Background in Advanced Composites (prior to Marshall Space Flight Center) *Randy Lee*

The Beginnings . . .

Started out in the shop as a fabricator (hands-on) around the age of 13 (1966) performing wet fiberglass lay-ups, adhesive bonding, sealing and spray painting in several family-owned vehicle body restoration and rebuilding businesses. Throughout my youth, I also worked in numerous fiberglass production shops laminate manufacturing facilities as a composite fabricator, process technician and supervisor. Involvement in this activity continued off and on throughout high school, college and beyond (over 20 years total). Experiences included hands-on participation in dry fabric / wet hand lay-ups, spray-ups, glass fabric selection and preparation, custom fiber/fabric tailoring, improvised structural build-ups, bulk resin preparation and mixing, modified composite designs and process troubleshooting. After several years, my responsibilites broaden to include management, training and supervision over production and shop activities. Hired, fired and provided specialized training and hands-on instruction to a variety of employees over the years as I honed my the skills in the areas of metallic/nonmetallic surface preparation, fiber/fabric tailoring, custom hand lay-ups, polymer resin activation, application and manual fabric impregnation, machining/sanding and trimming, gelcoat formulation and application, and the preparation and application of acrylic and urethane primers, lacquers and enamels to article surfaces.

Extensive hands-on use of amine-cured epoxies, peroxide-initiated, styrene crosslinked polyester and vinyl ester resins as binders for glass fiber/fabric lay-ups, body fabrications and pre-coat surface modifications. A driving desire to understand the technology behind these materials inspired my pursuit of chemistry in college. Perhaps my greatest talents throughout these years, particularly during the operation of our family businesses, exploited my creative approaches during customized fabrication approaches, specialized structural build-ups and exaggerated surface features using polymer resins, tailored fibers, fabrics and body putties (powder-filled styrene crosslinked polyesters), expert body/structural repair and refurbishing techniques, artistic paint and coating applications utilizing multi-tone gradients, texturing, striping, lettering and paneling. Much of this activity was directed toward specialized automobile restorations and custom hot rod-type innovations. Daily experience using an array of industrial shop equipment and hand tools, including air compressors, welders, hoists, jacks, come-alongs, grinders, sanders, metal cutters, air ratchets, micrometers, drills, spray paint equipment, adhesive and caulking tools, etc . . .

From Professional to High Tech . . .

After graduating from college in early 1982, I was selected by LTV Aerospace & Defense Company (Vought Aircraft) to be the associate (surrogate) M&P Engineer to the principal scientist responsible for creating the original carbon-carbon composite ablative material back in the 1960’s for the Apollo program, who subsequently developed the now-famous rayon-based Reinforced Carbon-Carbon (RCC) composite system in the 1970's. LTV was well recognized as the leader in carbon-carbon technology and by that time, my supervisor was well regarded as one of the most adept carbon-carbon professionals within the industry – the person everyone called upon when the tough problems came up. As his protégé and under his guiding mentorship, my position was somewhat unique relative to other members in the organization who came along throughout the 1970’s and 1980's during development of the next generation PAN-based Advanced Carbon-Carbon (ACC) composite thermal protection system. (After several ownership changes over the years, this division of LTV is now part of Lockheed Martin).

After about a year of service, I begin to build a reputation as the principal laboratory ACC substrate technologist and eventually gained recognition as one of the distinguished carbon-carbon M&P specialists within the Advanced Carbon-Carbon Technologies (ACT) group and the Space Shuttle's Leading Edge Structural Subsystem (LESS) RCC program at LTV (out of a combined group of about 100-125 engineers and scientists). Headcount in the ACT group exploded during the early to mid 1980's and during that era, direct knowledge in carbon-carbon was a rare commodity, especially if it was from the industry's leading producer. Consequently, many of the group members would work a year or two at LTV and then move on to other lucrative opportunities in high demand for those kinds of skills – many of my peers went to Rocketdyne, Ultramet, Aerojet, Kaiser, Supertemp, Boeing, Northrop, Morton, Rohr, Fiberite and Hitco (some are still at those companies), but not me . . . I stayed at LTV and continued to learn from the master. The freedom and opportunity for hands-on R&D was prevalent here. Completion of assigned tasks above and beyond the call of duty and a passion for original, self-directed independent R&D (about 50% of my time) allowed me to learn, earn and develop an advanced level of understanding in the areas of carbon-carbon substrate fabrication and characterization throughout most of the 1980's.

