

Factors Contributing to Delaminations in RCC Joggle Regions

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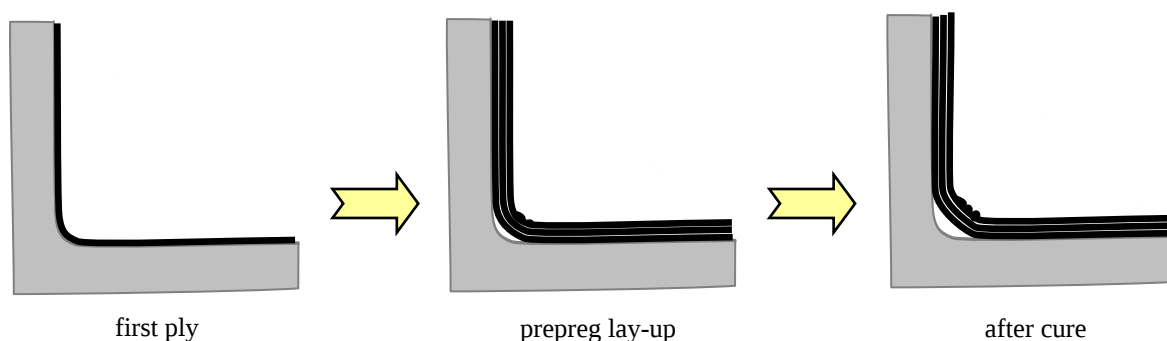
This discussion includes an elaboration of plausible factors that may facilitate delaminations, sub-coating separations or fractures along the lower OML slip side joggle section in some of the RCC panels which are located near the mid-wing region of the leading edge or LESS TPS system. The premise of some of these ideas was issued in a report last year (Oct. 2007). The approach here is based on the assertion that coating spallations do not occur spontaneously but are only one of several possible events that could follow substrate delaminations or coating-to-substrate interface fractures in this region of the RCC panels.

With this basis, it is postulated that a delamination/fracture will always precede, or at least coincide, with a spallation event (if one occurs) and that a delamination/fracture is a necessary precursor to spallation. On the other hand, the occurrence of delamination/fractures does not automatically mean that spallation of the coating is imminent. Thus, the issue then becomes one of exploring likely factors or root causes leading to substrate delaminations or interface separations in these critical areas. Potentially, spallation is a catastrophic event, so the objective should be to preclude this stage of the failure process by better understanding the most prominent factors likely to contribute to the formation of these kinds of sub-coating defects.

Several concepts are expounded on in this paper which may or may not have direct bearing on the current RCC root cause effort. It is not always exactly clear which test methods could be employed to unequivocally validate some of these factors. They are proposed here as a contribution to the RCC information pool, and are based on direct experiences in the composites and ceramics manufacturing industry along with several years of daily, hands-on engineering involvement as a principal in the design, fabrication and R&D of RCC panel trials and ACC structures throughout the 1980's (the most active period for LESS RCC production and ACC development at LTV Aerospace & Defense Co.). Thus, most of the following ideas are professional opinions based on first hand knowledge . . . but no guarantee is given here that any or all statements are correct, precise, error-free or non-controversial.

Scenario 1: The first factor of relevance occurs early in the RCC fabrication process where conditions are generated that could potentially lead to subsequent OML delaminations or 'weak planes'. During the composite lay-up stage, prepreg plies are visually positioned onto the mold contour and manually worked into position using the hands, soft teflon rubbing tools and/or rollers. An IPA spray bottle and a hot air gun are also used intermittently to improve localized prepreg tack, drape and placement control.

At one time, a more robust approach of differentially staging the plies *in place* was experimentally practiced to try and facilitate balanced and even curing across the laminate thickness during the subsequent autoclave cure (hot air staging of each individual ply as it was hand-crafted into the contour). In general, it is known that after the first ply of prepreg is placed and worked onto/into a curved female mold surface, the continued action of working the next few plies into position in and around the area starts causing the lower plies to try and lift up along the apex length forming a 'bridge' of prepreg across the angle. Moreover, continued migrational movements of the material during autoclave cure can substantially worsen the effect. Sometimes bridging becomes visually apparent during the lay-up process, but more often, the full effect is not seen until after the cured article is de-bagged and removed from the mold tool. The phenomenon is illustrated below . . .



In some cases, the resulting gap fills with resin. That is, thermal/physical movement (bleeding) of prepreg resin into the bridged area often causes the outer apex region to become 'resin rich' lengthwise along the apex. At one time, LESS manufacturing utilized specially shaped rubber tooling aids in the joggle areas during bagging/debulking procedures to help keep the material down and to minimize springback effects as the phenolic resin underwent staging reactions (these were silicone rubber block sections previously fabricated from the OML joggle apex mold contour). It is vaguely recalled that, at one time, these special tools were used in either one or both IML joggle contours during all pre-cure debulking operations.

Another technique that was developed and eventually incorporated into the joggle region lay-up procedure was a system of strategically cut and tapered strips of bleeder canvas precisely positioned along the apex length. During the final bagging operation prior to cure, pieces of bleeder canvas were stacked in graduating sizes with narrow strips placed first along the bag side (IML) apex length (on top of the perforated tedlar barrier film) followed by strips of gradually increasing radial width. No continuous canvas layers were laid completely across the apex section since this would compound the bridging effect. It was shown that this technique had positive benefits in terms of localized pressure application by effectively focusing the compaction forces along the apex. The procedure was adopted as standard practice for all joggle sections in the 1970's and used throughout the 1980's and beyond (the exact techniques and bagging configurations utilized in more recent lay-ups are not known at this time).

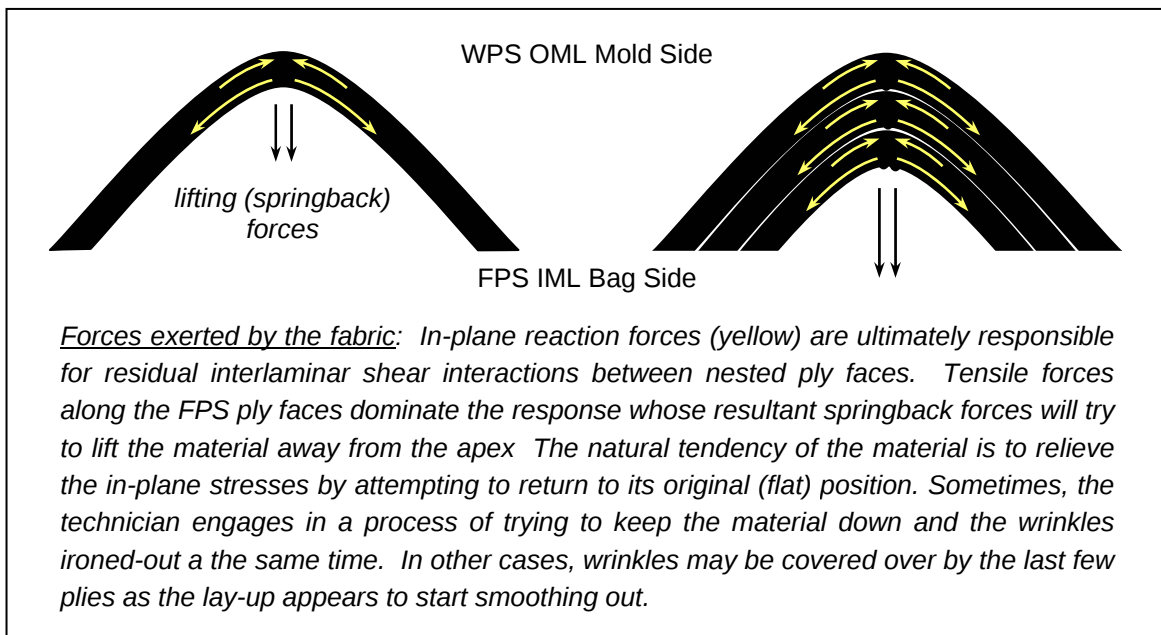
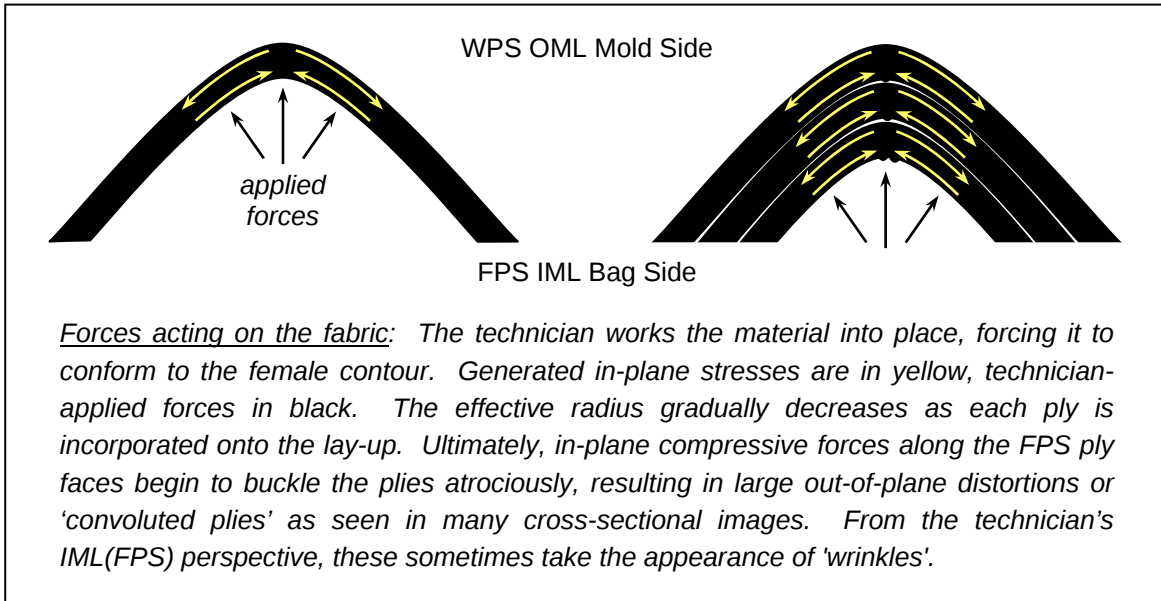
Historical records might show (circa 1970's-80's) that it was often difficult to get adequate pressure along many of the joggle contours during the lay-up and autoclave molding process. This radial lifting effect is not uncommon in the laminated composites industry when trying to lay-up carbon fiber prepregs into female mold shapes. The effect is further complicated in structural designs that have 3-D contours such as those of the joggle regions under study (a typical joggle contour is analogous to a curved cylindrical section).

