High Temperature Lightweight Self-Healing Ceramic Composites for Aircraft Engine Applications

Project WBS Number: 694478.02.93.02.11.10.22.

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Purpose

The overall objective of this proposal is to develop a new class of high temperature, lightweight, self-healing, SiC fiber-reinforced ceramic composites. Two new proofs-of-concepts studies will be conducted on simple shapes under Phase I. First, Engineered Matrix Composites (EMCs) designed to match the coefficient of thermal expansion (CTE) of the SiC fiber will fabricated. Second, the matrix composition will be designed to convert any ingressed oxygen into low viscosity oxides or silicates, so that they can flow into the cracks due to capillary action and seal them thereby activating its self-healing properties.

Background

Nickel-based superalloys have been successfully used in aircraft engines as blades, combustor liners and vanes for several decades. However, designing these hot sections of gas turbine engines with lighter weight silicon carbide fiber-reinforced silicon carbide (SiC/SiC) ceramic matrix composites (CMCs) allows them to operate at higher temperatures and higher pressure ratios with reduced cooling air while leading to lower fuel burn and reduced CO_2 emissions. The use of reliable, high temperature, lightweight materials in the manufacture of aircraft engines is expected to result in lower fossil and bio-fuel consumption thereby leading to cost savings and lower carbon emissions due to air travel.

The present generation SiC/SiC CMCs possesses a SiC matrix, where the design stresses are limited by a low matrix cracking stress of about 138 MPa. Above this matrix cracking stress, these composites show poor durability because of oxygen ingression from the external surfaces through interconnected matrix cracks to the fiber/matrix interface, oxidation of the boron nitride interfacial coating and premature strength degradation of the reinforcing fibers. This puts severe constraints on the design of CMCs for highly stressed components, such as the high-pressure turbine blade.

These CMCs rely almost entirely on the SiC fibers to carry the load owing to the premature cracking of the matrix during loading. Thus, the high temperature usefulness of these CMCs falls well below their theoretical capabilities. Irrespective of the other manufacturing details, the final step of the melt infiltration (MI) fabrication of many CMCs generally involves infiltrating the space between the SiC fibers forming the preforms with molten silicon. Although these CMCs are denser than those prepared by non-MI methods, the presence of free silicon in the matrix restricts their use to below 1589 K (2400° F) due to a low creep strength above this temperature. In the case of CMCs fabricated by chemical vapor infiltration (CVI), the presence of free silicon in the grain boundaries of the CVI deposited SiC can react with the protective boron nitride coating on the SiC fibers. Additionally, oxygen ingression from the external surfaces through surface-connected voids and cracks in the matrix can lead to the oxidation of the protective fiber coatings, thereby degrading the creep life of the CMCs. Thus, CMC life is dependent on the life of the protective environmental barrier coatings (EBCs). The current challenge in CMC

technology development is to develop matrices, which allow CMCs to be used at or above 1755 K (2700° F). Developing CMCs for this high temperature use, and meet NASA's current aeronautic goals, requires the development of a new class of ceramic composites with self-healing capabilities to mitigate these issues.

The present investigation aligns with the FY11 Seedling Fund solicitation relating to lightweight materials and structural concepts. In contrast to current technical developments, this research intends to use an engineered matrix consisting of silicides, SiC and Si_3N_4 to develop a range of EMCs capable of withstanding stresses and temperatures higher than current generation SiC/SiC CMCs. Additionally, it is intended to provide the matrix with self-healing capabilities to seal matrix cracks after they develop under loading.

The present concept proposes to use fundamental principles of physics and materials science to develop a new class of high temperature lightweight self-healing ceramic composites (SHCCs). Unlike current SiC/SiC CMC technology, the present concept proposes to develop SiC fiber-reinforced SiC-Si_3N_4-silicide matrix composites with a composition formulated to match the CTE of the fibers, and with an ability to getter ingressed oxygen and self-heal cracks by filling them with low viscosity oxides. If successful, the proposed concept is expected to advance the development of matrices suitably engineered to be compatible with BN-coated SiC/SiC woven preforms and advance ceramic composite technology for applications at or above 1755 K (2700° F).

Potential impact on NASA and national aeronautics challenges: Carbon dioxide emissions from air travel is expected to increase from the current 2% to 5% of total global CO_2 emissions within the next 20 years. Clearly, a reduction in the global emission of greenhouse gases and increased engine efficiency is of immediate importance for NASA, the United States and the global community. A successful development of the proposed concept to TRL 9 can significantly increase engine efficiency, and considerably reduce fuel consumption and CO_2 greenhouse gas emissions due to air travel.