While team-oriented activities were enjoyable and quite productive, I was also given the opportunity to work independently. After completing all my required tasks each day, I begin to conduct my own experiments investigating the nuts and bolts of this innovative material and the processes required for improvement and optimisation. During the first couple of years, I was committed to understanding the nature of the composite fabrication process and the subsequent carbon-carbon densification process while concurrently developing the analytical tools necessary to effectively characterize these process and the associated material changes. Carbon-carbon 2-D substrate starts out as a typical carbon cloth / phenolic resin laminated composite that is pyrolyzed and densified over several cycles before the outer layers are subjected to a process that transforms them into a highly oxidation-resistant, functional gradient ceramic conversion coating. However, during the basic composite fabrication (molding) stage, it becomes absolutely mandatory to develop, refine and apply the most appropriate assembly schemes, precision lay-up and bagging configurations and carefully controlled autoclave curing cycles in order to generate an as-molded polymer matrix composite (PMC) article that is acceptible for all the post-fab treatments and processes the composite substrate will be subjected to. The freshly molded products must survive numerous high temperature cycles (up to 3100°F) transforming their inner cores and outer surfaces before reaching the end of the manufacturing process. Thus, the conditions required to properly mold these articles are much more critical that standard PMC articles. Consequently, the PMC properties achieved from a properly optimised molding process are substantially higher and more robust than those associated with the more common carbon/epoxy or carbon/phenolic PMC structures.

In conjunction with task-assigned R&D projects, a multitude of experimental process trials were performed in order to develop the critical improvements and optimization parameters required to meet ACC performance expectations for NASA and the military branches. Some of my activities included experimental studies into alternative techniques for fabric lay-up, fiber (tow) placement, resin inpregnation into fabrics and porous substrates, augmented vacuum bag configurations, alternative breather/bleeder concepts and materials, atypical autoclave cure cycle variations, pyrolytic substrate conversion (into carbon-carbon), substrate/matrix densification (successive pyrolysis and resin impregnation/cure), porosity intrusion and infiltration, enhanced matrix-fiber interface compatibility and binding, concerted efforts aimed at improvements in interlaminar tensile (ILT) strengths and delamination prevention techniques, C/C substrate / SiC ceramic phase interactions and CTE compatibility effects between the carbonized matrix, the fibrous reinforcement phase and the surface-fused SiC conversion coating phase.

Eventually, I became regarded as the principal substrate technologist and local specialist for composite manufacturing characterization, innovative process development, physical property analysis, mechanical testing and chemical characterization – the person my peers came to for customized substrate fabrication, precise physical property analysis and expert problem resolution (that is, when my boss was not readily available). Independently formulated and developed analytical models directly associating composite material properties with process parameters (essentially 'wrote the book' on carbon-carbon process modeling and related manufacturing science at LTV). Pioneered new techniques for determination and precision characterization of composite bulk density, true density, open porosity, matrix content, matrix volume, matrix density, fiber volume, resin weight gain, pyrolysis weight loss, cumulative carbon gain, 3 and 4-point flexure, lap shear, double notched shear, short beam shear and ILT strength. Given the opportunity and facility space, I created and managed the LESS ACC R&D process development laboratory and pilot line for experimental composite manufacturing, substrate densification, physical/mechanical testing and materials analysis throughout the 1980's.

Project lead for chemical characterization of polymer matrix thermoset resins with heavy emphasis on novel phenol-formaldehyde-based phenolic resoles and novolacs along with advanced studies in resin process chemistry, matrix polymerization and pyrolytic conversion into inorganic carbon char. Conducted extensive characterization studies on carbonized 2-D rayon and PAN fibers and fabrics, and the reinforcement benefits of 3-D PAN preforms. Special studies also included characterizations involving the pyrolytic conversion of thermoset polymers into glassy (vitreous) carbon matrices and their attributes in terms of carbon matrix binding power, porosity creation, residual volatiles, residual stress, matrix continuity and effective char yield. Investigated novel and alternative thermoset and thermoplastic matrix precursors including thermoset pitches, polyphenylenes and functional vinylbenzenes, all of which can be engineered to form highly crosslinked, thermally stable glassy carbon matrices. Some of these candidates showed great potential as stronger reinforcement binders requiring fewer densification cycles and lower cure requirements. However, due to time constraints, not all viable matrix concepts were fully investigated. This one area in which improvements could greatly advance the current state-of-the art.