Radius bridging issues were notorious for 8 harness satin PAN fabric (ACC) but less problematic for plain weave rayon (RCC). This was one of the primary challenges never completely resolved during the period when we (LTV) were gearing up to retrofit the Shuttle's RCC entirely with ACC (mid 1980's). Bear in mind however, even when there is no visible lifting, these types of radial cross-sections almost certainly retain a certain level of bending stresses which eventually become molded-in with the contours as interlaminar residual stresses. Now after the first few plies are incorporated and the lay-up is continued, the cross-sectional thickness is built up while the effective IML radius gradually decreases. Consequently, in-plane buckling of fiber bundles comprising the plies closer to the bag side becomes progressively more pronounced, sometimes resulting in out-of-plane distortions or 'ply convolutions'.

Consider the scenario from a ply-to-ply perspective. During the lay-up process, the first ply of prepreg is hand-worked into the surface contour causing the fabric to become slightly warped in order to conform to the contour. But the forces acting on each face of the ply are not the same. For instance, along protruding or male (convex) mold surfaces (if there were any), the material must be stretched across the contour causing in-plane tension across the outside face of the ply and in-plane compression across the mold side face of the fabric. Since fiber tensile strength is many times greater than its compressive strength, there is a tendency for the mold side to experience microbuckling. Sometimes, visible wrinkles are manifested, depending on the radial angles that define the contour, and these are often hand-worked or rubbed out using the soft teflon tools. With opposing forces acting on either side of the ply, the tendency is for the ply to straighten itself out through a relaxation process that tries to lift the material out of the apex.

For RCC configurations, all tooling is comprised exclusively of female (concave) lay-up surfaces, in which the two fabric sides are often designated as the warp-predominant surface (WPS) and the fill-predominant surface (FPS), where the WPS is typically oriented toward the OML mold surface throughout the entire 0°-90° cross-ply lay-up sequence (the WPS was originally designed to face toward the outside leading edge of all RCC panels and articles). Thus, the WPS of all prepreg layers faces the OML mold/tool side of the lay-up while the FPS is oriented toward the IML bag side of the laminate (the side which faces the technician). So as the first ply is compacted onto the mold surface, WPS side down, the FPS side tends to microbuckle in accordance with the contour. As the technician works the material into position, tensile forces on the WPS side oppose the compressive forces on the FPS side, and when left undisturbed, the material attempts to relax back toward its original shape.

The effects are cumulative. After several plies are applied, and stacked on top of each other, a state of interlaminar ply-to-ply interfacial shear is established along the apex region as a result of the nestling between compressive forces along WPS ply faces and tensile forces along adjoining FPS faces. Consider the following descriptive illustrations . . .



As a consequence all this, residual bending stresses are incorporated into most hand-laid contoured sections as they are 'molded in' during the autoclave curing process, particularly in regions without the benefits of mitigating techniques such as the use of embedded 'filler strips' (discussed later). Weakened interlaminar or ply-to-ply interactions (sometimes called 'weak planes') which are fixed into curved laminate sections have been shown repeatedly to impart a degradative effect on regional interlaminar strengths, resulting in substandard ILT and ILS properties. Since there is no adequate energy release mechanism that can subsequently be imposed on the cured system, reduced ILS and ILT properties across the apex thickness likely become permanent attributes in the substrate throughout its service life. These stresses are long range in nature and their in-plane effects probably interact with the lamina well away from the apex region. Thus, mechanical isolation, regional machining or sample sectioning along the perimeters of the affected regions will provide a certain degree of stress relief as often observed during machining and extraction of test samples for destructive materials analysis.

It should be realized that this state of residual stress is almost purely a mechanical one, essentially independent of temperature (however, fiber-to-matrix chemical bonding between matrix and fiber surface functional groups plays a partial role in the total interface binding picture and could exhibit some thermal dependencies). The plies may move infinitesimally before reaching their final positions during the hardening stage of the phenolic curing process, and the interlaminar stresses could conceivably undergo slight changes due to out-of-plane expansion during subsequent high temperature processing (R120 and most phenolic resoles will typically gel above about 180°F and begin to harden in the 225°-250° range). However, *there is no subsequent temperature that can be later applied to reduce these stresses to zero*. The first 1500°F pyrolysis, which converts the as-molded composite to the RCC-0 state, transforms the phenolic matrix/binder into glassy carbon and reduces the matrix content by about 50% (for instance, an as-molded resin content of 35% is converted into a carbon char content of about 15-17%). Even though binder-to-fiber surface area is significantly reduced during the first pyrolysis, interlaminar stress relief is probably minuscule, if any at all.

Thus, the nature of chemical binding between the matrix phase and the fiber surfaces is altered by pyrolysis . . . most of the ether and ester links, which were prominent when the matrix was organo-phenolic, are destroyed and converted into van der Waals associations, pi overlap interactions and/or carbon-carbon sigma bonds between the amorphous structure of the reinforcement (carbonized rayon) and the glassy (amorphous) structure of the inorganic resin char. Subsequent densification cycles (each consisting of polyfurfuryl alcohol resin impregnation, 300° cure, 500° post-cure and 1500° pyrolysis) may have a slight general effect on thermal/mechanical stress relief within the composite body but again, the majority of the as-molded residual bending stresses along contours is retained in the substrate throughout the coating process and the lifetime of the panel.

