

Innovations for Graded Ceramicized Carbon/Carbon Composites

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Introduction and Background

It is well known that a ceramicized carbon composite material is used on the leading edges of the Space Shuttle orbiter. Specifically, the substrate is based on carbonized rayon fabric-reinforced – carbonized polymer matrix RCC (Reinforced Carbon/Carbon) and has been providing extraordinary, low maintenance thermal protection along the very hottest regions of the STS spacecraft since the late 1970's. Its next generation counterpart, carbonized PAN fabric-reinforced – carbonized polymer matrix ACC (Advanced Carbon/Carbon) offers greater structural capability but has never been unanimously proven to exceed or even realistically compete on the same level as RCC when it comes to reliability, processability/manufacturability, longevity, scalability or affordability. Even though ACC provides much higher in-plane tensile strength capabilities (4 to 5 times greater!), over the years, it has continually been plagued with inferior interlaminar properties, fabrication limitations and coatability challenges since its inception . . . issues that are essentially non-existent in the RCC platform. Similarly, mechanical and processability challenges have accompanied essentially all PAN-based composite structures throughout the entire industry in almost every application. The crenulated morphology and low modulus of porous carbonized rayon tow bundles along with result in low stress wovens weaving stress and soft fabric texture which and low weave stress characteristic of rayon-based fabrics greatly enhances ply-to-ply nesting and mechanical interlocking in 2-D laminates unlike any other continuous reinforcement readily available. In contrast, these properties are alarmingly lacking in most composite systems comprised of carbonized PAN fibers in which the bundles are generally straight, slick, stiff and less porous, often leading to inferior ply nesting and ultimately, to poor interlaminar properties in cured laminates. In a sense, ACC is still in the development phase.

Accelerated development of ACC, once a thriving enterprise at LTV/Vought Corporation (the originator of both RCC and ACC), has never fully reached the performance level initially envisioned by the founding fathers during the 1970's and 1980's when this activity was going strong. During this era, LTV had a tremendous advantage over all the other C/C developers throughout the industry . . . a large scale recurring application of C/C on a major space vehicle (and still the only re-usable, manned space vehicle in U.S. history), an associated full-time, daily production operation and dedicated facility for the fabrication of RCC structures from raw material to shipped product, a sister program to accommodate the extensive and expanding R&D effort for next generation ACC along with a substantial pilot line for production of ACC structures and experimental prototypes, as well as the mandate and funding to mature the ACC/RCC technology for the foreseeable future. Most importantly, we had RCC to use as a springboard for ACC concept development, fabrication modeling and production proofing. However, the impressive in-plane tensile properties associated with PAN-reinforced systems were hard to resist. It has now been a few decades since the entire carbon fiber-reinforced composites industry adopted PAN reinforcements as the choice for continued development, with visions aimed at advanced aerospace skin structures, substructural aeroframe components and next generation hypersonic engine concepts reminiscent of the National AeroSpace Plane and scramjet programs (applications in which rayon was deemed inadequate).

Today, while domestic sources of carbonized rayon fabric are rapidly vanishing, the need to overcome the challenges associated with PAN-based composites is more urgent than ever. Notably, lessons learned from RCC have not yet been fully realized and the transfer of knowledge, successes and lessons-learned from RCC to other C/C platforms is incomplete. For the most part, the composite fabrication stage, substrate densification and conversion coating of ACC have been highly successful *because* of the knowledge, expertise and benefits gained from daily, local RCC manufacturing activities, along with frequent field service feedback, and a program of

aggressive, on-going improvement efforts for both RCC and ACC. Without a doubt, a multitude of small-to-moderate sized PAN-based structures, prototypes and production articles have been extensively tested and placed into various service applications over the last two or three decades. Many of those utilizing 3-D enhancements and configurations, such as z-pinning, stitching, nanotubes and multi-weave preforms, have provided some unique and unusual results. However, 3-D concepts are often limited by manufacturability issues and constraints.

Now for traditional RCC and ACC systems, oxidation protection of the densified composite substrate is developed by the use of a pack mix cementation or pack cementation (PCM) process, where the bare (densified) C/C article is embedded in a powder mixture containing fine Si particles which subsequently react with the carbon constituents of the substrate transforming (or converting) the extreme outer regions of the material into SiC as the system is heated up to ceramic firing temperatures. In this process, a retort containing the 'packed' substrate article is ramped up to the 2900°-3000°F regime over a relatively quick reaction cycle (~5 hour ramp to 3000° with a total cycle time of about 10 hours . . . as compared to the standard 3-day calcined coke pyrolysis cycle which is utilized for each of the substrate densification cycles). The resulting ceramic reaction product is near stoichiometric SiC, which becomes chemically and mechanically fused with the carbonaceous substrate. Due to the nature of the solid state conversion process, the physical boundary between the substrate and ceramic phase is often relatively broad and diffuse. A gradient or gradual change in composition and micro/macrostructure characterizes the transition (conversion) zone between the fully converted ceramic phase and the completely unaltered composite substrate. A representative example of the composition gradient is given in Figure 1 below.

