

Survey of EDX Results on Anomalies in the HT-7 ACM Valve Failure

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This quick study was generated to provide some commentary in response to the unusually high levels of calcium detected during EDX analysis of globules found on the surface of the TZM Flow Distributor (FD) taken from the failed HT-7 ACM test valve, and to provide feedback regarding melting points for some of the internal valve constituents. Additionally, moderate levels of chlorine, oxygen and possibly aluminum and iron were also indicated. It may not be too surprising to see high atomic levels of silicon in these globules (given the fact that adjacent bodies in the valve are comprised of SiC), but the source of calcium is not fully obvious, particularly at a level comparable to silicon. These comments are not intended to support one possible contamination source over another, nor to draw conclusions concerning the failure mechanism but hopefully, provide some additional insight regarding potential sources for the extraordinarily high level of calcium (and chlorine) indicated in this particular analysis. A sample EDX scan for one of the globules found on the TZM surface is given in Figure 1.

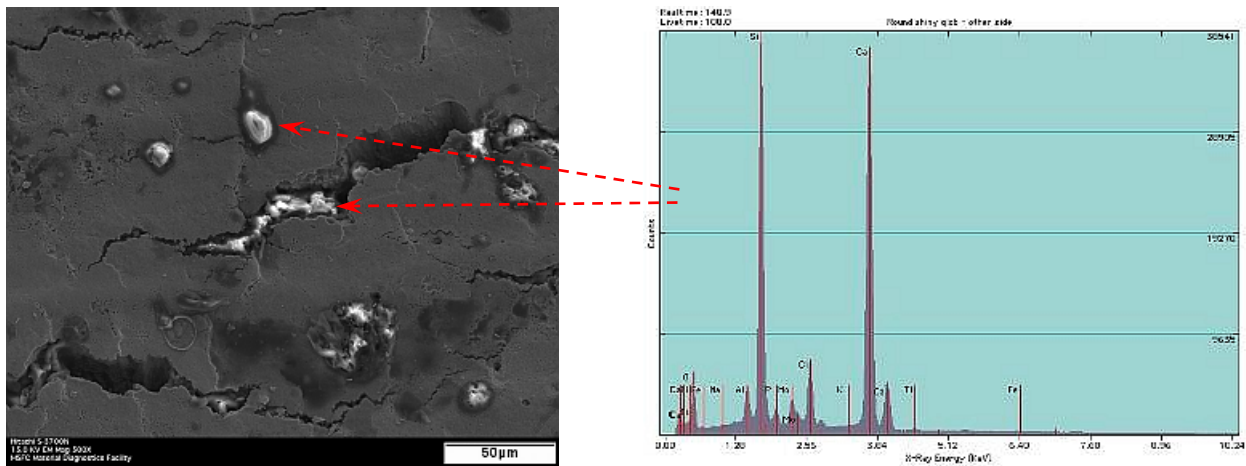


Figure 1. SEM microphotograph and corresponding EDX composition analysis of a globule on the surface of the tested Flow Distributor for HT-7.

