Evaluation of RCC Defects for STS-120

Response to the Presentation "STS-120 Flight Readiness Review, October 16 2007"

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The following discussion is in response to a request to provide comments regarding the presentation, "STS-120 Flight Readiness Review" presented on October 16, 2007 by Ralph Roe. This matter concerns degradative defects associated with several of the SiC coated Reinforced Carbon-Carbon (RCC) panels lining the Shuttle's wing leading edges which are part of the Leading Edge Structural Subsystem (LESS) program of Lockheed's Missiles & Electronics division in Dallas, TX (formerly Vought / LTV Missiles & Electronics). This 'semi-analysis' is my perspective of some of the available findings and without being able to actually participate in the investigation, ask questions or request specific tests, these comments are strictly opinion-based and may contain inaccuracies.

While there a several possible mechanism factors that seem viable, personally, I do not concur with one involving substrate oxidation followed by subsequent coating debonding (Slide 6, "Proposed Damage Mechanism with Flight Rationale for STS-117"). From the evidence presented, it does not appear that oxidation of the substrate (fibers) has occurred. This is supported by the visual condition of fiber edges presented in the photos and the presence of normal substrate fabrication voids (as opposed to those that might be created due to oxidation). I believe the team has now abandoned this scenario as well. From Slide 7 ("Other Hypothesized Mechanisms for Coating Separation"), it also my opinion that none of the effects associated with sealant depletion, volatile entrapment, pore pressure build-up or differential glass hardening played a major role in these failures. An occasional process discrepancy at the vendor during refurbishment services cannot be completely ruled out, but considering the cure procedures and temperatures used during these operations, I believe residual solvents and water are long gone before products leave the vendor's shop floor. In general, I do not believe that volatiles or solvents have any problem exiting the RCC system during any portion of the re-entry time cycle.

"Thermomechanical fatigue may result in large craze cracks and buckling of the coating over previously weakened areas" (from Slide 7). It would be difficult for anyone to disagree with this statement. Indeed, low density / high porosity areas are ever present in the radius areas of almost all composite structures, but for RCC (and ACC) systems, these properties vary from one side of the radius thickness to the other. As a result of the initial lay-up and autoclave fabrication process, the outer-most fabric layers may tend to be in tension along the mold tooling surface (the OML) and in compression at/near the bag side (the IML). Personally, I have seen many times, in both RCC and ACC articles, situations in which the fabric has bunched up (buckled) in the IML radius apex region creating large voids, fabric distortions and 'resin rich' IML radii visible to the naked eye. In many cases, the first few layers of prepreg will try to bridge across the radius angle causing a slight lifting or separation effect between plies and away from the OML surface. When frequent debulking, staging and special hand techniques are utilized throughout the lay-up process (working the material tightly into place, debulking after every ply, using a heat gun and RTV rubber packing tools), particularly with respect to the first few plies, OML bridging can be minimized and is often shifted toward the IML side of the radius where voids and porosity tend to increase. But these conditions also increase the level of interlaminar compression (or compactness) between the outermost OML plies and the female mold tool surface which tends to increase the regional OML density, all of which inevitably become incorporated into the cured product. Some of these effects are apparent in many of the 0.1" cross-sectional photos given on Slides 14, 19 and 26. Now examine more closely, the image on Slide 14, which has been reproduced below in Figure 1.