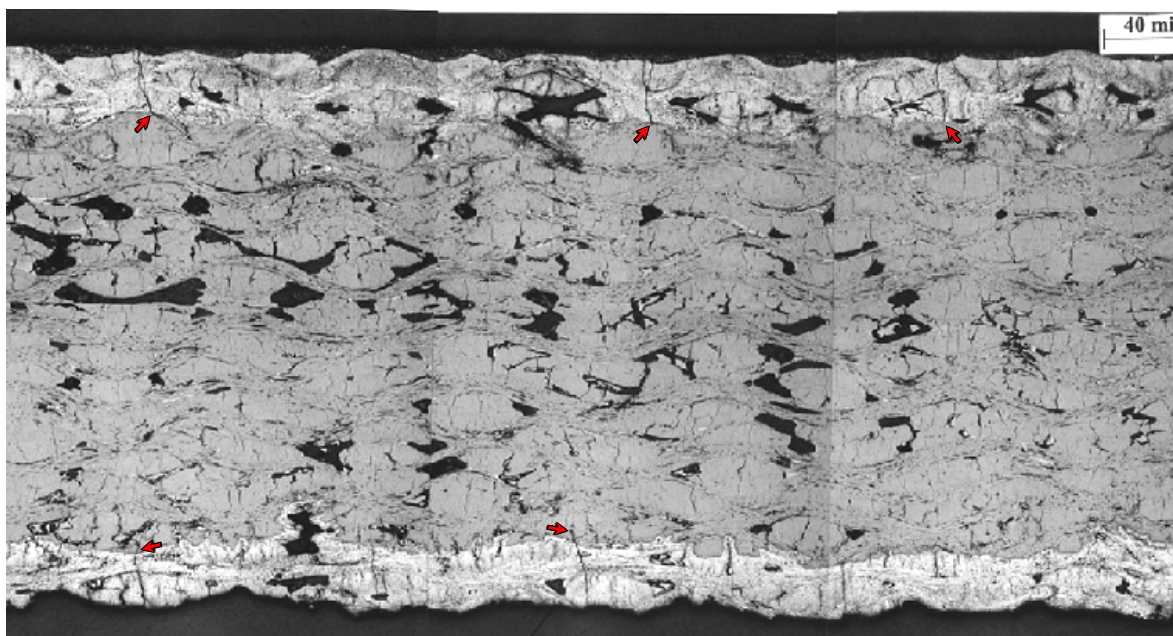
Scenario 2: Another possible factor which might be somewhat associated with the effects of Scenario 1 is the variation in material properties across the thickness (cross-section) of the apex. At the mold surface, plies are compressed against the hard fiberglass tool, due in part, because the bulk of the laminate body is stacked on top of these initial plies (in conjunction with the vacuum bag and autoclave pressures which are applied across the entire laminate). It has been shown that increased z compaction and nesting of the early OML plies will tend to modify the properties on this side of the laminate. In general, there is often a tendency for slight changes in mold side-to-bag side properties, and these will have an effect on the substrate's response to the conversion coating process. In contoured regions, the effect is further compounded by geometrical factors.

Effective surface conversion of the substrate is highly dependent on specific RCC-3 physical properties being within previously optimized ranges (determined many years ago). On the mold side of the laminate for instance, the per-ply thickness will tend to be slightly depressed while the substrate surface density is increased and micro/macro surface porosities are correspondingly lower. As a result, OML fiber volumes will tend to be a little higher with matrix contents slightly lower. In contrast, plies approaching the bag side are only opposed by the softer bagging material where the bulk density becomes increasingly lower and the porosity higher, along with corresponding decreases and increases in fiber volume and matrix content respectively. In concave apex regions, this effect is sometimes exacerbated abnormally and irregularly as out-of-plane ply distortions develop causing large voids and cavities, some of which become filled with subsequent densification matrix intrusions and others which are sealed off and contribute to the 'closed' porosity fraction of the material.

With some analogy to the OML side, ply distortions or kinking of the fabric layers approaching the IML side are due to in-plane compression and buckling of the prepreg plies as the material is forced into the decreasing concave radius. Unlike the OML side however, this condition is possibly augmented by a slight slipping of the IML plies during the autoclave cure. These irregularities will sometimes become apparent as IML 'wrinkles' to the lay-up technician who often tries to work them out using his teflon rubbing tools. The condition is not prominent on every joggle section and is not apparent on every delaminated cross-section evaluated in the RCC root cause study. For this particular joggle section, they seem to become most obvious within the last 5 to 10 plies of the apex region for some of the panels. In essence, IML-side distortions can be considered as an exaggerated extension of the ply face-to-face tension and compression effects described above for the OML side . . . an after-effect of the initial interlaminar shear stress condition generated as plies are incorporated into the laminate apex from the mold side up. Thus, the entire apex cross-section is subject to as-molded mechanical residual stresses whose magnitude gradually decreases across the OML-IML thickness. While energy is liberated on the softer bag side due to buckling distortions, stretched plies near the OML side retain most of their interlaminar stress energy which could, in extreme cases or when coupled with other factors, be released by a subsequent delamination event.

Not only do coating thicknesses vary from mold side to bag side but the quality of the gradient conversion zone is also affected. The greatest benefit from the classical RCC/ACC surface conversion approach (as opposed to say, CVD) is attributed to the compositional and microstructural gradient that is established during the conversion process (the transitional boundary zone separating the fully converted ceramic product from the unaltered C/C substrate). This ‘functional’ conversion zone is responsible for the quality and level of mitigation achieved in terms of CTE compatibility between the substrate phase and the ceramic phase.

Gradual conversion between these two phases is key to alleviating problems dealing with the differential coating-to-substrate CTE, the associated modulus mismatch and the coating’s oxidation protection capability, as well as extending the durability and service life of the panels. Transitional zones on the order of multiple lattice parameters vs. those traversing several tenths of a mil or even several mils can have enormous effects on coating-to-substrate adherence and CTE/modulus mitigation. These variations are often difficult to see visually. The following image somewhat reflects these conditions to a degree (courtesy of SRI), where there appears to be broad conversion zones across the upper half of the specimen and narrow or discrete boundaries separating the C/C substrate and SiC coating phase across the lower half . . .



Craze crack propagation through these two zones can also be characteristically different. For instance, within some of the narrow boundary zones, there may be a greater tendency for cracks to propagate directly into the substrate body. This would be understandable since broader conversion zones will have a heightened capability to absorb, dampen or retard propagating cracks due to the gradual change in the microstructure from crystalline SiC into amorphous C/C. Clearly, broad transition zones should be a primary objective in delivering a coated product that is optimized in terms of CTE mismatch mitigation. While it is typically measured as part of the total coating thickness, the transition zone is a graduating mixture of SiC ceramic and carbon substrate and should be considered as a separate multi-phase.

The carbonized rayon reinforcement and carbonized polymer matrix are both amorphous non-graphitizable 'hard' carbons while thermal reaction transformation into SiC likely converts both of these constituents into one of the crystalline SiC polymorphs, forming a fused monolithic SiC coating phase (either hexagonal α -SiC or cubic β -SiC). If amorphous SiC were formed, it would undergo irreversible crystallation above about 2000°-2200°F. The hexagonal SiC form is favored in this system since it will tend to mimic structures comprising the carbonized constituents of the substrate. Actually, the coating phase is not necessarily 100% SiC since about 10% Al₂O₃ is used in the pack mix. The ceramic product will inevitably contain 1-5% aluminum compound(s) to comprise a α -SiC/ α -Al₄SiC₄ 'composite' coating. The quality and condition of the transition zone can probably be substantiated and effectively mapped out using EDX line scans across the boundary zones at selected points. This technique has been suggested twice during the past year and is again strongly recommended here.

For reasons of clarity, classification of the ceramicized region of the C/C substrate as a 'ceramic fiber / ceramic matrix' composite may not be precisely correct. Since these two constituents lose their original identities at the molecular level, both phases inevitably assume the same SiC crystalline structure and become 'fused' together as a single ceramic body (otherwise, it would be feasible to physically isolate the two constituents and/or mechanically identify them as unique fiber and matrix phases; also, 'delaminations' exclusively within the ceramic coating phase are unheard of). Within the conversion phase, fibrous textures resembling the original unconverted fibers bear the same microstructure as newly converted matrix regions. A fracture front strictly within the ceramic region propagates almost equivalently through all the textural aberrations as though the phase was monolithic (that is, fronts or waves propagate *almost* equivalently, because the new coating phase generally does not exhibit uniform *bulk* density throughout since relative density distribution in the converted monolith will have a tendency to mimic that which was present in the unconverted substrate).

In addition to chemical conversion, mechanical integration of the coating phase with the substrate phase is manifested by the formation of coating dendrites into the porosity of the substrate. Mechanical interlocking via dendritic conversion features (or fingers) utilizes the macroporosity within the substrate periphery while chemical conversion is dependent on the substrate's microporosity. This is another illustration of how critical surface porosity is and helps to emphasize the need for tight control and optimization of this property to achieve consistent conversion of the substrate periphery. Above about 2600°-2700°F during the coating cycle, both vapor-solid and liquid-solid reactions take place between silicon atoms and substrate constituents (and carbonized cellulose will be more susceptible to ceramic conversion than the less reactive carbonized thermoset matrix which contains a higher level of 'hard' crosslinks). Chemical interactions between liquefied silicon particles in the pack mix, which are in intimate contact with open substrate surfaces, exposed cavities and large voids, could be characterized as 'reaction-controlled' processes while gaseous conversion reactions, which are wholly dependent on the substrate microporosity, tend to be 'diffusion-controlled'.