Objectives: The overall objective of the proposed research under Phases I is to develop a new class of high temperature, lightweight, self-healing, SiC fiber-reinforced ceramic composites. The desired technology development objective at the end of Phase I was to demonstrate proofs-of-concepts and advance the composite development to a TRL between 1 and 2.

Specific objectives identified for Phase I were as follows: (a) Develop and process several engineered matrices (EM) and demonstrate that their thermal strains match those of SiC as a function of absolute temperature, T, as proof-of-concept. (b) Evaluate the properties of these matrices to enable the down-selection of a few promising compositions for further optimization and development. (c) Demonstrate high temperature matrix plasticity. (d) Develop processing techniques to infiltrate BN-coated SiC/SiC preform coupons with the promising engineered self-healing matrices. (e) Evaluate the mechanical properties of these engineered matrix composites (EMCs) to demonstrate the self-healing capability of the composites.

Experimental Procedures

Figure 1 shows the schematic of the two-pronged work plan being followed in this investigation. Engineered matrices consisting of intermetallic silicide, SiC, Si_3N_4 powder mixtures, and designed to match the CTE of SiC fibers and suitably formulated to enable self-healing properties, were used to impregnate 2D SiC preforms using slurry casting techniques prior to melt infiltration with Si or SiGe to form the final EMCs.

One path of the work plan consisted of optimizing hot-pressing conditions for several silicide-based matrices, and characterizing them to enable the down selection of matrices with a desirable combination of properties. The other path of the work plan consists of developing methods for EMC fabrication. Both these paths were followed simultaneously in order to maximize the number of matrix compositions that can be studied within the one-year period for Phase I and to ensure that the technology development is cost effective with minimum risks. The chosen silicides included $CrSi_2$, CrMoSi, $MoSi_2$, $TiSi_2$ and WSi_2. The matrices were prepared without adding the self-healing constituents so as to characterize the properties of matrices to generate baseline data. Ball-milled or attrition-milled powder mixtures were hot-pressed into plates, which were later machined to produce the specimens used for determining CTE, oxidation, and bend and tensile data (Fig. 2(a)). The hot-pressed processing conditions were optimized for each matrix composition and plate dimensions.

Figure 2(b) shows the schematic processing steps involved in the fabrication of the EMCs. The engineered matrices were wet attrition milled to grind and mix the silicide, SiC and Si_3N_4 powders homogenously. Boron nitride-coated SiC/SiC tow preformed panels were machined into bend specimens[1]. Small specimens were also machined for conducting trial infiltration runs. Several attempts were made to infiltrate the preforms with different engineered matrix slurries before the specimens could be reproducibly infiltrated with epoxy-laden powder mixtures. These infiltrated specimens were pyrolized before melt infiltrating them with either Si or SiGe. The SiGe was used to develop the self-healing matrix. The methodology and processing parameters for melt infiltration could not be optimized before the termination date of Phase I. As a result, some bend specimens were not completely melt-infiltrated. The engineered matrices consisted of SiC-Si3N4-CrMoSi, where the volume fraction of each constituent was varied.

Generally, three bend specimens were tested for each engineered matrix. Four-point bend tests were conducted on the EMC specimens at room temperature and 1327^0 C. These specimens were tested to failure. The third specimen was pre-cracked in a 3-point bend fixture at room temperature, oxidized at 1327^0 C to try and heal the cracks and tested at 1327^0 C to evaluate the degree of self-healing. No attempt was made to verify the reproducibility of the test data.

Technical Accomplishments

The compositions of the matrices were engineered using the rule of mixtures (ROM) approach based on literature data. Figure 3(a) compares the predicted thermal strain, $\Delta L/L_0$, for a $CrMoSi/SiC/Si_3N_4$ engineered matrix with literature values for SiC and Si_3N_4 as a function of absolute temperature; Fig. 3(b) compares measured $\Delta L/L_0$ data for several silicides and engineered matrices determined in the present investigation with SiC and Si_3N_4. Clearly, the engineered matrices have similar $\Delta L/L_0$ are very similar to that of SiC. Fig. 3(b) compares measured $\Delta L/L_0$ data for several silicides and engineered matrices determined in the present investigation with SiC and Si_3N_4. Clearly, the engineered matrices have similar $\Delta L/L_0$ are very similar to that of SiC. The results in Fig. 3(b) proves the concept that matrices can be engineered to match the thermal strain of SiC fibers. The fact that different silicides can be added to SiC-Si_3N_4 powder mixtures in suitable amounts to ensure this match is particularly significant in that several EMCs can be fabricated in principle engineered to match desired properties as compared to conventional SiC/SiC CMCs.