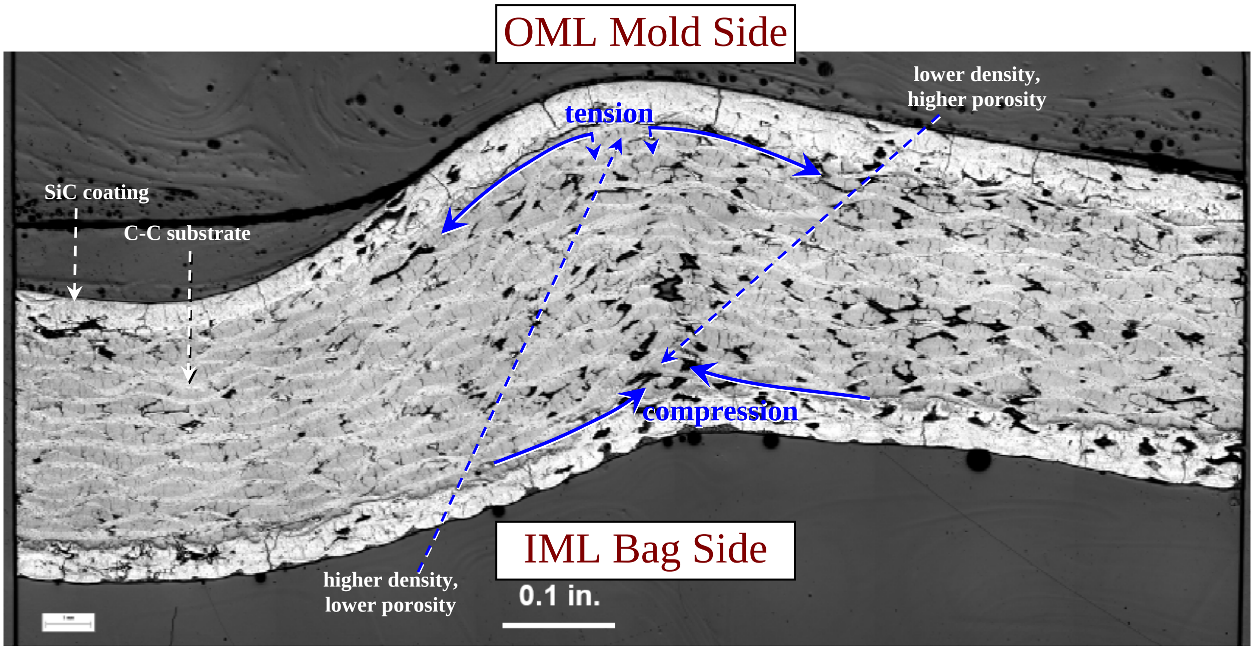


Figure 1. Cross-section of RCC joggle radius showing areas of high/low porosity and density and laminar regions under tensile/compressive forces within the substrate phase.

Thus, it is possible that, while the substrate IML region tends to buckle due to in-plane compressional forces (resulting in lower density and higher porosity in that area), along the OML curve, the outermost plies become stretched out across the contour and perhaps more compressed in the z-direction (resulting in slightly higher densities and lower porosities within the extreme OML region near coating interface and/or within the conversion zone). In a typical radius cross-section, a density gradient is often formed going from higher density at the OML substrate interface to lower density at the IML boundary. Subsequent densification cycles may tend to subdue the uneven porosity/density distribution across the thickness since the impregnating resin enters the substrate from all sides, but for the most part, the as-molded density/porosity structure throughout the composite is generally governed by the initial autoclave fabrication process (and subsequent pyrolysis) and is essentially maintained even after three or four densification cycles (after the porosity has been reduced), and (unfortunately) many of the pores are often closed off, sometimes becoming inaccessible to the intruding furfuryl alcohol resin.

Historically, the joggle radius regions on most of the LESS panels have been troublesome and difficult to fabricate, and technicians often had difficulty applying the right pressure to the OML radius region during the lay-up process. Over the years, various techniques were tested to try and mitigate the problems (some may or may not have been incorporated into the fabrication procedure). These included, pre-bleeding of specific plies during the lay-up sequence which proved to reduce excessive resin build-up or resin rich IML corners (particularly for ACC); differential staging of each ply (in place) while laying up to ensure progressive curing from the mold side to the bag side during the autoclave cure; time-delayed pressure increases during autoclave cure prior to gel of the phenolic resin, and based on prepreg out-time and debulk history (typically applied during the 175°F hold, this has helped to reduce voids and increase interlaminar strength); and post-curing of parts to ~500° (over a ~10 day cycle). Post-curing of RCC was indeed incorporated into the process after autoclave cure and after each impregnation cycle during the 1980's. Proper post-curing was found to eliminate catastrophic delamination problems and minimize excessive interlaminar voids. Many of these practices were transferred to the ACC platform where they found their greatest benefits. However there have been instances, in both RCC and ACC, where the regional OML per-ply thickness was visibly less than the IML per-ply thickness in highly contoured regions. This implies again, a situation like the one described above where the initial OML plies tend to stretch across the female mold surface as the lay-up progresses and become compacted more tightly together while fabric layers in the regional IML radius area tend to loosen and buckle or bunch up toward the apex. The extreme OML radius region then becomes slightly denser and less porous than the area just below which can sometimes have a negative effect on the depth and adherence of the SiC conversion coating along the OML radius curve. It has been proven that substrates exhibiting high densities / low porosities often make poor candidates for effective conversion coating. It is important to note that all the conditions and scenarios covered above pertain to the uncoated substrate and are inherent within the composite body *before it even enters the coating process*.