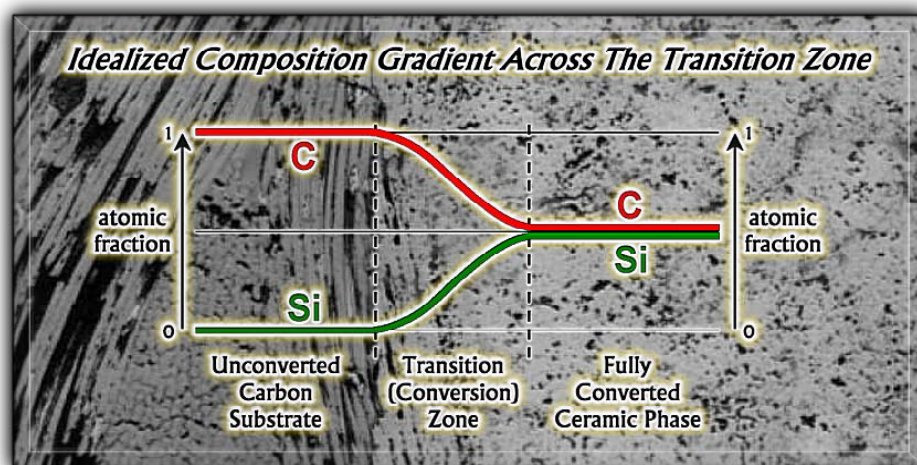


Figure 1. Example of idealized EDX overlay on a recent test sample which shows a cross-section of the RCC substrate-to-coating bimaterial interface.

More commonly used deposition-type coatings, such as CVD, are characterized by a discrete, narrow boundary separating the substrate and coating phases which are not joined together by any chemical means and whose physical interactions are easily degraded. With RCC/ACC systems however, a broadened, graduating boundary (conversion) zone is a natural consequence of the cementation reaction process and is responsible for the extraordinary degree of moderation incorporated into the product with respect to the substantial CTE/modulus mismatch that exists between the two phases. The conversion zone should not be confused with the overall coating thickness, but strictly refers to the chemical/structural transition region separating completely converted ceramic product from virgin (unaltered) substrate. It may run anywhere from several tenths of a mil to several mils, depending on the properties of the substrate and the processes employed. This transition zone is not a trivial concept . . . it is the single most important property directly affecting the degree of fusion between the two phases and thus, the quality/quantity of mitigation imparted to the ceramicized product addressing the CTE/modulus differential. Interestingly, the nature of the transition zone and its ability to effectively integrate the converted ceramic phase with

the unconverted substrate can be controlled, to a large degree, by engineering design and fabrication technique. That is, the transition/conversion zone between virgin carbon substrate and the monolithic ceramic phase can be modified by manipulating the chemical and physical properties of the substrate as it undergoes the various manufacturing steps. Properties such as the width (or depth) of the transition zone, the level of dendritic branching and the chemical composition (relative to the specific pack mix used) are of particular interest.

Microstructurally, there are a multitude of SiC crystal structures or polytypes. The designations, 3C and 6H, are a couple of the more common structures and refer generally to the cubic β -SiC and hexagonal α -SiC polytypes. The α -SiC form is more stable at higher temperatures and usually predominates above about 3100°-3300°F (that is, β -SiC transforms into α -SiC when heated above ~3100° . . . or possibly for prolonged periods above 3000°). Another more recent structure is the amorphous form, symbolized here by a-SiC, which is often associated with the low temperature glassy ceramic product produced when pre-ceramic polymer precursors are first pyrolyzed. During the synthesis of SiC from elemental sources of a-C and Si, glassy a-SiC ceramic begins to form around 800°-900°F and comprises the entire product up until about 1500°-1600° when it just starts to undergo crystallation, transforming itself into the β -SiC polytype (however, process temps greater than 2000°-2200° are typical practice). Ultimately, the beta structure begins to rearrange into the α -SiC form when the system temperature is elevated into the 3000°'s. While there is a notable volume and density difference between the glassy and crystalline forms, the hexagonal α -SiC and cubic β -SiC structures occupy about the same crystal volume and are almost equivalent in density.