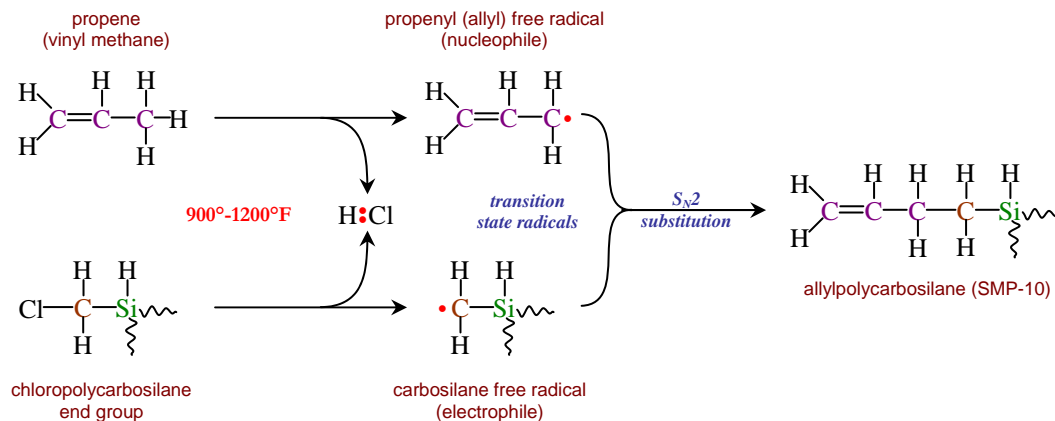
It has now been confirmed that Starfire Systems utilizes calcium compounds in the processing of SMP-10 preceramic polymer for the removal of water and halides in at least three different process steps. Although not much detail was provided and remnant levels of Ca on the order of ppm were suggested, it is known that multiple Ca sources are employed during synthesis and processing of the SMP-10 polymer, which could conceivably contribute to an overall level greater than ppm. It is also believed (by the author) that residual calcium compounds (or Ca atoms) can migrate or 'bloom' to the surface under high temperatures where they are capable of acting as reducing agents or alloying with other metals (such as Si). The SMP-10 polymer is extremely water-sensitive and extra efforts must be applied to ensure no/low water levels are achieved in the resinous product during synthesis and packaging at Starfire (likewise, the intermediary customer must minimize moisture absorption during process handling and end-product fabrications). Thus, calcium-laced materials and processes employed for the removal of water and chloride from the reaction/product system during polymer manufacturing are worth noting for the record.

- (1) Diatomaceous Earth compounds . . . Industrial grade DE is typically > 90% SiO₂ and contains a large variety of other elements at smaller levels. In common DE products, the secondary and tertiary constituents are often Ca (~ 1500ppm ≈ 0.15%) and Al (~1000ppm ≈ 0.10%). During SMP-10 processing, DE is used as a dehydrating agent (or filtering aid) for rough water removal from the virgin polymer intermediate.

(2) Reducing Agents . . . The SMP-10 polymer can be classified as an 'allyl carbo silane'. During the synthesis process, unsaturated allyl (or propenyl) groups are reacted with the Stage A SMP-10 precursor in which the allyl groups are chemically attached to accessible polymer branch ends along the virgin SMP-10 structure. During end-user processing (such as curing), these unsaturated groups induce thermoset crosslinking of the polymer which permits hardening of the resin prior to pyrolysis (< 2000°F pyrolysis converts the polymer into glassy/amorphous a-SiC). The exact chemistry involved during SMP-10 synthesis is Starfire proprietary however, it can be surmised that the original polymer is probably formed via a Grignard-type synthesis process using a chloroalkylsilane monomer to form a highly branched polymer structure. The resulting adduct consists of alternating (side-by-side) carbon and silicon atoms throughout the structure along with chlorine atoms at most of the branch ends (the intermediate is then a chlorocarbosilane).

In a subsequent step, the chlorine-laden product must undergo extensive reduction reactions in order to remove all the residual chlorine atoms from the virgin polymer. However, before application of any reducing agents, cure properties of the intermediate product are modified by the incorporation of these allyl groups (specifically, propene for the SMP-10 polymer). Now reaction of propene with the chlorocarbosilane macromolecule produces an allylchlorocarbosilane in which the allyl carbons^[1] undergo substitution with about 5%-10% of the chlorocarbon sites. Due to the highly branched nature of the SMP-10 structure, steric hindrance (structural shielding) is a primary factor responsible for limiting the number of sites available for substitution reactions. Particular aspects of this process were covered in a previous report, "Evaluation of C/C-SiC Composites for Small Motor Components" submitted by the author back in June of this year.

