslinked with interconnecting open microporous networks (for volatile release). Such techniques will eliminate matrix exudates, increase resin strength, increase resin T_g, and reduce resin CTE, providing greater resistance to microcracking and improved insulation properties.

★ In combination with rayon fabrics processed under the appropriate alternative conditions of carbonization, pre and post-carbonizations, such modifications will produce composite structures with enhanced ablative properties, greatly increased thermal stability and substantially improved matrix-to-fiber bonding.

Collaborations, Value to NASA and MSFC Rationale

★ Various NASA centers, the US military and commercial industries stand to benefit from optimized CCP materials which offer improved, more robust advantages over current methodologies.

★ MSFC currently has the engineering know-how and hands-on exper-tise to oversee, participate in and lead small to large scale fabrication efforts for both demonstration and production articles.

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Method for Producing Improved C-C/SiC Material for Small Motor Components

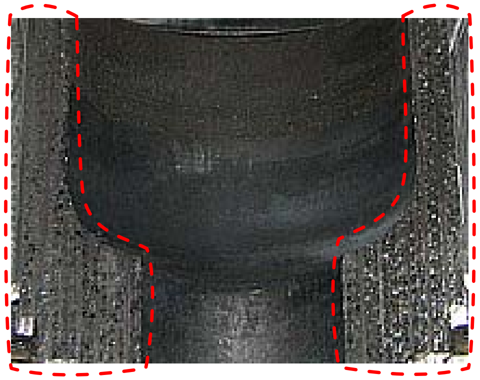
Randy Lee Jacobs ESTS / ICRC / EM40

Description of Issues and Problems

Current methodologies for manufacturing small C-C/SiC articles utilize practices which often lead to inferior thermomechanical properties and substandard high temperature performance when subjected to real life field environments.

- ★ Loose 3-D weaving styles currently used to fabricate these preforms which are then machined from large billets result in flagrant material inconsistencies, low fiber volumes, damaged and discontinuous fiber reinforcements along with corresponding losses in composite mechanical strengths and toughness attributes.
- ★ High levels of closed voids, large interstituals and localized pore clusters created by inadequate densification practices lead to poor mechanical properties throughout the substrate body and along periphery regions near substrate-to-coating interfaces.
- ★ Use of 'paint-on' slurry/particle-based ceramic seal coatings which are known to cause pore blockage, exhibit poor adhesion and thermal mismatch with substrate constituents during test cycles lead to ineffectual substrate protection and regions that become susceptible to spalling. When coupled with the factors above, these effects result in a final product that is much lower in quality than it could be.

Spalled coating showing localized, sub-surface inter-bundle porosity.



Exposed general porosity and voids typical within current 3-D C-C/SiC articles.

Objectives and Approach

Such practices may stem from efforts to save time and/or reduce costs. However, for critical motor and STS applications, these reductions may not be fully justified. There are alternative techniques and approaches readily available which are known to resolve these kinds of issues.

- ★ Improved preform configurations are feasible which could substantially increase mechanical strength and toughness factors of 3-D articles while reducing the level of closed inter-bundle porosity and completely eliminating the need for rough machining and sectioning. Such continuous fiber-reinforced ceramic matrix composites (CFCCs) offer vast improvements over the current methodology.
- ★ More robust densification techniques are known which would substantially reduce the level of closed porosity by preventing blockage and providing better control over pore dimensions and pore interconnectivity (interconnectivity is key in resolving major issues associated with defects in composite materials, including C-C/SiC).
- ★ Advanced coating procedures, surface conversion methods and micro-finishing techniques are available which can provide vastly improved coating-to-substrate adhesion, greater thermal stability and essentially eliminate the risk of spalling during flame exposure and cool down.

Collaborations, Value to NASA and MSFC Rationale

- ★ Various NASA centers, the US military and commercial industries stand to benefit from optimized C-C/SiC materials which offer improved, more robust advantages over current methodologies.
- ★ MSFC currently has the engineering know-how and hands-on expertise to oversee, participate in and lead the fabrication efforts for both demonstration and production articles.
- ★ MSFC may acquire state-of-the-art processing capabilities for C-C/SiC fabrication and densification in the near future.