Consider now possible bulk and mechanical effects associated with stresses generated during the cool down portion of the initial coating process. Along flat regions of the substrate, contractional CTE compression forces operate independently of the substrate geometry (disregarding interface mismatch for the moment). In contoured areas however, contractional stresses interact with the substrate in accordance with the part geometry. Along OML concave regions, the coating front diverges and craze cracks tend to squeeze together, but along OML convex curves, the coating front converges causing cracks with wider gaps at the periphery. In accordance with geometric CTE mismatch, components of these stresses can impart loads that tend to squeeze the radius in on itself which could easily contribute to coating-to-substrate buckling effects. Figure 2 below (a close-up of Panel 8R Sample 4 given on Slide 16) illustrates these effects. Coupled with the substrate lay-up and fabrication scenario given in the above discussion, these types of coating contraction effects would only exacerbate a possible delamination event on the substrate side of the conversion zone.

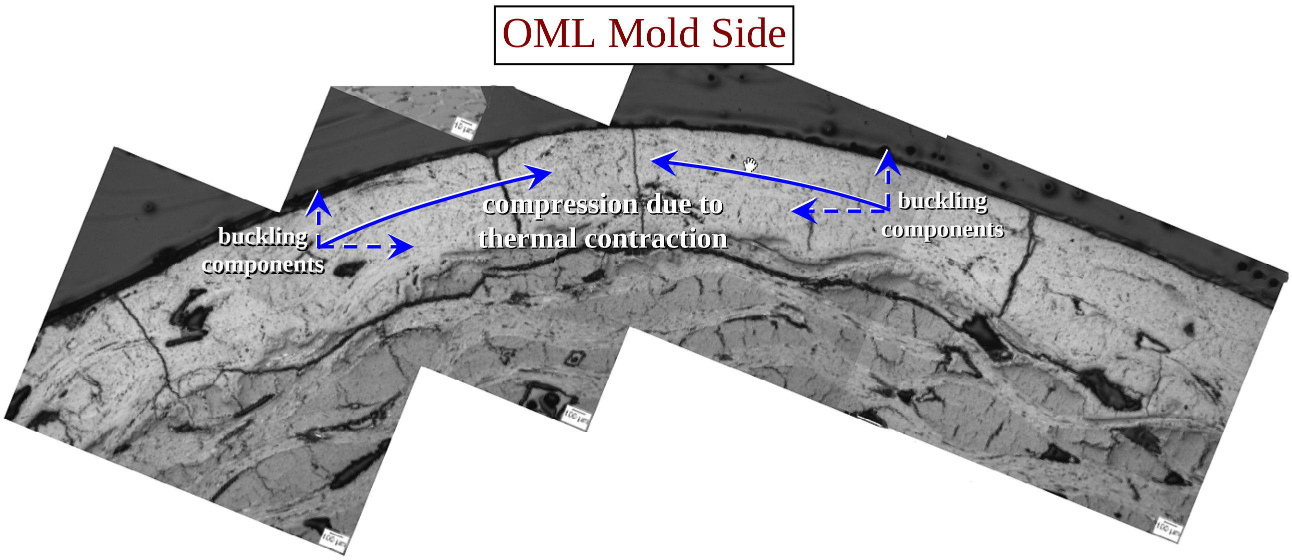


Figure 2. Close up of joggle radius curve showing coating contraction forces and associated stress components.

As another mechanism contributor, consider properties associated with the coating-to-substrate integration quality. Of particular interest is the depth or penetration (coating thickness) and the SiC-to-substrate conversion (gradient) zone relative to critical substrate properties. Examine Figure 3 below.