Before delving into Scenario 3, it is interesting to make note of some of the average thermal expansion/contraction coefficients for each of the components in the coated RCC system. Due to the advanced post-cure that autoclave-fabricated (as-molded) RCC is subjected to, the median (pre-char) CTE of the cured isotropic phenolic resin matrix is relatively low (for a polymer thermoset) and may run from around 20 to 40 ppm/°C (one of the primary benefits of post-curing phenolic and furfuryl products is that it raises and diminishes the cured T_g while lowering the CTE accordingly). After pyrolysis of the phenolic fraction into inorganic glassy (vitreous) carbon char, the matrix CTE drops to about 2.5–3.5. This is also reflective of the expansion/contraction CTE for carbonized polyfurfuryl alcohol resin which comprises the bulk of the RCC-3 matrix fraction (functionally, the carbonized versions of these two resins are virtually identical). The longitudinal CTE for high temperature carbonized rayon fibers is almost nil, being about to 0–1 over a wide temperature range. This is primarily due to the rigid nature of the 2-D hexagonal carbon ring system comprising the graphene layers of the carbonized fiber structure, many of which are oriented longitudinally or parallel to the fiber length.

Both the matrix and fiber precursors here are highly crosslinked polymers that are converted into sp^2 -bonded 'amorphous' carbons which do not pass into liquid crystal mesophase and are thus non-graphitizable carbon forms (at least up to $> 3000^\circ\text{C}$). However, the 2-D graphene fiber structure will still contain regions of limited 3-D indexing or 'pseudo-d spacings', which permit transverse expansion/contraction along the fiber diameter several times greater than its longitudinal CTE. Thus, the transverse fiber CTE probably runs around 4–5. While pure SiC has been measured as high as 6, the sometimes carbon-rich aluminum-modified SiC phase comprising RCC/ACC coatings probably runs around 4.5–5 in the median temperature regimes ($\sim 500^\circ\text{C}$ – 1000°C). The matrix and ceramic coating phases are essentially isotropic while the fiber is highly orthotropic . . . that is, the fiber gets fatter while its length remains relatively unchanged. (Note: The term 'amorphous' is not exactly correct when describing carbon forms. It is used here with the understanding that these allotropes actually consist of 2-D graphene planes or layers with no 'z' indexing or formal 'd' links and so they are not truly amorphous in a 3-D sense . . . they are highly ordered 2-D structures with very little 3-D organization).

Thus, for the RCC composite substrate, through-the-thickness expansion/contractions can be substantial, with contributions from both the carbon matrix and transverse fiber CTE. The magnitude and direction of these movements are somewhat compatible with that of the ceramic phase. In-plane CTE is dominated by longitudinal fiber movements, which are very small, but . . . the effects of transverse fiber movements along the cross-ply direction will tend to compliment the in-plane longitudinal CTE of the substrate, possibly raising it a point or two. Matrix microcracks are probably influenced by expansion/contraction differentials with both the longitudinal and transverse fiber CTEs. Finally, the ceramic coating phase heavily interfaces the warp and fill fiber bundles and thus, the primary interface mismatch in the coated RCC system is between the isotropic SiC phase and the longitudinal (warp and fill) orientations of the reinforcement with a median coating-to-substrate differential ratio of about 2.5-3.

Scenario 3: Differential CTE interactions between the SiC coating and the RCC substrate have been the subject of many studies and analysis over the years. Most recently, coating-to-substrate interface mismatch in flat, coated RCC samples has been well characterized by Vaughn, Walker and Koenig in terms of craze crack behavior and the concept of 'Stress-Free Temperature' (SFT). This excellent study reveals some very interesting and critical information pertaining to conditions at the SiC-C/C interface and craze crack closure over a wide temperature range in non-curved regions. It has been difficult for this and other recent studies to confirm an approximate value for the RCC SFT, whose uncertainty is now projected to lie somewhere between 525° and 1707°F. A value of 1350° is currently being used for on-going root cause analysis studies. As noted in Vaughn's report, the expected value is dependent on coating thickness. However, contributions to the actual SFT may also come from variations in regional contours, geometrical factors, mold side to bag side differences and location to location variations . . . and it may even decrease over the service life of the product.

Perhaps it would be helpful here to reiterate that differential coating-to-substrate interface CTE is not the only source of residual stresses in the RCC system. In general, even for the simpler non-coated laminated fiber-reinforced composite systems comprised of multiple phases (constituents), several levels of internal stresses are almost always present, including those at the constituent level (due to CTE differences, for instance) . . . and at the lamina or ply level because of differing ply orientations and the anisotropy of specific lamina properties. At the panel level, residual forces and moments are also expected due to built-in manufacturing stresses, constraints imposed by the tooling and the material's resistance to changes in curvature. Some of the factors specific to RCC have already been described.

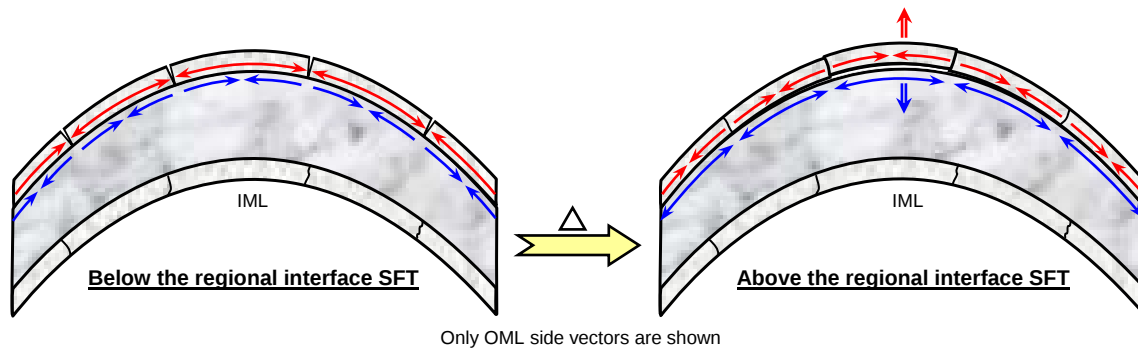
One of the consequences of ignoring or not accounting for all of the residual stresses in a system is a misinterpretation of the material's toughness properties . . . measured toughness values will tend to reflect apparent values rather than the true toughness. It goes without saying, residual stresses, whether they be thermal or mechanical in nature, lower the true toughness and strength characteristics of a material. It is interesting to note that any given LESS/RCC panel can be described as a complex-shaped, ceramic-converted, charred polymer matrix-densified, hand-laminated 2-D carbon fiber-reinforced composite system . . . and a complete stress picture may not be fully realized based on the premise that the material can simply be heated to a singlet state of net zero stress at some parametrically-defined SFT. A more inclusive approach should also recognize all the other stress contributions, such as the purely mechanical (temperature-independent) residual stresses and particularly, the critical geometrical factors which can influence the behavior of delamination/fracture events along curved, non-flat contours (the type of contours relevant to the RCC study). The shape of the substrate can have a profound influence on both the initiation and growth of interfacial fractures. Perhaps the SFT definition for RCC could be modified just for this paper, and identified as the 'coating-to-substrate interface SFT', or for short . . . the 'interface SFT'.

Now, reiterating and then expanding upon Vaughn's report . . . During the original coating process, the anisotropic (orthotropic) substrate is heated to high temperature as a binary inorganic carbon body where the outer layers are chemically (and physically) transformed into a new material which assumes the full identity and properties of an isotropic ceramic monolith as it passively cools down. On the average, the ceramic phase contracts 2-3 times more than the substrate phase (that is, relative to the longitudinally oriented warp and fill fiber bundle directions), but movement of the ceramic interface is restrained by its strong attachment (fusion) with the substrate. As a result, the contracting ceramic phase subjects the substrate interface to in-plane compressive stresses while the ceramic interface itself becomes diametrically loaded under tension. These conditions cause the coating-to-substrate (bimaterial) interface to experience in-plane shear forces. Along flat acreage areas, the interface is dominated by Mode II (shear) forces since the angle of loading is exclusively *in-plane*.

For the coated RCC system, there is a differential thermal (CTE) mismatch *and* an elastic (modulus) mismatch, both of which are substantial. While moduli generally decrease with temperature, strengths of the carbon fiber and SiC phase both increase upon heating. Generally, the ceramic monolith is about ten times stiffer than the composite substrate . . . and while the ceramic phase is quite high in compressive strength, its tensile strength is rather low, reflective of most ceramics. As a result of the thermal mismatch, the elastic mismatch begins to dominate the contraction process by the formation of through-the-thickness coating fractures, or craze cracks, which permit the release of tensile energy through the ceramic phase. As Vaughn has elucidated, this energy-releasing process likely proceeds through several steps or levels of crack development as the product gradually cools to ambient. However, not all the interface stresses are relieved during this multi-step cool down process. The interface remains under stress at the end of the production process while cracks continue to develop and evolve as panels are thermally cycled throughout their service life. When freshly manufactured product is heated back up, crack gaps begin to close, interface stresses decrease and at some point, a practical *interface* SFT may be reached (an interface SFT pertaining to fresh product).