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Experimental Laboratory/Facility for the Synthesis of Unique Matrix and Fiber Polymers for Applications in Composites, Ceramics and Adhesives

Randy Lee   Jacobs ESTS / ICRC / EM40

Description/Objectives/Approach

- ★ This laboratory would permit experimental synthesis of new and innovative monomers and polymers which have the capability to provide improved and advanced properties for heterogeneous nonmetallic material formulations.
- ★ High temperature elastomers, glassy matrices, fiber precursors, pre-ceramic polymers multifunctional binders, and environmentally friendly polymer systems are some of the materials that can be derived.
- ★ In addition to small scale laboratory synthesis, this facility would include the capacity/capability to produce small batches of spinning resins or matrix materials (quarts) for incorporation into hetergeneous material systems (composites, adhesives, coatings) and for the production of demonstration articles.

Rationale for MSFC Technology Development

- ★ MSFC has the engineering/scientific expertise to the lead technical efforts for experimental laboratory processing and developmental polymer synthesis required for small batch processing.
- ★ MSFC possesses extensive composite fabrication capabilites, resin mixing and application facilities, and a dedicated clean room for prepreg preparation and tailoring with the potential for experimental matrix prepregging and fiber/fabric evaluations.
- ★ MSFC possesses various support capabilites and extensive testing facilities for organic/inorganic analysis of monomers and polymers.

Value to NASA/Commercial

- ★ Next generation fibers and matrix systems will offer improved thermal and mechanical properties, high T_g, and low CTE (increased resistance to cryogenic microcracking). Others may utilize the benefits of mesogenic side chains, facilitate smart technology or permit *non-autoclave curing processes* and low temp crosslinking mechanisms which can offer portability. Still others can provide greater toughness, high temperature elasticity, hermeticity, and the ability to transform into a different material when exposed to energy.
- ★ For high performance composites, adhesives and coatings, such fiber and matrix systems would be of enormous benefit to many current and future NASA programs and commercial endeavors.

Readiness Level

- ★ TBD

JACOBS ESTS Group

ICRC A Subsidiary of VSE Corporation

Experimental Facility for Spinning and Processing Alternative Polymer Precursors in the Production of Rayon-Like Textile Fibers

Randy Lee   Jacobs ESTS / ICRC / EM40

Description/Objectives/Approach

- ★ This laboratory/facility would facilitate the processing of white textile fibers with emphasis on producing rayon-like prototypes, but would also include the capabilites to generate traditional and non-traditional fiber types for other composite and nonmetallic applications requiring fibrous reinforcements.
- ★ Process capabilites would include wet (solution) spinning, melt spinning, dry spinning, dry-jet wet spinning and some of the other newer techniques for producing advanced fibers (electro-spinning, reaction spinning, etc...). The facility would also include capabilites for multiple step coagulation/precipitaion operations, solution treatments and post-process treatments, as well as mechanical and physical processing in preparation for precarbonization operations.
- ★ This facility would compliment the fiber carbonization developmental laboratory operation already planned for the nonmetallics group.

Rationale for MSFC Technology Development

- ★ MSFC has the engineering and scientific expertise to lead development activities for prototype fiber production and has plans to construct state-of-the-art processing laboratory facilities for fiber carbonization and associated processing in the near future.
- ★ MSFC possesses extensive capabilites for process characterization and materials analysis of monomers, polymers, organic and inorganic fiber precursors which may become candidates of interest.

Value to NASA/Commercial

- ★ With the vanishing of domestic classic rayon sources, development of acceptible alternatives is mandatory. This facility would help to address those concerns.
- ★ Additionally, advanced alternative fibrous reinforcements for high performance materials would provide substantial benefits to various NASA centers, commercial STS endeavors and the US military.