Daily hands-on fabrication and direct manufacturing oversight of hundreds of carbon-carbon structures and test development articles. Daily hands-on materials characterization, test methods development and processing oversight for several thousand composite and C/C test specimens and samples (acquired, managed and scrutinized a tremendous level of C/C data during my tenure). Types of articles included sub-scale prototype composite structures, secondarily bonded and co-cured assemblies, flight developmental panels, basic and complex angled sections and shapes, and ordinary flat panels (from one ply to 2" thickness). Project lead for the design, fabrication and characterization of multi-stemmed compression panel prototypes, non-coated impact panels, stitched and 3-D enhanced concept panels (all NASA LaRC); body flap panels, chin panel trials and multiple ACC materials development test articles for the Space Shuttle (NASA, Rockwell); scramjet ducts and turbine blade prototypes (USAF); radiator prototypes and concept panels for SDI (DOD); ceramic matrix and ceramic fiber test panel trials (IR&D, B-2 development); numerous 3-D braided preforms and 3-D woven test articles for the National Aerospace Plane concept (General Dynamics), and many others. Also provided daily support as Process Engineer during manufacturing and process development trials of LESS RCC panels, nose caps and associated hardware for the Space Shuttle orbiter throughout the 1980’s.

As the principal densification specialist in the group, some of my most intense studies centered around techniques and innovations to control substrate porosity and permeability and its characterization, particularly in terms of the specific parameters employed during the early composite fabrication stages. Some of these efforts addressed the limits associated with traditional laminate lay-up and fabrication approaches, curing and post-curing, intrusion, infiltration and impregnation of fluids into porous fabrics and hardened substrates (not limited just to viscous polymer resins). Other studies investigated comparative aspects of slow and rapid matrix carbonization (pyrolytic conversion with new porosity generated), development and enhancement of mechancial properties throughout the densification process, control and characterization of *surface* porosity (particularly as it correlates to the requirements for subsequent diffusion coating of the porous substrate). Since the fibrous reinforcement is already fully carbonized prior to the manufacturing process in both PAN-based ACC and rayon-based RCC, substrate C/C densification is more appropriately defined as *matrix densification*, but the intent is to optimise adhesive interactions between fiber surface functional groups and matrix atoms.

Effective conversion of the outer 30-50 mils of the carbon substrate into β-SiC ceramic is accomplished via diffusion-reactions in the 2900°-2950°F temperature regime after the article has been intricately packed and embedded in a precisely formulated particle/powder pack mix. This extraordinary process creates a unique functional gradient between the SiC conversion phase and the porous carbon substrate . . . a 'new' phase comprised of both compositional and microstructural gradients. The effects and benefits of a properly formed gradient conversion phase are immeasurable in helping to mitigate the fourfold lateral CTE difference between the perpheral SiC phase and the C/C substrate.

Per organizational directives, a considerable amount of effort was focused on exploring new and innovative concepts for fabricating ACC. This activity involved experimental investigations into alternative fibrous reinforcements (including fibers comprized of silica, mullite, unsual carbon forms and hybrid blends), augmented matrix formulations, unconventional refractory and ceramic processing concepts as well as alternative fabrication approaches including compression molding, slip casting, pultrusion, and manual fiber/fabric placement techniques (this was before 'fiber placement' methods became popular in the 1990's). Again, these conceptual approaches were often associated with efforts at improving interlaminar properties and optimization of differential CTE effects between the reinforcement and matrix phases as well as investigating new ways to reduce cost and processing time. Many of the manufacturing approaches and characterization techniques developed during this period were adopted by various companies in the field where they have become standard practice throughout the advanced composites industry, and LTV Vought certainly had its share of contributions. Today, the issue of poor interlaminar properties now involves the entire PAN-based composites industry world wide.

Some of my latter experimental studies included advanced fiber heat treating (HT) effects, tow interlocking concepts and developmental weave designs, alternatives to wet lay-up methodolgy, enhanced fabric impregnation approaches and optimization of thermal staging cycles on prepreg, modifications of prepreg control factors such as tack, drape and springback, particularly in and around complex contours, optimization of cure cycles and novel crosslinking approaches examining variations in time/temperature/vacuum/pressure profiles (including time-delayed pressure application effects), the impact and control of residual volatiles, the benefits and consequences of post-cure processing, alternative matrix polymers and densification concepts, rapid inert pyrolysis (10 hr vs. standard 3 day), CVD/CVI densification and coating experiments, development of analytical correlations between composite density and porosity and NDE (ultrasonic) data, and many more topics. Throughout my tenue, whenever innovative material samples, new processing concepts and instrumental (characterization) systems came in house, program managers generally handed these tasks directly to me as the principal experimentalist assigned to investigate their feasibility first hand.