As ceramic conversion reactions permeate into the substrate during the original factory process, a substantial, dynamic temperature gradient is established which plays a dominant role in the particular structures that form across the gradient prior to cool down. While the basic elemental composition simply changes from SiC to C, there is a vast structural difference and associated material property gradient between the fully converted isotropic SiC phase in the extreme periphery and the highly anisotropic, fiber/matrix laminated composite phase underneath. It could be suggested that a-SiC is the first reaction product formed along the conversion front followed by crystalline transformations into β -SiC which probably dominates the conversion product all around. A ceramic microstructure mixture with increasing levels of α -SiC could be possible in the outer surface regions of the coating phase which see the highest temperatures for the longest amount of time as indicated in Figure 2.

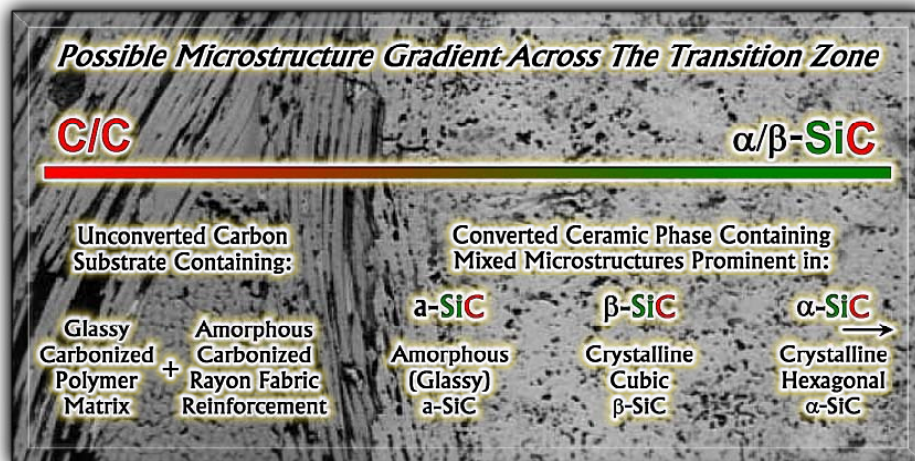


Figure 2. Cross-section of RCC bimaterial interface with suggested microstructure distribution across the conversion zone

The conversion product is expected to be essentially monolithic at the extreme periphery (again, the region which experiences the highest temperatures and the longest time exposures, as well as the greatest reactant availability). So, progressing from the fully converted regions inward, the transition zone begins to exhibit more of the

orthotropic laminar properties of the substrate as the composition gradually changes from the siliconized carbon phase (SiC) into the unaltered composite phase (C/C) and the micro/macrostructure evolves from monolithic-like α -/ β -SiC into the amorphous, highly anisotropic carbon fiber / carbon matrix lamina. Thus, the nature of the final transition zone is a function of the interconnectivity of the pre-converted substrate micro/macro-porosity leading from the surface of the article inward, as well as the thermal gradients that are established in the substrate periphery during the conversion process. Both of these factors drive the gradual transition from monolithic ceramic into orthotropic laminate. It should be noted that composition and microstructure do not necessarily overlap, and this applies to other properties. Some properties may overlap approximately along the transition line, others may not.

During the factory conversion process, thermally motivated Si particles react with the fibrous reinforcement and glassy matrix in two modes: (1) Diffusion of vaporized Si atoms into the microporosity of the substrate, terminated by gas-solid conversion reactions, and (2) Direct melt-solid fusion reactions between liquefied Si particles and open/accessible substrate surfaces. Both reaction modes result in the same α/β -SiC product mixture (final structures are temperature-dependent rather than reactant-dependent). Near its melting point, the vapor pressure of Si rapidly increases ($\sim 2600^\circ$) so diffusion processes begin before the melt phase is reached. There are literally a hundred different reactions that could take place within both the substrate zone and pack mix phase during the conversion process. Obviously, the primary reaction responsible for the ceramic conversion product is simply $\text{Si} + \text{C} \implies \text{SiC}$ but there are several other prominent reactions which must be considered to tell the whole story. Pore diameters large enough to accommodate Si atoms and their agglomerates ($> \sim \frac{1}{2} - 1 \text{ nm}$) and the degree of pore interconnectivity (in terms of depth and branching) play dominant roles in the availability of reactants and the uniformity of penetration directly along the conversion front. Conversion depth is not only dependent on the nature of substrate micro/macro-porosity, but on the peak temperature and the reaction time provided by the cycle. The longer the reaction time (and the higher the temperature), the greater the penetration/conversion into the substrate. However, the final depth may be influenced by growth kinetics not too different than those of more common oxide conversion coatings which tend to follow parabolic and semi-parabolic growth laws. In these situations, conversion growth consumes the substrate body as it works its way inward resulting in little overall dimensional change.