Readiness Level

- ★ TBD

Experimental Process Facility for Producing Small C-C, C-C/SiC and CMC Articles and Post-Fabrication Composite Substrate Modifications

Randy Lee Jacobs ESTS / ICRC / EM40

Description/Objectives/Approach

- ★ Small size process development facility/laboratory/pilot line designed to demonstrate methods and optimization parameters for transforming smaller, molded composite articles into advanced, high performance components comprised of C/C, SiC/SiC, C-C/SiC and SiC/C/SiC, with the capacity for porous substrate densification, matrix gradient deposition, secondary bonding and thermal converiosn coating.
- ★ Operational capabilites are not limited to C-C or ceramic concepts. A multitude of ideas, materials and processes are viable. Ordinary PMC composites as well as a variety of polymer-based molded articles, bonded assemblies, foam-based substrates and semi-metallics may be candidates for such post-fab modifications which can vastly enhance their TPS performance value.
- ★ Such candidates might include, but are not limited to, small motor components including pintles, throat inserts, exit cones, body liners, housings, insulators and guide structures, small radiator concepts, and external vehicle TPS articles such as nosecaps and leading edges.
- ★ Process capabilities will include, but are not limited to, liquid polymer densification, in-situ polymerization, sol-gel processing, hyperthermal treatments and converisons, porosity control techniques, ceramicization and carbon matrix densification, powder sintering, reaction bonding, diffusion bonding, CVC, gradient substrate transformations, alternative seal coating process, bimaterial surface conversion coatings, and integration of metallic/nonmetallic constituents.

Rationale for MSFC Technology Development

- ★ MSFC has the capacity for renovation of existing facilities to provide the necessary 800-1000 sq ft of processing floor space, as well as the technical expertise to specifiy and facilitate the design requirements and processing equipment for such activites.
- ★ MSFC currently has the techical know-how and hands-on expertise to oversee, participate in and lead comprehensive development efforts and fabrication operations for demonstration and production articles.
- ★ MSFC possesses various support capabilites and extensive testing facilities for high temperature characterization and materials analysis.

Value to NASA/Commercial

- ★ Improved versions of C-C and C-C/SiC are of great interest throughout NASA, the US military and commercial industries for future launch vehicles, space planes and STS platforms. Motor, nozzle and leading edge components derived from improved C-C and C-C/SiC materials would provide substantial benefits to risk and safety factors.

Readiness Level

- ★ Existing or new floorspace would need to be updated or prepared to accommodate such processing activities and the necessary equipment would have to be fabricated and/or procured (~1-2M$).

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Experimental Process Facility for Scaled-Up Production of C-C, C-C/SiC, CMC and Post-Fabrication Modified Composite Substrate Structures

Randy Lee   Jacobs ESTS / ICRC / EM40

Description/Objectives/Approach

- ★ This facility would encompass the same capabilities covered under the proposal, “Experimental Process Facility for Producing Small C-C, C-C/SiC and CMC Articles and Post-Fabrication Composite Substrate Modifications”, but with greatly expanded floor space to accommodate full scale production articles for nozzle components, leading edges and other high temperature TPS hardware.
- ★ Additionally, the facility would include a full scale pilot line for production development and the capabilites to precisely determine the engineering requirements and design criteria for the manufacturing scale-up of advanced C-C and CMC structures.
- ★ In conjunction with the smaller C-C/CMC facility, this line would attempt to eliminate scale-up gaps with the intent to streamline the process of scaling up from concept to production.

Rationale for MSFC Technology Development

- ★ MSFC has the potential to support the necessary facilities for producing large C-C and CMC experimental structures and prototypes (~10,000 sq ft), as well as the technical expertise to specifiy the design requirements and processing equipment for such activites.
- ★ MSFC currently has the techical know-how and hands-on expertise to oversee, participate in and lead comprehensive development efforts and fabrication operations for demonstration and production articles.
- ★ MSFC possesses various support capabilites and extensive testing facilities for high temperature characterization and materials analysis.

Value to NASA/Commercial

- ★ Large and full scale structures comprised of improved versions of C-C and C-C/SiC are of great interest through-out NASA, the US military and commercial industries for future launch vehicles, space planes and STS platforms. Compared to other more common TPS structures, motor, nozzle and leading edge components derived from improved C-C and C-C/SiC materials would provide substantial benefits to risk and safety factors.

Readiness Level

- ★ TBD

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