As a result of funding issues, the ACT group begin to scale down in the late 1980's and was eventually dissolved around 1990-91 after I had already moved on to another company. My boss retired in 1991, a couple of years after one of our engineering colleagues acquired the available equipment (from LTV and General Dynamics, all now part of Lockheed) and started the company C-CAT (Carbon-Carbon Advanced Technologies), which became a made-to-order production service for ACC products. Since their charter focused exclusively on ACC production using current state-of-the-art methodologies, further development, refinement and improvement of the ACC platform was drastically reduced. Once the principal resource for both RCC and ACC production and R&D within the industry, by 1991-92, the development era of LTV's C/C branch was all but vanished with ACC capabilities liquidated and the LESS RCC program relegated to making a few spare leading edge panels and associated hardware for the remaining four Shuttle crafts (post-Challenger).

Even to this day, some of the major problems have still not been adequately resolved, particularly issues pertaining to sub-standard interlaminar strengths and coating-to-substrate CTE mismatch concerns (differential CTE is directly associated with the *modulus* mismatch between the isotropic β-SiC phase and the orthotropic carbonized fibrous reinforcement). The global implications of mediocre interlaminar interactions in PAN-based composites are undeniable. Unfortuantely, little progress has been made in this area. As it was twenty years ago, the entire PAN-based composites industry is still plagued by poor interlaminar tensile (ILT) and interlaminar shear (ILS) properties which are inherent to the nature of PAN fibers from all genres (PAN fibers generally exhibit smooth/straight fiber morphologies). The potentially devastating effects of as-molded 'weak planes' which are associated with inadequate ILT/ILS properties is a condition that cannot be ignored. For structural PAN-based composites, improvements in this area have been and are still the number one mechanical-related project topic under pursuit throughout the industry. This includes the ever-expanding carbon fiber / epoxy matrix industry, aerospace and non-aerospace products alike.

In general, the binding scenario in laminated composites is defined by two varying microscopic contributions or fractions and one very important macroscopic effect . . . (a) chemical bonding between the fiber surface and the matrix, (b) mechanical bonding or interlocking as the matrix interacts with the fiber morphology (regular and irregular surface features, fiber bundle porosity, gaps and interstices), and (c) ply-to-ply nesting effects between neighboring laminate layers (layer-to-layer meshing and nestling). The latter is a function almost entirely of the fabric weave (and the fabric modulus) as well as the regularity of the fiber bundle morphology but is it may also be controlled, to some degree, by the appropriate fabrication techniques employed. While both chemical binding and mechanical interlocking can influence both interlaminar tensile (ILT) and interlaminar shear (ILS), nesting may have its greatest benefit in ILS. The majority of functional (coupling) groups developed on typical carbon fiber surfaces from oxidation treatments applied during fiber processing are carboxyl based. If toughening properties are being optimized for a given composite system (notably ceramic composite systems), content levels of these coupling groups can be controlled to facilitate the toughening effects, but in general, carbon fiber-based composites, especially C/C systems based on glassy carbon matrices, need as much chemical and physical binding power as can be incorporated.

Over the years, as industry requirements called for higher strength / higher modulus reinforcements, carbon fiber/fabric vendors begin to apply higher temperatures and tensioning effects during processing. Common grades of PAN fibers available nowadays are catagorized as low, intermediate and high modulus fibers. However, high heat treatments make the carbon fibers stiffer, more brittle and harder to weave. Bulk mechanical properties for carbonized PAN fibers are typically four to five times greater than those of rayon-based carbon fibers. One of the unique characteristics of rayon fibers is their propensity to form regular morphological features or *crenulations* as they swell and contract disproportionally during the spinning process. These crenulations are retained throughout the fiber carbonization process and are ultimately responsible for the extraordinary nesting effects imparted to fabricated rayon-based composite articles.

On the other hand, PAN fibers do not form such features but rather their surfaces are smooth, slick and straight. In addition, PAN fibers are comparatively stiff and brittle . . . their bundles must be woven in multi-harness configurations in order to minimize fiber breakage (5 and 8 harness satin weaves are typical for PAN fibers). All these limitations lead to poor interlaminar nesting effects in continous PAN fabric-reinforced systems. They are directly attributable to the frequently occuring weak planes characteristic to PAN systems and ultimately lead to inferior ILT/ILS properties all around. While PAN systems provide longitudinal (tensional) strengths which are several orders of magnitude greater than rayon systems, rayon laminates exhibit ILT/ILS properties that PAN laminates cannot compete with. These comparisons may help to provide some insights into the challenges faced during platform conversions from the older rayon-based systems (such as RCC) to the more modern PAN-based reinforcements (ACC, carbon/epoxy, carbon/phenolic, etc...) which now dominate the carbon fiber-reinforced composites industry. Structural conversions from rayon to PAN started several decades back when business leaders, exexutives and politicians got wind that PAN fibers were many times stronger than rayon (albeit in straight tensile strength only). Over the last two decades, the conversion effort has accelerated exponentially throughout the entire industrial base world wide. Now that all the domestic rayon sources have vanished, we are stuck with PAN reinforcements, for better or for worse.