Above the interface SFT, the stress situation is reversed. During heating, the ceramic phase expands more than the substrate (that is, more than the longitudinally oriented fiber bundles), and when the craze cracks close up, the coating interface goes into compression while tensile stresses are imposed along the substrate interface. Again, this subjects the bimaterial interface to in-plane shear (Mode II) forces . . . in flat areas. The compressive strength of the ceramic is very high but so is the longitudinal tensile strength of the substrate. Even though the craze cracks may be butted together under in-plane compression, they represent potential bifurcation points with the remote possibility that the angle of loading could shift, altering mode mixity and introducing out-of-plane (Mode I) forces into the interface region. Certain interface defects or substrate surface morphological imperfections could also lead to bifurcation. However, buckling-driven interface separations are extremely rare within flat areas of RCC. The typical response is generally a slight textural effect imparted by the craze crack patterns.

In contours and curved regions, the situation is substantially different and geometrical factors come into play which impact the system similar to a defect. The most relevant geometrical factors are direct functions of the various radii defining the specific contour shapes which may be ellipsoid-like or curved cylindrical sections such as the RCC joggle sections of interest. Geometrical factors become increasingly significant as the contours become more complex and sharper (they are inversely related to the regional radii and coating thicknesses). In a joggle section, the apex itself serves as a geometrical defect which can introduce out-of-plane forces into the bimaterial interfacial region. Above the regional interface SFT, inward/IML-directed out-of-plane tensile components along the substrate interface will try to resist the outward compression components along the coating interface, changing the mixity to Mode I-dominated stresses directly along the point or length of the apex . . .

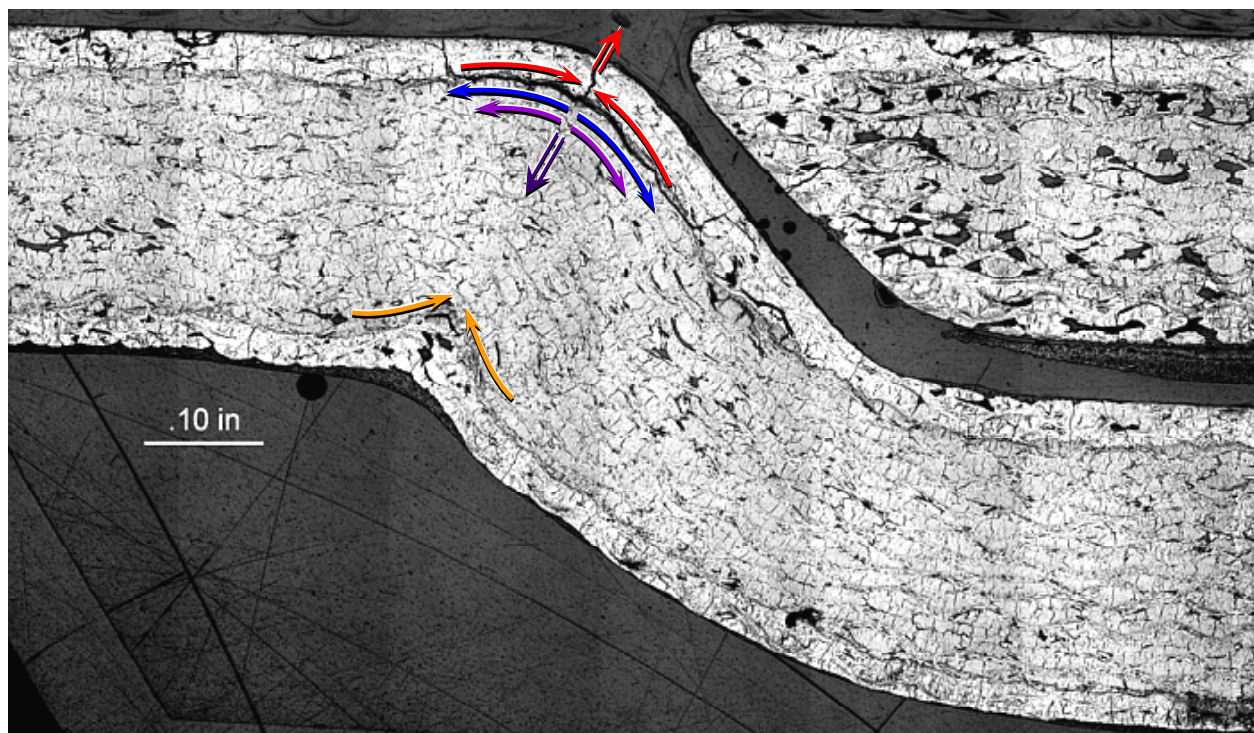


On the substrate side, the effect will combine with the pre-existing bending stresses incorporated during the composite molding process (Scenario 1). During a separation event, regional craze cracks along the contour could act as defects, possibly allowing segments (or islands) of the coating to shift slightly, facilitating a pre-buckling effect along the radial interface. A buckling-driven fracture would likely originate very near the apex point as a Mode I separation while the crack progressed outward on either side of the apex as Mode II-augmented fracture fronts leaving unloaded interfaces behind. Regardless of whether a separation actually materializes or not, it should be realized that the very apex is subjected to out-of-plane forces unlike any of the surrounding acreage areas due to the associated geometrical factors.

In flat regions, a critical stress level for planar buckling or delamination must be exceeded before deflection can occur. Prior to the formation of any out-of-plane components, these cases are characterized by Mode II (ILS) stresses in which the geometrical factors are zero, the loading angle is zero (in-plane) and the energy release rate is essentially zero . . . until an interface defect or bifurcation point is encountered in which the mode mixity changes. However, along contoured interfaces defined by radii, Mode I (ILT) components become prominent in accordance with phase angle changes and increases in energy dissipation rate, which makes curved regions more prone to buckling-driven delaminations. Also, along both flat and contoured regions, outer warp and fill fiber bundles become stress concentration points from the original coating process, so craze cracks will tend to form and develop along many of these ridges generating the familiar checkered pattern associated with the crazing effect.

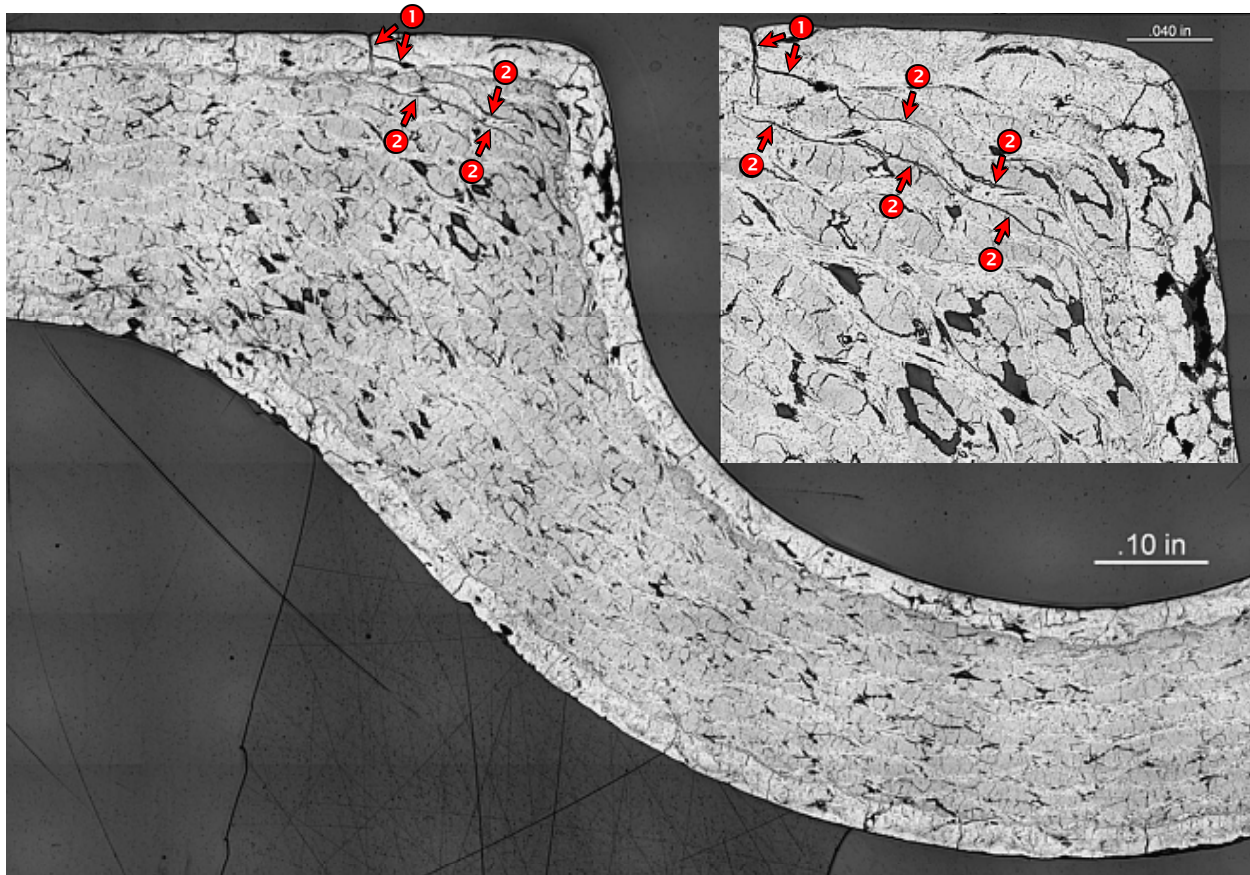
Mode I dominance at the apex can also be attributed to the large elastic mismatch between the ceramic phase and the composite substrate, and is probably a factor above and below the interface SFT. Because the modulus (stiffness) of the coating is so much greater than that of the substrate, thermal excursions can increase interface stresses to the point where the more flexible phase tries to separate from the stiffer phase. While both thermal and elastic mismatches decrease with increasing distance from the interface, thermal mismatch is longer range, so elastic mismatch has its greatest effect near the interface. For convex geometries (such as the joggle substrate OML), buckling-driven separations are uniquely possible since only small levels of residual stress can drastically change the loading angle, promoting out-of-plane micro-deflections. On the concave side of the joggle section (the substrate IML), constraining interface contact between the substrate and coating as well as wedging effects associated with the orientation of the craze cracks prevent deflections altogether.