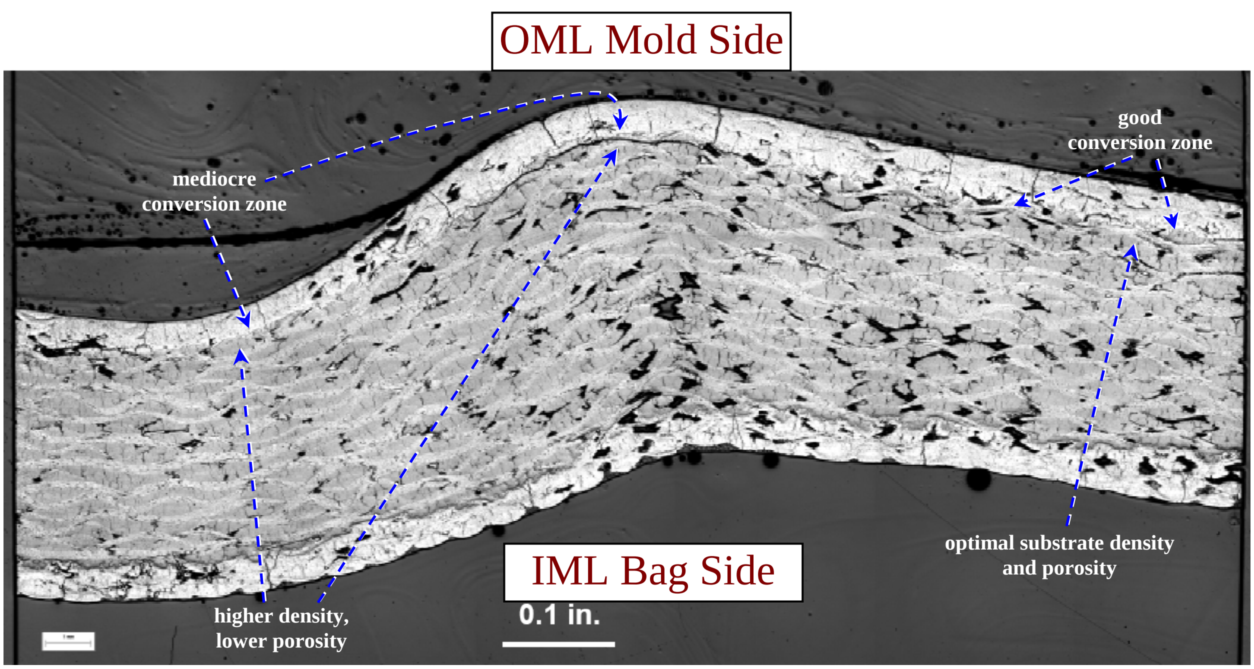


Figure 3. Cross-section of RCC joggle radius showing SiC gradient conversion coating zones and associated substrate property observations.

Along the OML apex region where the delam occurred, there appears to be a fairly fine distinction between the coating phase and the substrate which could be indicative of less-than-optimal conversion of the substrate. In some of the flatter areas however, particularly the OML zone far to the right of the apex, blending between the two phases is more pronounced. Here, the characteristic functional gradient unique to coated RCC/ACC materials is quite apparent. This part of the interface region is a good representation of how the coating should diffuse and graduate into the substrate body (of course, if the conversion zone is too deep in thin regions of the substrate, the product could become brittle). Successful conversion coating is heavily dependent on the level and nature of porosity near the surface of the substrate after the densification phase is complete (peripheral porosity). A long history of trial and error has repeatedly proven that substrate densified to the RCC-3 (and ACC-4) state generally provides the most suitable bulk properties for successful coating-to-substrate integration, as indicated along the extreme right of the OML radius curve in this image. It is a major responsibility of the substrate technologist to deliver the most optimum properties for coating operations and, while I cannot decisively make a definitive judgment on the some of the narrower interface zones, it is my opinion that the density and porosity of the substrate in this flatter area were exceptional and quite receptive to the coating.

Whether or not localized pack mix pressure, mix composition, particle size distribution or heating variations played a major role in these failures cannot be ascertain at this point with this data. However, due to the critical requirements associated with the coating process, these parameters can have a pronounced effect on the final coating thickness, gradient composition, pin hole formation and the nature of crazing. Perhaps EDX line scans across some of the conversion zones (from the SiC phase into the C-C body) would shed some light in this area. Results from this type of test might indicate possible anomalies associated with the chemical make-up of the conversion zone since gradual transformation of the C-C substrate into SiC is the key to producing adherent coatings in which the CTE mismatch is mitigated and stabilized. Ideally, the SiC phase and the C-C substrate should become almost mechanically inseparable as they blend together.