Today, the C/C market seems to be dominated by products that are densified via pyrolytic carbon CVI (infiltration) which may then be SiC coated on the outer surface of the article via CVD (deposition) for added oxidation protection. However, articles generated from this approach have some notable impediments, even when considering the major problems associated with ACC and RCC. In many recent studies, mechanical property differences between systems containing impregnated glassy resin char matrices and those that are vapor-densified via graphitizable CVI carbon infiltration are often obscured and not fully representative of either. During CVI densification, if process parameters are not precisely optimized (temperature, vacuum, residence time, gas composition, etc...), reactant CVD gases may tend to 'crack' before permeating into the substrate's pore channels (sometimes they react on the outside surfaces). This results in an unknown level of closed porosity within the substrate. Additionally, CVI densification is extremely time-consuming, sometimes taking several months to attain the required level of matrix densification. Below about ~4000°F, pyrolytic amorphous carbon is deposited and above that, pyrolytic graphite is formed (pyrocarbons are converted to pyrographite when heated above 4000°-4200°). Thus, with subsequent heat treatments to >4000°F, amorphous CVI carbon matrices are converted into crystalline graphite. (The term 'amorphous' is not entirely accurate, it is used here with the understanding that these allotropes actually consist of 2-D graphene planes or layers with no 'z' indexing or 'd' links and so they are not truely amorphous in a 3-D sense).

Unfortunately, closed voids, occlusions and porosity are also likely in many resin-densification processes. There is some evidence however, that unoccupied voids provide a certain level of long term fatigue and stress relief for the composite over its use life. Upon initial pyrolysis, thermoset polymer matrices are transformed into 'hard' carbons. These are a special class of amorphous carbon more precisely defined as ‘glassy’ or ‘vitreous’ carbon which are non-graphitizable carbon forms – even at temperatures >5000°F (hence, the term ‘hard’ carbon). Now, upon initial carbonization, petroleum and coal tar pitch-based materials, are converted into ‘soft’ amorphous carbons (comprized of 2-D graphene layers) . . . and all soft carbons easily undergo full graphitization above 4000°F. As such, essentially all soft carbon forms must pass through liquid crystal mesophase somewhere in their thermal history in order to acquire the mobility for rearrangement into 3-D graphitic-like structures. Conversely, glassy (vitreous) carbons remain in their amorphous 'hard' state permanently (a result of the rigid crosslinks established during the thermosetting cure process).

In general, amorphous carbon matrices have a tendency to absorb or dampen rapid mechanical propagations into the composite and thus provide the system with a unique form of thermal shock and fracture protection. Consequently, amorphous matrix composites generally exhibit properties of lower thermal conductivity. Crystalline (graphitized) matrices, on the other hand, respond just the opposite. They will transfer slowly-applied mechanical loads to the fibrous reinforcement much more efficiently (where they belong during normal structural applications) . . . but in high impulse situations, the fronts of thermal and mechanical shock waves will often propagate right through the reinforcement fibers. These particular properties must be taken into consideration during design phases for the specific carbon-carbon application. Amorphous CVI and pitch binders may soften during heating cycles and this could have detrimental effects on fiber-matrix bonding at higher temperatures. At exposure temperatures >4000°F, these matrices will crystallize irreversibly, substantially increasing their conductivity and mechanical transport properties into the fibrous reinforcement (a property that may be beneficial or unfavorable, depending on the application). In contrast, matrices comprized of glassy carbon not only provide strong binding power but deliver excellent shock resistance and low conductivity *at all temperatures*. As a matter of fact, glassy carbonized phenolic resin (such as that used in ACC and the early states of RCC) is a unique carbon form that is chemically inert, undergoes no further thermal phase transitons, and may be formulated with special matrix enhancement ad-mixtures and oxidation protection agents.