As a result of the ceramic conversion process, the carbon fabric identity is destroyed and all as-molded interlaminar stresses vanish as the region is transformed into a fused monolithic SiC phase. However, built-in residual stresses in the *unaltered* substrate remain. The unconverted substrate is never completely stress-free and retains the original as-molded stresses. These are probably most intense along the first couple of unconverted plies directly interfacing the transition zone (the plies are where most of the separation/fractures seem to occur). The coating phase is hard, stiff and brittle, while the laminated interface immediately on the substrate side of the transition zone is vulnerable to the powerful geometrical factors as it is already laden with weak planes. The following cross-sectional image illustrates a possible situation in which both Scenarios 1 and 3 are active *above the regional interface SFT* . . .



- ➡ In-plane compressive forces generated along the coating interface as a result of the CTE/modulus bimaterial mismatch relative to the geometry of the contour. Present only when but every time the section is heated above the SFT value specific to this particular regional interface. Stress magnitudes are thus temperature-dependent.
- ➡ Diametric in-plane tensile forces generated along the substrate interface due to the CTE/modulus bimaterial mismatch relative to the geometry of the contour. Present only when but every time the section is heated above the regional interface SFT specific to this contour. Stress magnitudes are thus temperature-dependent.
- ➡ In-plane tensile forces generated along OML-side FPS ply surfaces during the initial substrate molding process as a result of the material's interaction or resistance to the convex OML contour imparted by the tooling or shape geometry. Since these are exclusively mechanical stresses, their magnitude is completely independent of temperature.
- ➡ In-plane compressive forces along IML-side WPS ply surfaces generated during the initial substrate molding process as a result of the material's interaction with the decreasing concave IML radius. Facilitates loose ply nesting (high porosity, low density) and convolutions/distortions. The magnitude is completely independent of temperature.
- ➡ Unbalanced resultant of the combined bimaterial interface and substrate stresses illustrating likely Mode I forces responsible for an apex-centered interface fracture and substrate delamination adjacent to the transition zone. (Note: The separation gap height depicted in the above cross-section is indicative of a relaxed gap after cooling to ambient . . . the actual gap height at peak temperature is unknown).

If contributions from Scenario 2 become significant along the apex (unusually narrow gradient transition zones), the situation can only be exacerbated. Possible implications are that Scenario 1 dominated situations would tend to favor fractures within the substrate lamina (delaminations), and the effects of Scenario 2 will tend to focus along the bimaterial interface (or transition zone), while Scenario 3 can aggravate either scenario. Of course, contributions from Scenario 3 require that the product be subjected to one or more temperature excursions above the regional interface SFT, which could happen in the field or conceivably during post-coating operations. It should be emphasized however, it is not just the thermal CTE difference that is responsible for fractures, separations or even craze cracks . . . but the substantial elastic mismatch between the two phases (indeed, if the elastic properties of the ceramic phase could somehow be improved, craze cracks might never form). In extreme cases, due just to the modulus mismatch alone, Scenario 1 could feasibly generate enough Mode I stress to initiate an apex-centered separation. For certain contours, it is also possible that these as-molded residual substrate stresses could potentially overwhelm other stress contributions enough to instigate, not an interface separation, but a substrate delamination several plies away from the primary coating interface. Fractures of this type have been seen in cross-sectional samples examined in years past. For the moment, consider the more current image below which is one of the cross-sectioned micrographs of samples removed from the 8R *lock side* joggle . . .

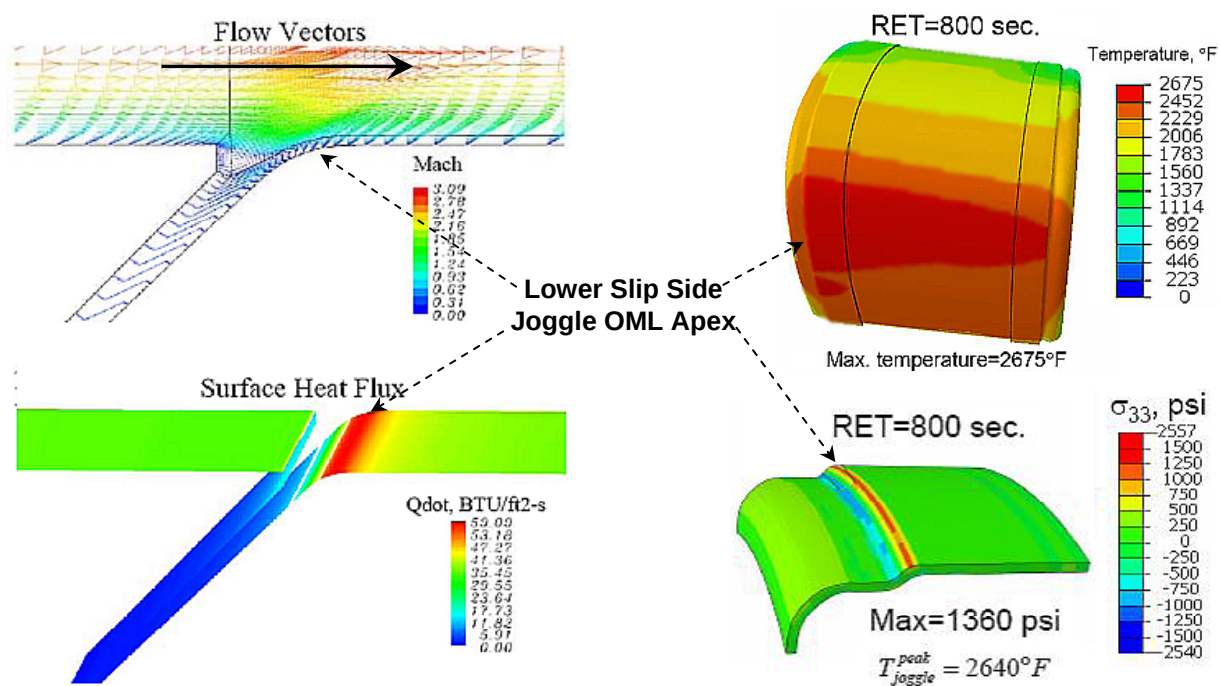


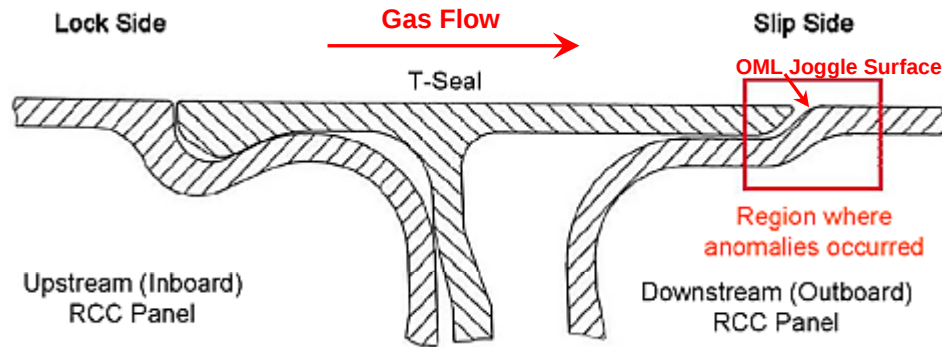
While a multitude of slip side joggle sections have been examined over the last year, panel 8R is the only known lock-side evaluation that has been made available for this particular study. It might be interesting and informative to examine additional lock-side cross-sections from other panels. Obviously, the OML lock-side radius is notably sharper than that on the OML slip-side and this might lead to the expectation that a much higher propensity exists for lock side delaminations. During field service however, air flow and heat flux distributions across slip side joggle regions may be several times greater than those across the lock side.