Low temperature CTE differences between isotropic β-SiC and the orthotropic C-C substrate may be close to 3:1, but around the 3000° regime, moderate increases in substrate CTE subdue this mismatch notably (more on the order of 2:1). However, during the cool down phase of re-entry, contractional mismatches increase substantially and the coating-to-substrate conversion zone is again placed under higher stresses. Historically, lower temperature oxidation protection (2000°- 2300°) of SiC coated RCC-3 has been a concern since the early development days of the 1970's. It goes without saying, repetitive cycles of re-entry impart cumulative fatigue effects to the coating-substrate interface, particularly in sharp contour areas which also see higher temperature extremes . . . and the expansion/contraction cycles probably exhibit an appreciable degree of hysteresis which likely aggravates the fatigue effects. It is my opinion that thermomechanical fatigue of the OML SiC-to-C/C conversion zone is the most prominent driver leading to these delaminations. I would not necessarily attribute these failures to any particular manufacturing inadequacy, rather, they are more reflective of age, wear and tear. They are indicative of aging panels near the end of their use life. Perhaps the wishful 100 mission life capability originally postulated in the early days for the Orbiter's siliconized RCC was a little over-optimistic. Realistically however, you must admit, 25 to 30+ low maintenance missions is not a bad performance record for any TPS material, especially for applications to the very hottest regions of the ship. All in all, most of these panels have served their duty very well. In terms of performance, maintenance and longivity, it would be hard to beat this record with any other known material system currently available.

Summary and ranking of the most likely factors contributing to these failures:

– Thermomechanical fatigue of the radial coating-to-substrate conversion zone (with respect to the hysteretic CTE mismatch) due to repetitive thermal cycling (re-entry episodes) coupled with contributions from one or more of the following factors:

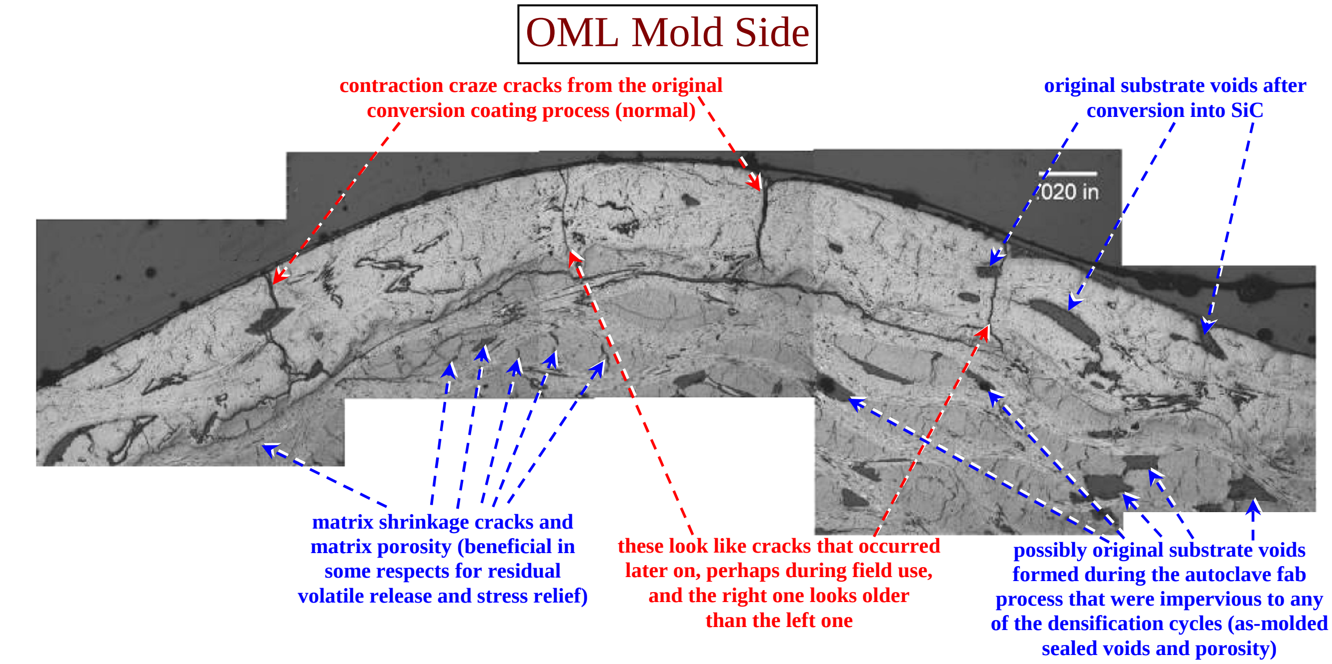
– Stresses associated with CTE contraction of the SiC coating phase during cool down of the coating process which generates compressive buckling forces in accordance with radial part geometry in contoured regions (the part leaves the factory floor with these stresses inherently built in).