On the outside, oxidation protection provided by a functional gradient ceramic conversion or phase transformation of the outer substrate layers has no rival. The exact techniques and skills used in this process were a closely guarded secret of the inventor of the original SiC conversion coating operation for both RCC in the 1970’s and ACC in the 1980’s (LTV’s long time coating technologist, now retired). Since that time, no one has ever yet been able to successfully duplicate this process to its full and original potential (including C-CAT). It seems that for the past few decades, the research community has expended a considerable amount effort attempting to develop robust oxidation protection mechanisms based primarily on CVD (surface deposition) concepts. However, when applied correctly, surface conversion produces a coating phase that is fused with the substrate (they are essentially inseparatable, mechanically). In conjunction with an adequate sealant system, this method of oxidation protection mitigates the substrate-coating CTE difference unlike any other technique currently in practice. The 3000° conversion process utilizes a functional powder/particle pack mixture surrounding the article in which Si atoms undergo diffusion reaction-cementation with carbonaceous substrate constituents (fibers first, then the matrix) transforming the substrate periphery into an Al-SiC composite coating phase (highly dominated by β-SiC). From my perspective, the industry should be focusing its innovative efforts on improvements to this approach, such as identifying techniques to minimize or eliminate craze cracking or the sealant requirements, rather than continuing the pursuance of mediocre CVD methodologies. We should be exploring oxidation protection concepts that offer the longevity and permanence of *surface conversion* rather than the short-lived and potentially catastrophic fate of *surface deposition*. Extensive plasma and oxidation testing over the years have repeatedly proven that CVD SiC coated carbon-carbon is quite inferior to gradient conversion coated products . . . there is simply no comparison.

In my mind, there is still an abundance of un-tested ideas and potential solutions capable of making this material better than it ever has been, but there are still major problems which have simply not been effectively resolved. Unfortunately, as each new generation of technologists enters the field, it seems we tend to 're-invent the wheel' over and over again and the problems of yesterday often become the same issues we face today. It shouldn't always have to be that way. Given the opportunity, I believe I can help 'jump start' some of the challenges and problems facing the current state-of-the-art in carbon-carbon technology and ceramic matrix composite concepts. Many of the solutions and future discoveries in this area of the composites world will undoubtedly offer break-through benefits to leading edge structures, troublesome nozzle configurations and thermal protection challenges in other STS areas, as well as the advanced composites industry as a whole.

Related Corporate Publications (incomplete list)

> Design, Fabrication and Testing of Stitched C/C Compression Panels . . . Jun 1987
> Resin Process Chemistry & Analysis of Phenolic Matrix Resins . . . Apr 1987
> Advanced Data Analysis Techniques for Reinforced Carbon-Carbon . . . Apr 1987
> A Model for Polymer Composite Fab & Carbon-Carbon Densification . . . Oct 1986
> Fabrication and Analysis of 3-D Fibrous Preforms for Carbon-Carbon . . . Jul 1986
> Analysis of Carbon-Carbon Bladed Disks for Engine Applications . . . Mar 1986
> Fabrication & Analysis of NASA Langley Carbon-Carbon Impact Panels . . . Dec 1985
> Cure Cycle Optimization for Molding Carbon Fabric Phenolic Laminates . . . Jul 1985
> Math Methods for Composite Fabrication & Carbon-Carbon Processing . . . Feb 1985
> Optimization Techniques for the Fabrication of Carbon-Composites . . . Nov 1983
> Physical Property Data Analysis of Primary Carbon-Carbon Panel Stock . . . Jun 1983
> Statistical Process Data Analysis of Primary Carbon-Carbon Panel Stock . . . Dec 1982

Related References

Name1 – Founder/inventor of the original carbon-carbon substrate material at LTV in Grand Prairie, TX; one of the earliest forms of carbon-carbon developed in the world (originally known as Reinforced Pyrolyzed Plastic). My supervisor and mentor at LTV throughout the 1980's. Professional colleague and close friend since 1982. Co-developers included Name2 (substrate) and Name3 (SiC coating). Worked with each of these innovators regularly during this era (all three are long retired or deceased). Name1 (and Name3) also developed the Space Shuttle's SiC coated Reinforced Carbon-Carbon LESS system. Now retired. Frequency of contact: several times per year. Currently resides in Bedford, TX. Currently active and in very good health. XXX-XXX-XXXX.

Name4 – Founder, owner and President of Carbon-Carbon Advanced Technologies Inc. (C-CAT) in Fort Worth, TX. Member of the ACT team at LTV during the 1970's and 1980's. Professional colleague and close friend since 1982. Name2, Name5 and Name4 begin purchasing equipment and started the company C-CAT in 1987; Francis ended up with the company a year later which he now runs exclusively with personal family members. Frequency of contact: once or twice a year. Last contact: November 2007. Currently resides in Fort Worth, TX. XXX-XXX-XXXX.