During prepreg lay-up of slip-side joggle sections, all 22 plies are laid continuously across the contour apex extending several inches on either side (there are no butt splices, overlaps, staggered plies or filler strips along the apex normal). However, during lock-side lay-up procedures, after about 5 or 6 plies have been laid across the contour, a system of graduating-width prepreg filler strips is tapered and strategically positioned along the apex centerline, one piece at a time. These embedded filler plies help to alleviate in-plane compressive stresses which influence the formation of IML fabric distortions but most importantly, they facilitate the concentration of molding pressure into the apex, thus helping to mitigate far side OML out-of-plane stresses which might otherwise become more problematic (not to be confused with the bleeder canvas strips discussed earlier . . . while both provide similar effects in terms of pressure localization along the apex, the prepreg filler strips are permanently molded in with the composite while the canvas strips are removed with the bagging materials after cure).

Also noted in the previous image are: ❶ Monolithic ceramic fractures . . . these and all craze cracks propagate directly through the ceramic phase unperturbed by fiber textures and former fiber-matrix boundaries. They are guided primarily by: (a) substrate weaknesses near the interface, (b) width of the transition (gradient) zone, and (c) density/porosity variations within the ceramic phase . . . these factors influence the formation of diagonal cracks and branching, but most importantly, along contours and radii, they can interact *directionally* with substrate interlaminar weaknesses connecting craze cracks with substrate delaminations as shown; ❷ Classical substrate delaminations . . . these occur along fiber-to-matrix interfaces and are reflective of pre-existing weak planes, laminate level and panel level residual stresses including some of those already covered.

One question that has been difficult to answer is why the fear of spallation is most heavily attributed to slip side joggle sections rather than the lock side. There have been several thermal and CFD models introduced during the investigation strongly indicating that the lower slip side joggle apex is a particular hot spot that bears the brunt of hot gas flow impingement. Illustrative results from some of those models are presented below . . .





The lower slip side joggle section is the region where all the separations of concern have occurred and these models indicate that it is wide open to the hot gas flow with localized heating concentrated directly along the apex length. On the other hand, the corresponding lock side joggle apex on the adjacent panel is not only cooler and oriented opposite to the flow, but may actually be shielded from the heat by its close association and intimate proximity with the T-Seal. During re-entry, as the slip side opens up and exposes the joggle OML apex surface, the lock side closes up and remains locked in place. Relative to the slip side, the lock side apex is not subjected to the same air flow vectors or localized heating and may essentially be protected by the interlocking T-Seal structure. The accuracy of these models to effectively characterize the two joggle sections is not fully known but it is convincingly apparent that the heating and impingement profiles are significantly different for the two sections with the implication that the slip side is several times more vulnerable to these degradative effects than the lock side.

Thermomechanical cycling and testing of RCC joggle samples over the past year have established that repetitive exposures to simulated re-entry flight conditions are able to both initiate separations and exacerbate pre-existing ones (both with correspondingly drastic increases in IR line scan indication). Rodriguez's recent Arc Jet Test Summary covered results from cyclic testing designed to simulate re-entry conditions as best as possible and has demonstrated both initiation and propagation of cracks in all samples tested with drastic increases in separation gap height in most samples after only one cycle. One of the interesting observations noted from this testing included 'the development of coating interface separations in the absence of detectable underlying defects'.

With all this information, a plausible failure mechanism for recurring delaminations in the lower OML joggle regions can be envisioned. Firstly, it is surmised that permanent residual bending stresses associated with weakened interlaminar interactions (weak planes) are incorporated into contoured sections, and concentrated along the apex, as a natural result of the material's resistance to the various radii and tooling contours (Scenario 1). These stresses may be considered to originate at the *ply level* and are completely independent of temperature applications, excursions or thermal history.

After panels are finally coated and cooled to room temperature, it is suspected that coating transition/gradient conversion zones (not just coating thickness) vary from region to region, particularly along contoured interfaces as opposed to flat acreage areas (Scenario 2). This effect acts at the *constituent level* and may result in minimal (narrow) conversion zones which subdue the benefits of gradual phase transition from ceramic coating to composite substrate. The condition is not necessarily associated with any residual stresses nor can it be altered by subsequent heat applications, thus it is also temperature-independent

When panels are subjected to high temperature excursions above the relevant interface SFT, such as from multiple re-entry events in the field (or possibly from sealant, reliability or other post-coat/pre-flight operations), it is believed that the resulting compressive effects within the coating phase have the potential to lead to buckling-driven substrate delaminations or sub-coating interface separations very near the transition zone (Scenario 3). While this condition originates at the constituent level, perhaps it is ultimately manifested at the *panel level*. It is the combined result of the CTE interface differential and bulk elastic mismatch between the two phases which likely initiates and/or propagates during the temperature up-ramp, reaching the maximum stress level (and gap height) at peak temperature.

Each and every RCC panel is hand-crafted and unique. Thus, the level and nature of any of these conditions can be influenced by specific manufacturing practices or inconsistencies. Due to material, equipment, manpower and skill variations, no two panels are identical. Likewise, no two joggle sections are the same either. Some may contain higher levels of defects and residual stresses than others. Additionally, there may be other stresses inherent within the coated RCC system which have not been taken into account here. While Scenario 1 by itself could conceivably result in substrate delamination (in extreme cases), a situation which also includes even a small contribution from Scenario 2 or 3 could heighten the potential for fracture initiation, resulting in buckling-driven separations along the apex of tendentious contoured sections. This implies a remote possibility that separations of unknown gap height could conceivably exist intermittently in certain virgin products on the factory floor or at the OPF.

However, it is believed that the repeated exposure of these vulnerable regions to the conditions of atmospheric re-entry provides a catalyst for both initiation and propagation of fractures (as the evidence has clearly shown). While separation gaps of increasing height eventually become detectable via NDE procedures, pre-existing separations of some unknown minimum threshold are not detectable (nondestructively) and most importantly, current state-of-the-art NDE techniques are completely oblivious to the presence of weak planes, residual stresses and substandard interlaminar interactions within composite materials (unfortunately). Disregarding any strong indications or confirmation of recent factory discrepancies pertaining to these defects, it is proposed that the final factor necessary for fractures to occur *in the field*, is repetitive or gradual mechanical degradation due to the thermal cycling effects imposed on the panels during their normal service lives, or in short . . . thermomechanical fatigue.

Thus, the contention is that the thermomechanical factor will exacerbate a pre-existing separation or even initiate a separation in a region containing weak planes whose interlaminar strength or toughness is below some critical threshold. Due to the resilient and unique nature of the conversion coating approach for these forms of carbon-carbon, delamination/separations which may already be present in a panel before the Shuttle leaves the ground do not necessarily lead to coating spallation (as flight history and simulated mission cycling tests have clearly shown). It is believed that spallation is only one potentially catastrophic event that could ultimately occur to regions containing pre-existing fractures, propagating delaminations or even weakened interlaminar strengths, particularly in apex regions where the actions of interfacial buckling fatigue could eventually liberate a small piece of the coating phase. However, the essence of this report is the root cause and consequences of sub-coating fractures since they are believed to be the precursor to subsequent spallation and are considered to be the primary culprit that differentiates a good panel from a bad one, regardless of what the ultimate demise of a given defect may turn out to be.

It is interesting to note a few of the results, conclusions and events that have transpired over the last year or two pertaining to RCC spallation and the activities of the Root Cause effort.

- (1) During the STS-120 FRR (August, 2007), the following results were presented: (a) Spallation events occurred on two panels after flight and on one nose cap during factory processing (STS-102, STS-103 and OV-105 respectively); (b) Room temperature IR Thermography (NDE) indications for panel 8R changed from 0.15-0.2 to above 0.6 (Wf) before and after STS-114 (that is, > 0.4 in one flight) . . . however, the panel did not spall.
- (2) None of the testing programs conducted over the last year have been able to produce (or reproduce) an actual or obvious spalling event.
- (3) Microscopy of cross-sectioned joggle regions have shown that, in general, IR indications in the single digits do not appear contain *visible* separations while those with indications equal to or greater than 0.1 do, in fact, contain visibly detectable fractures or delaminations.
- (4) Microscopy and CT scans have shown that Thermography can detect separation gap heights as low as ~1 mil spacing.
- (5) The overwhelming majority of pre- and post- flight indications show little change in Winfree IR measurements (taken at or near room temperature), even after several missions.
- (6) Panel 8R data suggests a Thermography indication greater than 0.2 is an excellent indicator of subsurface delamination.
- (7) Panel 12R, an unused panel with no flight history, gave an indication of 0.13 (Nov. 2007). More recent factory data indicates an intermittent history of other panels with > 0.1 indications.
- (8) Line scan indications are very repeatable (within 0.05), given consistent testing conditions. This implies a per-scan variability of ± 0.05 for the current IR Thermography method in use.
- (9) The professional assessment of the RCC NDE experts (Dr. Bill Winfree and his team) has been documented . . . readings as low as 0.1 most likely represent sub-coating separations.