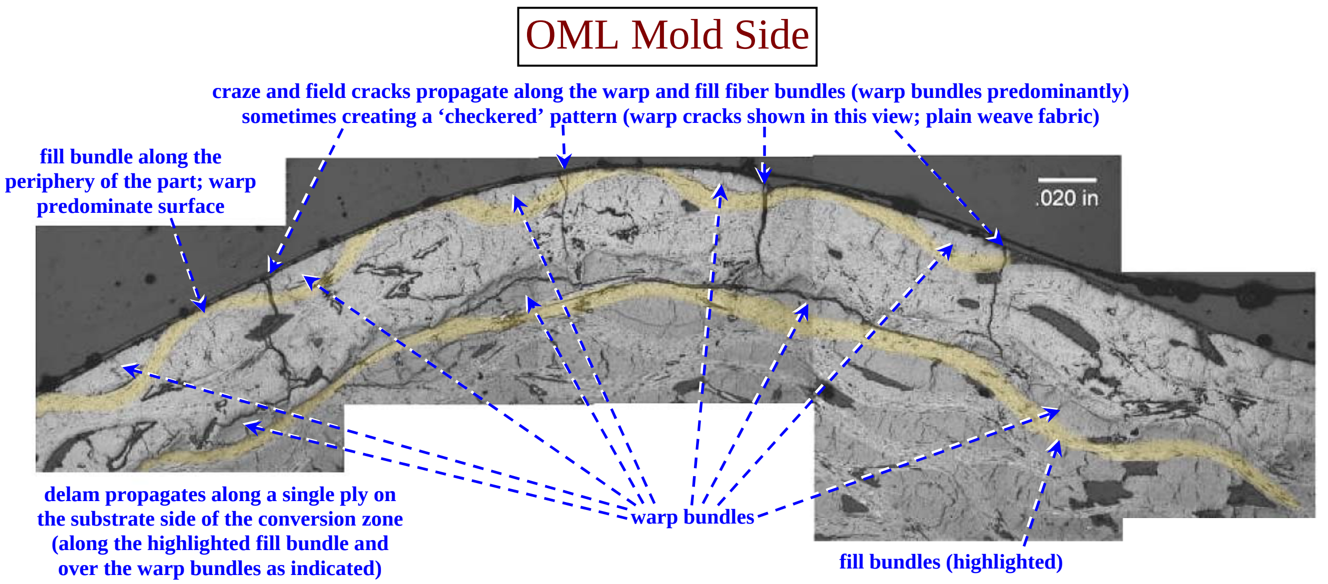
– Stresses inadvertently built into the difficult contour region of the joggle radius during the early fabrication (lay-up) stages. Note that stresses are incorporated into all laminated structures and while some may eventually be eliminated or reduced by design or fabrication methodology, they are not necessarily abnormal in these types of complex material systems. However, as with the condition defined above, the part leaves the factory with these residual (latent) stresses built in, probably for the lifetime of the part.

– Less-than-optimal SiC conversion of the C-C substrate in higher density regions resulting in narrow gradient zones and mediocre coating-to-substrate integration (adhesion). This condition can depend on RCC-3 substrate properties as well as variations in pack mix attributes and/or coating temperature distribution.

Additional Observations and Notes:

Image below taken from Slide 23, Sample 5D





as a part ages, the number and extent of stress cracks increase while the spacing between them decreases accordingly; stress cracks are wider in OML radii and contoured regions making them more vulnerable to oxygen intrusion