Contact names and numbers available upon special request

Additional Experiences with Advanced Ceramics, CVD & Carbon Forms

Recruited into the research department at Poco Graphite during the mid 1990's as Project Scientist for hands-on R&D and experimental development of CVD/CVI processes and ceramic bonding technologies, as well as engineering support for Poco's 24 hour ceramics/carbon CVD/CVI coating and graphite manufacturing operations which included ten independent 200 cu. ft. vacuum furnaces and associated support facilities. Principal involvement in SiC CVD processes, pyrolytic carbon CVD and pyrolytic graphite formation. Lead scientist for experimental process trials investigating reaction-bonding, sintering and adhesive joining utilizing developmental bonding formulations based on innovative pre-ceramic polymer materials. Characterized the processing requirements and chemical/physical properties of Starfire's new AHPCS (SMP-10) polycarbosilane ceramic precursor, Dupont's Lanxide Ceraset ureasilazane pre-ceramic polymer resin, Allied Signal's polysiloxane and phenolic refractory adhesive admixtures under various process conditions leading to glassy and polycrystalline ceramic products.

About 45% of my activities involved ceramics CVD/CVI coatings development and ceramics fabrication as associate scientist to Poco's senior staff CVD expert; about 45% as the Lead Project Scientist over carbon/ceramic bonding technologies & ceramics formation from polymer precursors, and about 10% in graphite/carbon manufacturing development. Heavy participation in product/process characterization for large scale ceramics fabrication via 3500°F gaseous conversion of bulk graphite articles into β-SiC (Poco is the originator and largest practitioner of this unique process for the formation of porous β-SiC products from machined graphite billets). Headed up experimental trials examining complete gaseous conversion of ACC substrate samples into monolithic SiC (non-coated PAN-based Advanced Carbon-Carbon test samples acquired from C-CAT). Designed and conducted pilot line R&D experiments investigating the process requirements and chemical/physical properties of SiC CVD/CVI coatings onto SiC substrates. Examined a host of variables including coating thickness distribution, CVD/CVI deposition rate, porosity infiltration vs. surface deposition, residence time, modified gas compositions, flow rate, pressure/temperature profiles and various attributes for monolithic SiC crystal growth formation. Ceramic CVD/CVI processes generally utilized pre-cursors derived from one of the methylchlorosilanes (with variable H_2 spoiler) which generated hot HCl as a by-product, while pyrolytic carbon CVD operations were carried out under methane atmospheres with variable H_2 and/or N_2 dilutents. CVD process temperatures and pressures varied from 1500° to 3500°F and 0.001 to 0.1 torr. Lower temperatures and pressures promote porosity infiltration (CVI) while higher temps and pressures favor surface deposition (CVD). Daily involvement in large scale CVD/CVI pyrolytic and graphitization operations, bulk carbon billet fabrication, large graphitization production operations and all the associated furnaces and vacuum processing facilities.

As technical lead, I formulated and tested numerous high temperature adhesive formulations and associated pyrolytic bonding processes for joining ceramic and carbon/graphite components together in complex assemblies. Studied the thermal converson of linear polycarbosilane thermosets into polycrystalline β-SiC, reaction-bonding of particle/powder mixtures & phenolic char precursors, reactive gas sintering with SiC particles, the transfomation of cyclic polyureasilazane thermosets into SiC/Si_3N_4 and then to stochiometric SiC. Resident materials chemist for characterization of these organic/inorganic polymer systems and their pyrolytic conversion into amorphous (glassy) ceramic and crystalline β-SiC. Also studied petroleum crude and mesophase pitch chemistry. Acquired in-depth understanding of the various forms of carbon including conventional bulk hexagonal d-spaced graphite, pyrolytic CVD carbons and amorphous 2-D graphene (carbon blacks) which pass through mesophase around 800°F and then graphitize above 4000°. Also became very familiar with the various polymorphs of SiC and Si_3N_4 including their glassy forms which are predominate below 2500°- 2600F; the fcc β-SiC and hcp β-Si_3N_4

structures (β-SiC begins to form above ~2500° while β-Si_3N_4 becomes unstable below 3000°); and the >3600° hexagonal α-SiC which finally sublimes around 5000°.

Experience in other industries utilizing CVD/PVD processes include heavy involvement in the fabrication of semiconductor devices and silicon wafers. I have been employed, at two separate companies, as Process Development Engineer and Materials Engineer over day-to-day operations involving epitaxial CVD processing, diffusion deposition, photolithography and wet chemistry in the manufacturing of silicon wafers for power devices. At another firm, I was specifically selected by the senior staff to fill the position of Failure Analysis Engineering Manager involved in sputtering and PVD fabrication of Al-Ti metalized quartz substrates used in RF transceiver components (3½ years; I was hired by and reported directly to the VP of Corporate Development with 2 direct reports).