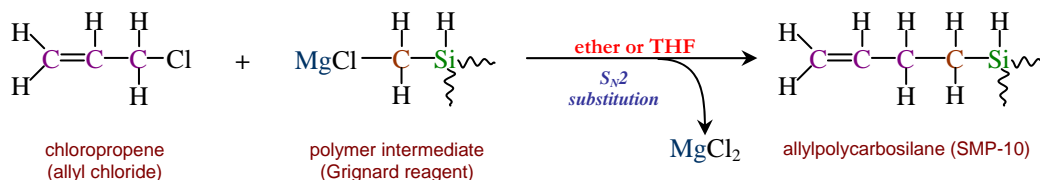
As a supplement to that discussion, consider a likely method employed by Starfire to attach propenyl groups onto carbosilane end-branches via free radical S_N2 substitution reactions with accessible chlorocarbon end groups along the polymer structure ($S_N2 = 2^{nd}$ order Nucleophilic Substitution). As propene gas is bubbled through the virgin SMP-10 polymer system at elevated temperature, HCl gas is generated when allylic carbons^[1] displace chlorine in the mother structure, accordingly . . .



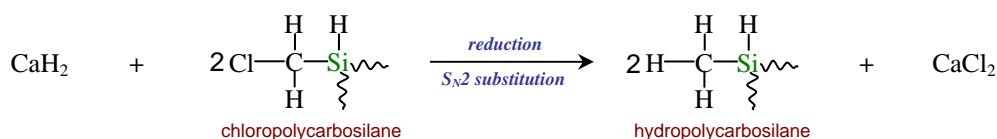
Here, propene and the chlorocarbosilane end-group dissociate into their respective free radicals where nucleophilic propenyl radicals instigate back-side attack of available (unhindered) electrophilic carbosilane radical end-groups. Chlorine functions as the 'leaving group' in the one step S_N2 process and the radicalized carbosilane end-groups easily terminate via reaction with local allyl radicals (again, the highly branched polymer structure limits S_N2 reaction availability). There is no confirmation however, that this is the particular scenario utilized by Starfire for rendering crosslink capability to the material.

[1] An allylic carbon is a carbon adjacent to a double bond. Propene (or vinyl methane) is the simplest allylic compound. Due to resonance, allyl compounds easily form very stable radicals (low bond dissociation energy) which accounts for their high reactivity towards substitution. However, ionic addition to the double bond is a competing reaction which must be minimized by careful selection of the reaction conditions utilized. As the nucleophilic propenyl radical is formed, bonding between all three carbon atoms is converted from sp^3 hybridization to sp^2 . In general, the allyl radical is a hybrid of two resonance structures where the π bond and the unpaired electron are delocalized across molecule allowing substitution to occur at either end-carbon.

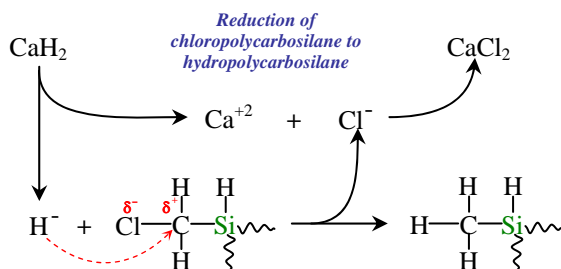
The other likely method that might be feasible for incorporation of allyl groups into the SMP-10 structure involves an extension of the original virgin polymer Grignard synthesis process where allylation is carried out prior to extraction of the Grignard organometallic reagent groups.



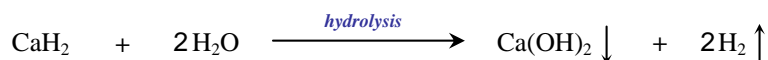
Here, the polymer adduct (the Grignard agent) is the nucleophile where propene is halogenated beforehand via allylic substitution to give the appropriate electrophile. Depending on its polarity and hydrogen activity, the particular solvent medium used in the process can have profound effects on the mixture of end-products and the dominance or balance of $\text{S}_\text{N}2$ vs. $\text{S}_\text{N}1$ reactivity. In any case, there are many end groups throughout the polymer structure containing residual chloride and possibly MgCl groups which must be extracted from the system. In accordance with information provided by Starfire, the reducing agent most likely utilized for removing bound residual chloride atoms from the system would be calcium hydride CaH_2 , and a likely reaction for reduction of the chlorocarbosilane could be represented by . . .