Not only is there the obvious and well known CTE differential between the two phases, but there is an enormous elastic modulus difference as well. The brittle ceramic phase may be up to ten times higher in stiffness than the carbon composite to which it is attached and, for all practical purposes, the modulus mismatch is the primary factor responsible for the formation of craze cracks and the detrimental consequences of what is often referred to as "CTE mismatch". It goes without saying . . . a broad or gradual transition between the two materials is absolutely essential in order to produce a successful conversion product that can repeatedly see the aggressive thermal conditions of atmospheric re-entry or nozzle burn with little to no maintenance. Varying depths of substrate thickness can be transformed ('ceramicized' or 'siliconized') into SiC depending on the degree of open, interconnected porosity at and near the surface of the substrate, as well as the effects of certain critical reaction/process conditions.

Now the nature of the porosity within the pre-converted RCC-3/ACC-4 substrate is dependent on the particular conditions and parameters applied during the initial composite autoclave fabrication process and subsequent densification cycles. Thus, this property is entirely controlled by design innovations, equipment limitations and the specific processing techniques utilized. The basic macro/micro-porosity network within the substrate is completely established within the article long before the conversion process (i.e., RCC/ACC porosity is engineered into the material by design and by the control and manipulation of specific fabrication techniques). It has never been a result of haphazard or random processing, otherwise the conversion (coating) process would have never succeeded. Now the nature of the thermal gradients formed within the material during the process are also heavily influenced by the pre-established density and porosity conditions and their variations throughout the composite periphery. However, these gradients are highly dependent on the maximum temperature, up-ramp and

hold time applied during the conversion cycle and they generally go from higher to lower as heat moves into the material from the outside. Broader conversion zones might tend to be favored by fast up-ramps, lower temperatures and shorter hold times. However, the latter two will also lead to incomplete conversion and poor oxidation protection. Across-the-thickness variations resulting in typical higher density (lower porosity) regions along the outer few plies lacing certain mold surfaces can sometimes lead to more narrow transition zones (as well as thinner coatings). Bear in mind however, every converted ply is one ply less to contribute to the product's strength capability (that is, the thicker the coating, the less composite there is for structural purposes). So the intent is to make the coating as thin as possible in order to provide the oxidation protection needed for as many service cycles as possible.

Since CVD coatings flake or burn off after one or two firings, the surface conversion (or fusion) approach is clearly superior. A CVD approach was tested in the early RCC days (and again during ACC development). It was determined to be inadequate for both RCC and ACC in terms of processability, cost and cycle time, but most importantly, CVD approaches are wholly inadequate for imparting re-usable oxidation protection to C/C substrates. In many cases, CVD deposits simply burn off during the first or second cycle in plasma or arc jet testing. Over the years, CVD has been repeatedly proven itself to be quite inferior to surface conversion approaches. Contrary to stoichiometric expectations, Si-starved powder mixtures have yielded the best conversion products. Other experiences have also supported these concepts. For example, boron diffusion into carbon/graphite substrates. It seems that boron atoms tend to migrate into the region between the graphene layers producing an effect that retards crystallization of SiC; boron also increases the ceramic yield; In more than one occasion during the 1970's and 1980's, experiments using boron compounds formulated in the powder pack mix were found to promote vast reductions in craze cracks; an improve coating process was loosely proposed in the late 1980's under this concept but funding issues prevented its maturation; this approach is still a viable alternative to the current crack-laden ceramic product and miles ahead of any CVD or CVR approach.

Fluidized-Bed Cementation and Vapor-Streaming Cementation

Several pack cementation approaches have employed for conversion coating of superalloys (i.e... chromium, aluminum, zinc onto low alloy steels). Many of these involve of gaseous diffusion of the individual metal atoms into the crystal structure comprising the outer regions of the substrate often with reactions proceeding in both directions to form a complex mixture of intermetallics across the transition zone. However, the RCC/ACC process is exclusively reaction-oriented and might be called 'reaction pack cementation' or reaction CVI. The two boundary phase do not diffuse or migrate into one another as with typical PC processes, but the process exclusively involves movement of both liquid and gaseous Si atoms into the carbonaceous substrate (carbon atoms do not diffuse outward into the pack mix).

To be continued . . .