Related Corporate Publications

> Overview of Alternate Bonding Methods for Joining of SiC Components . . . Nov 1997
> Reaction Sintered Techniques for Bonding/Joining of Carbon Articles . . . Aug 1997
> Study of Pre-Ceramic Polymers for SiC Bonding and Joining Processes . . . Mar 1997

Additional Experiences with Polymer Matrix Composites

Throughout much of the period 1998-2006, I held various positions as Lead Process Engineer, Lead Quality Engineer and Principal Materials Engineer at companies such as Lockheed Martin Aeronautics and Bell Helicopter Textron for the production, manufacturing development and characterization of primary and secondary composite structures during the assembly and design of various military aircraft. These included direct involvement in hand lay-up, filament winding and fiber placement of thick carbon/epoxy, glass/epoxy, BMI and polyimide matrix composite structures within the sub-systems, drive systems and body panels for the all-composite F-22 Raptor, all-composite Joint Strike Fighter (F-35), and part-composite F-16 Falcon (all Lockheed Martin Aeronautics), the all composite V-22 Osprey and 609 Tiltrotor aircraft (Bell Helicopter Textron). Indirect experience also included manufacturing design and analysis for the composites, adhesives, sealants, metals and coatings used in the assembly of the F-117 Nighthawk, B-2 Spirit and F-18 Hornet airplanes.

Provided independent consultant services Impact Composites Inc., 2001. Characterized the performance and formulation effects of a new, innovative natural fibrous filler additive for enhancement of styrene crosslinked polyester resins used in Fiberglass Reinforced Plastic systems. Documented cure-altering characteristics in terms of gel point delay, early exotherm, viscosity modification, extended pot life and workability/processability. Issued the publication "*Reactions of Polyester Resins and the Effects of Lignin Fillers*".

Provided independent consultant services Composite Technology Inc, 1991. Evaluated the process parameters, resin chemistry and fiber/fabrics for large FRP structures fabricated via pultrusion, automated panel fabrication, spray lay-up and conventional hand lay-up using styrene crosslinked polyesters and vinyl esters with chopped fibers and continuous E-glass reinforcements. Explored innovative material alternatives and environmentally-leaning manufacturing improvements.

One year independent study and research into composite concrete materials and process involving investigations into lightweight polymer concrete formulations and concrete composite materials technology. Investigated properties and reactions of Portland cement, latex copolymers (vinyl acetate & acrylate), plastic, carbon and steel fiber reinforcements, pozzolanic powders, cement hydration chemistry, particle size distributions, mechanical, thermal and aging characteristics.

Project member of the consulting services company, Composites-Consulting.com, as part time technical contributor for special topics and projects (since 2000).

Related Corporate Publications (incomplete list)

> Overview of Sealing & Shimming Technologies for the JSF Concept . . . Dec 1999
> Evaluation of Liquid & Solid Shimming Options for the JSF Concept . . . Dec 1999
> Study of Pre-Ceramic Polymers for SiC Bonding and Joining Processes . . . Mar 1997
> Reactions of Polyester Fiberglass Resins & the Effects of Natural Fillers . . . Jan 2001
> A Model for Polymer Composite Fab & Carbon-Carbon Densification . . . Jan 2001
> Formulations for Polymer/Fiber Modified Lightweight Concrete . . . Jun 2003
> Proposed Mechanism for Thermal Degradation of Phenolic Matrices . . . Jul 2007
> Evaluation of Spalling on RCC Leading Edge Panels Post Flight STS-120 . . . Oct 2007

> Overview of Shuttle Reinforced Carbon-Carbon (RCC) Composites . . . May2008
> Analysis of Post-Fired C-C/SiC Composite Motor Components . . . June 2008
> Failure Mechanism of Post-Fired C-C/SiC Motor Components . . . Aug 2008
> EDX Analysis of Anomalies on Post-Fired C-C/SiC Motor Components . . . Sep 2008
> Factors Contributing to Joggle Delaminations on Shuttle RCC Panels . . . Nov 2008
> Failure Analysis of Anomalies on Post-Fired C-C/SiC Motor Components . . . Mar 2009
> Density & Porosity Factors in Ceramic & Polymer Matrix Composites . . . Jun 2009
> Reactions & Mechanisms of Pre-Ceramic Polymers for C-C/SiC Systems . . . Jul 2009

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