Here, the nucleophilic hydride (H^-) is formed opposite to the more electropositive calcium ion Ca^{+2} and behaves almost like a halogen or a hydroxyl group displacing chloride from the polymer, sort of like . . .



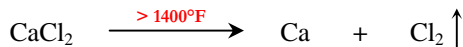
Now, all the CaCl_2 must be removed from the system as well as any residual reducing agent, and water is the most optimum washing agent available for this step. Since CaCl_2 is highly soluble in water and residual CaH_2 readily undergoes hydrolytic destruction, washing the intermediate product with water removes both CaCl_2 and residual CaH_2 in one step, the former simply by solvation and the latter via hydrolysis which expels hydrogen gas from the system while calcium hydroxide falls out of solution as given by . . .



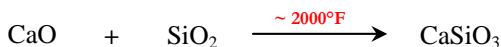
- (3) **Drying Agents . . .** Now the product must be dehydrated and treated to remove all the water from the system. While a series of steps and materials are likely used in this process, it is now known that at least one of these materials contains calcium. One of the most prevalent drying agents is CaCl_2 which has a very high affinity for water. In practice, the reaction product is often passed directly through a bed of anhydrous CaCl_2 particles which are quite hygroscopic and readily absorb water forming the corresponding hydrates (i.e. . . . $\text{CaCl}_2 \cdot x\text{H}_2\text{O}$). Obviously, it is conceivable that trace levels of both calcium and chlorine could be incorporated into the polymer adduct from this step.

Thus, these processing materials represent potential sources for both Ca and Cl, and collectively, they could contribute to levels higher than 'trace' quantities . . . but that does not mean that they are responsible for the results indicated in the EDX analysis for the globule given in Figure 1, nor are they necessarily associated with the failure mechanism for the HT-7. They are considered here only in efforts to explore potential sources for some of the contaminants detected in the post-test analysis

The peripheral phases of the C/C-SiC components in the ACM valve consist almost exclusively of glassy a-SiC. In an oxidizing environment, a thin layer of amorphous silica (a-SiO₂) will develop on these surfaces, and since both phases are amorphous, there will be a tendency for the a-SiO₂ to diffuse or dissolve into the a-SiC phase creating a composite mixture of SiC-SiO₂. When the temperature is increased, the a-SiC phase does not melt or soften but rather it hardens and condenses as it crystallizes and finally converts into its cubic β-SiC counterpart starting at around 2000°F. The silica phase begins melting around 3200°-3300° and becomes a viscous glassy liquid on the SiC surfaces (its melting point is slightly raised while the valve chamber is pressurized). But SiO₂ does not have to be in the liquid phase in order react chemically . . . SiO₂ becomes reactive well below its melting point, closer to its sintering temperature which starts around 1800°-1900°F. Reaction with water would give silicates, hydrates and hydroxides, most of which are opaque to white in appearance and which are not apparent in any of the analysis. However, residual CaCl₂ within the SiC matrix (if it is present) will begin to melt in the 1400°-1500°F range releasing elemental (reduced) calcium according to . . .



The solid calcium generated will itself melt around 1500°-1600°F, and molten calcium will tend to coalesce and start flowing outward toward the periphery (a process sometimes referred to as 'blooming') where it becomes oxidized (the resulting CaO or amorphous lime melts well above 4500°). However, sintering temperatures for SiO₂ begin around 1800°-1900°F where reactions with CaO also become possible, perhaps generating one of the oxide compounds/mixtures shown in Figure 2 (reactions between amorphous solids occurs more readily than with crystalline structures since no crystal bonds need to be broken). Considering the large number of possible stoichiometries, one could find a given composition for just about any temperature of interest. On the other hand, considering the limited source of calcium readily available, lower melting, silicon-dominant compositions are probably more likely. Perhaps, a relevant example could be represented by considering the simple calciosilica CaSiO₃ eutectic . . .