Thus, the overwhelming majority of pre-to-post flight IR data indications appear to show little change in Winfree value. However, some of the results developed during the last few months have indicated that *outliers* to this trend may be more substantial than conventional expectations seem to indicate. For example, Rodriguez's Arc Jet Test Summary, which evaluated seven samples from two field panels, contained three specimens that exhibited quite unusual results. One sample changed from 0.02 to 0.67 after only one cycle (defect initiation). Another changed from 0.26 to 0.82 after one cycle and then to 0.95 after three cycles, while the third changed from 0.32 to 0.49 after one cycle and then to 1.3 after three cycles (both defect propagation). All three of these samples exhibited drastic changes after only one cycle. A fourth sample, which was extracted directly adjacent to one of the three samples above, required six cycles to change from a 0.11 to 0.36 (only moderate change after several cycles).

Both of these panels had been through multiple repair and/or refurbishment procedures during their service life. Factors such as repair and refurbishment however, are likely to exacerbate almost any kind of pre-existing local damage in RCC panels. Redistribution of liquid-to-solid glass/silicate residues or wedging of SiC particles into temporarily opened cracks could certainly facilitate the intensification of potential fractures already under the influence of weak planes or localized residual stresses. A similar inference could be made regarding the detrimental effects of trapped volatiles incorporated during the refurb process. However, attempts to tie these processes directly to the root cause of fracture initiation or the on-going recurrence of joggle delamination/separations has not been entirely consistent. It is definitely possible that either or both refurb and thermal cycling could accelerate defect development or aggravate conditions of inferiority already established in panel regions beforehand.

From another perspective, a multitude of mechanical testing conducted on RCC and ACC over the years (as well as many other composite systems), has documented one important aspect time and time again . . . composite fractures (especially interlaminar fractures) do not always progress or propagate consistently, or follow prediction models according to expectations. Unlike isotropic metals or lamellar metallic alloys, *fracture growth in laminated composite structures is not 100% predictable*. This is especially true for ceramic converted / carbon matrix / carbon fiber reinforced composites which are known to deviate frequently from traditional PMC models. While the majority of mechanical test sample failure processes seem to take place consistently and predictably up until the ultimate stress point, some 5 to 10% of the tests have always failed prematurely and unexpectedly for no apparent reason.

Analogous to the discussion above, there have been an untold number of cases when two composite samples, extracted side-by-side from the mother panel, gave drastically different results, with one following prediction models quite well and the other failing catastrophically at a fraction of the expected maximum stress level. While the exact causes for the majority of these precocious failures often go unconfirmed, a common factor which seems to be prevalent in many cases is the presence of localized weak planes or weakened interlaminar interactions.

Poor fiber-to-matrix bonding, substandard ply-to-ply nesting, residual stresses, trapped volatiles and excessive porosity (to name a few) have all been attributed to weak interlaminar interactions and eventually to delaminations at some point or another using destructive test methods such as ILS and ILT. Throughout the industry and history of laminated composites, it has been shown many times that the precursor to ill-fated delaminations is often the presence or precondition of weak planes, and this also been proven for both RCC and ACC. So in a sense, the root cause objective could be further defined to include the elucidation and identification of sources or causes leading to weak interlaminar interactions in the regions of interest.

However, current NDE methods cannot detect weak planes (including Thermography). While new and innovative techniques will eventually be developed in the future, there is no NDE method yet available which can actually detect weak planes nor the latent propensity for delaminations *before they occur* (the inventor of such a technique would become a billionaire and the composites industry would be changed overnight). At best, current NDE tools can only indicate a fracture, separation or delamination that is well beyond the initiation stage and has now propagated (or increased in gap height) to the point where it has become physically detectable by the attenuation of energy waves passing through the material. From a structural perspective, a composite article that is known to contain one of these kinds of defects should be pulled out of service (or production). In essence, it does not matter if the separation gap height is one micron or 20 mils. An interfacial debond, delamination or areal separation, in and of itself, is a potentially catastrophic defect . . . a composite fracture just waiting for the right force or series of forces to finish off the job by separating the two interfaces into discrete bodies.

The current fly/no-fly methodology seems to be based on the philosophy that it is OK to fly a cracked panel on a manned Shuttle mission . . . as long as the crack is not too big. The premise is further extended to say that it is OK to repeatedly fly the same cracked panel on consecutive missions until the crack size gradually surpasses some arbitrary limit based essentially on flight-to-flight trending and group consensus. The following two axioms are not necessarily recommended but are given here to provide some thought-provocative insight from a radical or hard-line perspective . . .

(1) Never fly a panel containing a known fracture or delam on a *manned* Shuttle mission, regardless of the suspected gap height. It may or may not be acceptable to use such defects on a UAV, an automobile or a ground-based structure, but not on a crewed aerospace vehicle. This may not be a popular idea in terms of cost, scheduling or convenience, but given the unpredictable nature of fracture initiation and propagation, it may be folly to risk human lives on an approach that is known to have a limited and controversial degree of certainty.

(2) Do not use NDE as a means for assigning 'degree of risk' or placing a value on human flight worthiness with regards to manned flight safety. When it comes to the safety aspects of a delaminated or fractured composite structure, there is no gray area . . . there is only black and white. NDE tools can reveal and ascertain bad panels almost 100% of the time, but 'good' panels can only be inferred . . . with the hope that a suspect does not turn out to be an outlier.

At this point, there does not seem to be an abundance of convincing knowledge, at least which has been made readily available, that factory production articles are currently experiencing a trend of such defects. However, if factory panels are showing room temperature indications greater than 0.1-0.15 on an irregular basis, then there is a serious concern and it would be crucial to examine some of these further, perhaps extract a few cross-sectional samples for visual analysis. Examination of an occasional panel with ≥ 0.1 readings may turn out to be well worth the sacrifice. In a worse case scenario, it would not be the first time the LESS program has had to address wide spread RCC manufacturing-induced delaminations.

Since most of the other team members have already weighed-in on the matter, an opinion and recommendation will be given here as well. Firstly, an IR value of $0.05 < x < 0.1$ should be recognized for what it most likely is . . . a substrate delamination, coating interface fracture or sub-coating separation defect of some sort or another within the material. Gap heights at elevated temperatures, particularly peak temperatures when regional stress levels are at their highest, are almost certainly greater than their room temperature values. The source or cause of the defect is not inferred by the measurement, but one attribute can be absolutely surmised . . . the anomaly is well beyond the 'weak planes' stage and likely represents a defect that is already in the process of expanding in area and/or height. After all, the NDE professionals have practically insured us that 0.1 is a separation. Then, it comes to the question of whether or not it is OK to fly a panel that almost certainly has a delam/fracture in it, regardless of how advanced the separation may or may not be in size or shape. The opinion is also put forth here that it is unacceptable to fly critical TPS hardware with known defects of this nature on the very leading edges of a re-entry spacecraft carrying human life.

For decades, the composites industry has embarked on the noble challenge of enhancing and bolstering interlaminar properties and trying to improve ILT/ILS strengths in order make composite systems better, stronger and more acceptable for other wide-reaching applications. At the very least, our efforts have been aimed at the anticipated elimination or vast reduction in weak interlaminar properties. It seems ironic that we now find ourselves at a point of trying to justify the acceptance and presence of these kinds of defects within usable hardware for the sake of expediency. Better wisdom would mandate that an absolute maximum IR level of 0.1 be the pass/fail limit for any RCC panel . . . period. However, the value of 0.15 may be deemed admissible in concordance with other stakeholders. The logic behind these decisions should preclude the tendency to continue raising the bar from 0.2 to 0.3 to 0.4 and beyond as though the threshold were indeterminate. The 0.15 limit is not suggested because it is considered to be less severe than those at 0.2 and above . . . the mere presence of a defect should be the primary deciding factor, not the severity of it. For the sake of flexibility, readings of 0.15 ($0.1 + 0.05$ in reverse logic) might be considered as the maximum threshold between a borderline defect and one which has the potential to unexpectedly lead to catastrophe.