With phenolic resin impregnated carbonized rayon cloth, 2-D RCC substrate is fabricated utilizing lay-up techniques, autoclave curing methods and tooling not too different than those employed for common carbon/phenolic and graphite/epoxy composites throughout the aerospace field. Substrate fiber volume is established and controlled by regulating the degree of resin bleed-out during the autoclave cure (10-15% weight loss is typical for ACC, RCC is lower). Even though several cycles of subsequent densification may tend to subdue non-uniform property variations across the substrate, the rudimentary porosity/voids network and density distribution are essentially established by selections made for the specific lay-up materials and methods, bagging configurations, and time/temperature/vacuum/pressure cure cycle profiles utilized. After a post-cure operation to reduce residual volatiles and subsequent delaminations, the as-molded composite is converted to the first carbon state RCC-0 via pyrolysis at 1500° in a retort packed with calcined coke particles over a 3 day period. Pyrolysis (which results in a ~ 20-25% weight loss) converts the phenolic resin binder into a glassy carbon matrix at a content of about 15-20%. This highly porous C-C form (25-30% porosity) is then double impregnated via vacuum/pressure furfuryl alcohol resin impregnation and cured to the RCC-0 'bimatrix' state (25-30% cured resin weight gain) and then post-cured again (a typical post-cure slowly ramps the part up to the 500° range with multiple steps over about 10 days and results in about 1-3% weight loss). Each cycle of densification (impregnation/cure/postcure/pyrolysis) increases the substrate's density, matrix content and mechanical properties while reducing the open porosity. At the RCC-3 state, the composite bulk density runs around 1.45-1.55, open porosity about 10-15%, matrix (carbonized resin) content in the 30-35% range, fiber volume around 55-60%, flexural strength 15-30 ksi and interlaminar tensile (ILT) strength in the 800-1200 psi range. After the SiC coating process, ILT values drop 40-50% below the pre-coat RCC-3 level, and for properly coated material, the failure generally occurs in the body of the substrate laminate, not in the coating zone.

It was determined long ago that the properties of the substrate at the RCC-3 state consistently provided optimal conversion of the outer 30-50 mils of the substrate surface. In preparation for the pack mix cementation diffusion coating operation, the substrate is secured in a graphite/SiC retort and a specially formulated particle/powder mix is precisely packed around all surfaces of the part, contours, radii, corners and edges. It took several years to refine the optimum pack mix composition, particle size distributions, packing pressure and temperature profile suitable for successful surface conversion of densified RCC substrate. Eventually, an approximate powder formulation of 10%Al_2O_3/60%SiC/30%Si was found to consistently produce the best results using different particle size distributions for each of the three components. With modifications in the retort design to facilitate mix conductivity, initial reaction temperatures in the 3200°- 3400° range were reduced to 3000°- 3100° and produced substrate weight gains of about 25-35%. Further improvements eventually led to reduction of the peak processing temperature to 2950°-3000°. In this process, Si atoms diffuse into the porosity of the substrate where they react with both the fibrous carbon reinforcement (firstly) and the glassy carbon matrix (secondly) producing reaction-cemented β-SiC (in actuality, small amounts of Al-SiC products result in a 'composite' coating phase which is predominantly SiC). As a result of the substrate-coating differential CTE, craze cracks develop in the SiC coating phase during the cool down portion of the conversion cycle.

While the presence and precise level of Al_2O_3, as well as higher processing temperatures and/or a post-coating heat treatment step were found to reduce crazing, a system of sealants and application processes were eventually developed. Tetraethylorthosilicate (TEOS, tetraethoxysilane) was selected as the primary glass-ceramic-forming sealant. It is impregnated into the coated substrate 4 or 5 times and is intended to fill the craze cracks with SiO_2 and/or silicon oxycarbides upon firing. Finally, several applications of one or more low temperature, glass-forming, inorganic sealant mixtures (Type A, Type Fh, etc...) are painted on the part to provide additional (low temperature) oxidation protection. Basically, these are custom C/SiC powder blends dispersed in aqueous alkali silicate solution (Sermabond Part I). Early during the development of RCC (or Reinforced Pyrolyzed Plastic, RPP), a craze-free coating process was inadvertently achieved and extensively tested but details of the run conditions are vague at this time. Also in the early days, Vought experimented with various coating options for primary oxidation protection of the RPP substrate including slurry forms of boron-zirconium-silicon, hafnium-tantalum melt coating, and other materials applied via plasma spray overlay, resin 'ad-mix', and CVD. CVD approaches repeatedly failed plasma arc testing and were projected to last only 1 or 2 missions. Thirty five years later, these findings still hold true. Despite its shortcomings and ill perceptions, particle pack mix cementation/diffusion still provides the most effective means for rendering long lasting, low maintenance oxidation protection to C-C substrates. The next generation of this material may still not yet be able to (realistically) offer 100 mission life capability (whether based on rayon, PAN or some synergistic form of fibrous reinforcement), but it should provide some vast improvements in terms of processability (and cost), survivability (oxidation protection, impact resistance), versatility (suitable for both skins and substructures, re-usability), field maintenance and reliability. The best is yet to come . . .