This amorphous oxide (sometimes identified as wollastonite) gives a balanced atomic ratio of Ca/Si as reflected (approximately) in the EDX scan (cristobalite and tridymite are allotropes of SiO₂). Note that CaSiO₃ will liquefy around 2800°-2900°F (under pressure this will be a little higher according to Simon's law) and increased levels of Ca (or CaO) are required for higher melting points.

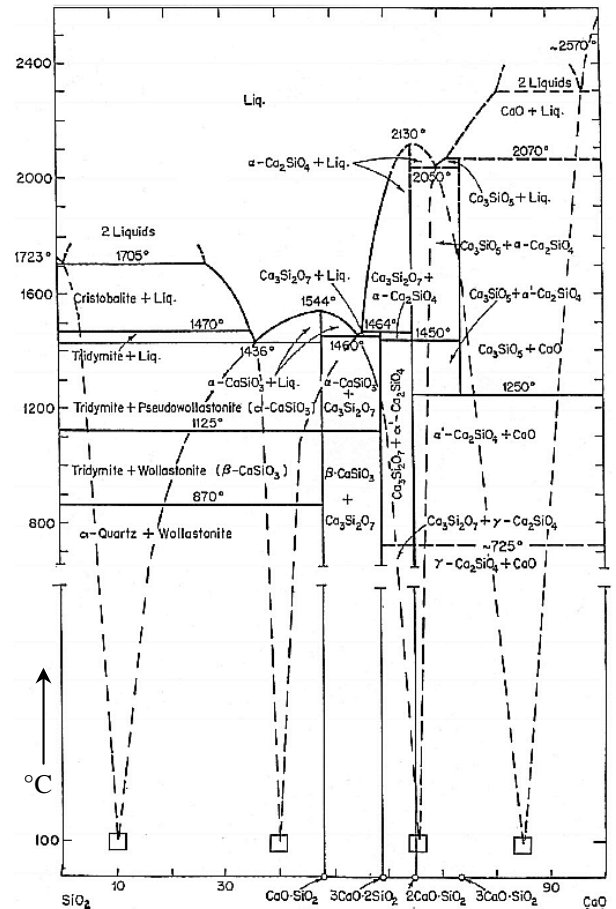


Figure 2. CaO-SiO₂ phase diagram showing the wide variety of CaO-SiO₂ compounds and mixtures possible as well as several deep eutectics. Taken from 'Science Direct', Frans J.M. Rietmeijer, Aurora Pun, Yuki Kimura, Joseph A. Nuth III

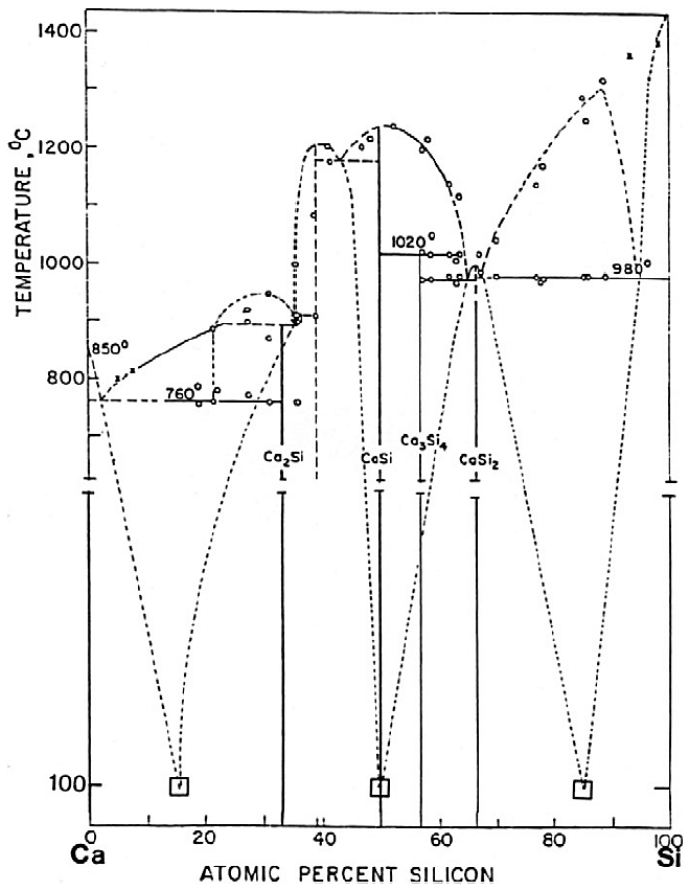
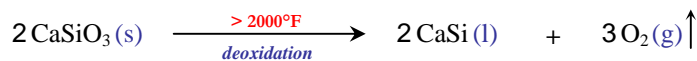


Figure 3. Ca-Si phase diagram showing the characteristic Ca-Si compounds and mixtures possible as well as a few deep eutectics. Taken from 'Science Direct', Frans J.M. Rietmeijer, Aurora Pun, Yuki Kimura, Joseph A. Nuth III

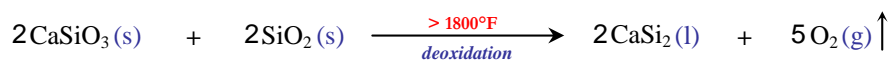
If the oxygen level in the EDX scan of Figure 1 was substantially higher, CaSiO_3 might be a feasible description of the dominate composition. However, even though EDX data is sometimes considered to be semi-quantitative, constituent levels in this scan imply an obvious lack of oxygen contribution in the apparent composition. Also, the globules seem to have more of a lustrous appearance characteristic of a metal, not an oxide. Thus, this would suggest that the globule composition is dominated by an intermetallic phase rather than an oxide. Perhaps this is a slightly oxidized Ca-Si alloy. Figure 3 gives the corresponding phase diagram for Ca-Si equilibrium compositions and note that the 1:1 CaSi alloy exhibits a deep eutectic which melts around 2200°-2400°F. The CaSi_2 eutectic should also be considered a candidate for one of the components in this composition. These compositions would imply that the globule in Figure 1 may have formed (or at least cooled down) within an environment that was oxygen-starved, perhaps in the form of a reducing or a *deoxidizing* environment.

The TP-H-3174B propellant used in the ACM motor utilizes a polymer (butadiene) as the primary fuel component (along with the customary ammonium perchlorate as oxidizer). Typical

oxidation products here would include CO_2 and H_2O along with lesser amounts of HCl (gas, not acid) and nitrogen (or ammonia, a reducing agent). While water vapor may provide oxidation power in certain reactions (via oxidative hydrolysis) and act as a micromedium for HCl acidification, HCl decomposes into its elemental gases around 2700°-2800°F producing Cl_2 and H_2 (another reducing agent). During late burning, near the end of the burn cycle or when the polymer momentarily became depleted, it is conceivable that the balance of redox components within the chamber atmosphere favored reduction (or deoxidation) over the action of available oxidation species. If calciosilica was formed as an early product on internal valve surfaces, subsequent loss of oxygen within the surface environment could have resulted in formation of the intermetallic . . .

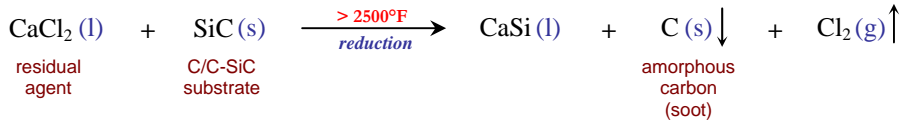


or . . .

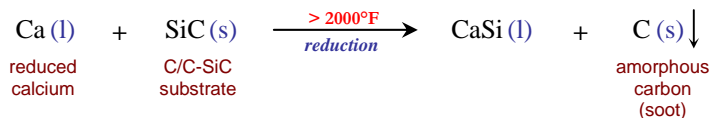


Note that, as with SiO_2 , CaSiO_3 does not have to be in the melted state in order to react or undergo solid phase deoxidation. Also note that under the appropriate conditions, both calcium silicide and the disilicide are themselves effective deoxidizing agents.

In a case involving the complete absence of oxygen or in localized pockets of depleted oxygen, reduced calcium or its precursor compounds could react directly with the SiC substrate to give the intermetallic . . .



or . . .



In closing, it is not believed that any of these species were in the gaseous state or participated in any form of CVD to give the products indicated in Figure1 (during motor operation, the valve cavity is not a stagnant CVD environment – once they vaporize, they're out of there). Rather, the CaSi alloy(s) probably behaved much like molten solder during the moderate to higher temperature stages of the burn cycle and then solidified, during cool down, on the surfaces that they were attracted to or forced to interact with (molten solder always flows from a cooler surface to a hotter one). Liquefied Ca-Si alloy could have been transferred to the hotter FD surface facilitated by the powerful jet flow. However, a meaningful mechanism cannot be elucidated here at this time.

Notes: In the C/C-SiC material system under study for the ACM valve, the matrix consists of three portions: (a) an amorphous carbonized pitch fraction (hardened mesophase) which is essentially a thick fiber coating since it is the first densification material deposited onto the pore walls of the substrate, (b) crystallized SiC (derived from SMP-10 polymer), and (c) amorphous/glassy SiC (also derived from SMP-10 polymer). Crystallized (cubic) SiC (or β -SiC) is formed when the densified substrate is subjected to temperatures greater than about 2000°-2200°F, otherwise, the SiC phase remains in the glassy phase. Since the last formal heat treat during the densification process is 2200°, some of the subterranean matrix phase consists of glassy SiC (or α -SiC). Most likely, the intent here is to functionally graduate from hard β -SiC near the core to soft α -SiC at the periphery, which may actually be manifested as a solid dispersion of β -SiC domains within in the α -SiC outer matrix phase. During the formal seal coating stage however, process temperatures are never taken over 1500°, so the outer regions of the matrix and the entire seal coat phase are 100% α -SiC. The high modulus carbonized PAN fiber comprising the reinforcement phase will behave much the same as other long range ordered carbon forms and graphites, which do not ordinarily exhibit melting points but sublime around 6500°-7000°F (however, under high pressures (greater than about 1500-2000psi), graphites may enter a liquid phase above 7000°F). Since the carbonized pitch matrix phase is a 'soft' carbon, it will easily graphitize at temps greater than about 4000°-4500°F and then follow the same path as the carbon fiber phase. SiC will tend convert into its alpha (hexagonal) form, α -SiC around 3500°-3600° and then decompose into carbon and a silicon-rich melt at temps greater than about 4500°F, but this will immediately volatilize (sublime). In some of these situations, the production of various carbon-silicon gaseous compounds is possible, including such species as Si₂C, SiC₂, Si₃C, etc... In an open system, SiC will simply sublime, but under higher pressures, sublimation can be deferred. Under only a couple of hundred psi, vaporization of either Si or C can be completely inhibited until about 6000°F. As long as the pressure is greater than the total vapor pressure for Si and C combined, volatilization will be prevented and their ratio should remain stoichiometric. In the ACM valve environment, liquification of SiC phases is probably nonexistent. Bear in mind however, exposed carbon, silicon and SiC will have a tendency to react with available O₂, H₂O or N₂ at elevated temperatures in the solid, liquid or gaseous states. Unprotected carbon forms will begin oxidation around 900°-1000°F, while the native/thermal oxide SiO₂ will form on the SiC surfaces, but this will begin to break down in the 2500°-3000° range above which crystalline SiC forms become vulnerable to oxidative degradation (at lower temperatures, α -SiC is even more susceptible to oxidation than its crystalline counterparts). Also bear in mind that neither C, SiC or SiO₂ need to be in the melt phase to sinter, react with each other or react with particular interface metals that may be present. Intermetallic silicides with alkaline earth or transition metals are well known.