Figure 4(a) shows a photograph of a 50 x 50 x 4 mm hot-pressed $CrMoSi/SiC/Si_3N_4$ plate used for machining bend specimens; Fig. 4(b) represents the corresponding internal microstructure. The CTE

[1] Although tensile specimens were also machined, these could not be epoxy infiltrated since molds of suitable dimensions were not commercially available.

specimens were thermally cycled three times between room temperature and about 1500 K. Except for $MoSi_2/SiC/Si_3N_4$, which showed extensive cracks, the other engineered matrices were observed to be robust (Fig. 5). Thus, $MoSi_2/SiC/Si_3N_4$ was dropped from further consideration.

Figure 6 compares the specific weight change data from preliminary isothermal oxidation studies for several engineered matrices oxidized in air at 1600 K. The data for SiC and Si_3N_4 were reported at a lower temperature of 1573 K[2]. Several observations can be made from Fig. 6. First, the observed specific weight changes were higher for the silicide-engineered specimens than monolithic SiC and Si_3N_4 although it is noted that they were oxidized at a higher temperature of 1600 K. These observations suggest that the silicides oxidize first before the oxidation of SiC and Si_3N_4 results in the formation of a protective oxide layer. Second, the two $CrSi_2/SiC/Si_3N_4$ specimens, which were hot-pressed under different conditions, oxidize at vastly different rates so that processing conditions influence matrix oxidation rates. Third, the oxide layer for the $TiSi_2/SiC/Si_3N_4$ specimen spalled while $WSi_2/SiC/Si_3N_4$ specimen fell apart, and therefore, these compositions may not be suitable as a matrix compositions. Fourth, $ZrSi_2/SiC$ shows a much reduced oxidation behavior than the other engineered matrices.

Figure 7 shows the bend stress-strain data for CrMoSi-SiC-Si_3N_4, $CrSi_2$-SiC-Si_3N_4 and WSi_2-SiC-Si_3N_4 specimens deformed at room temperature (RT), 1643 and 1698 K. In the case of the CrMoSi-SiC-Si_3N_4 material, the bend stress-strain curve at 1698 K reveals that the material begins to exhibit some plasticity and an ability to slow down crack propagation at this temperature. The fracture surface of this specimen was undulated, which is consistent with the observed stress-strain curves. Thus, this matrix material is likely to be compliant in a composite and thereby increase its life and reliability by either resisting or slowing crack propagation. Similarly, as the $CrSi_2$ deforms at 1473 K, the bend stress-strain curves for $CrSi_2$-SiC-Si_3N_4 exhibit a relatively larger amount of strain than for tests conducted below 1473 K. The WSi_2-SiC-Si_3N_4 specimens oxidized catastrophically while being heated and they could not be tested at high temperatures. Thus, WSi_2-SiC-Si_3N_4 was dropped from the program.

Figure 8(a) shows a photograph of an uninfiltrated SiC/SiC woven preform, while Fig. 8(b & c) show the cross-sectional microstructures of a specimen after slurry infiltrating with a mixture of $TiSi_2$+SiC+Si_3N_4. Figures 9(a-d) show computer tomographic (CT) sectional scans through uninfiltrated and infiltrated preforms after different stages of EMC fabrication. These micrographs and CT scans reveal almost complete infiltration of the preforms with the area fractions of the porosity in the uninfiltrated and melt-infiltrated preforms being about 21-23% and 1.8%, respectively.

Figure 10 compares the room temperature three and four-point bend data for several EMCs. The data from the three-point tests represent those obtained from specimens which were pre-cracked. The four-point data represent those from specimens, which were taken to fracture.

Summary of Research

Table 1 compares the accomplishments for the matrix development and EMC fabrication with the proposed milestones and summarizes the current status of each milestone.

[2] L. U. J. T. Ogbuji and E. J. Opila, J. Electrochem. Soc. Vol. 142, 925-930 (1995).

Table 1. Summary of Phase I Accomplishments.

Milestone	**Status**
Demonstrate thermal strains for engineered matrices match those of SiC.	Completed.
Generation of matrix properties and down-selection of promising compositions.	Completed.
Demonstrate high temperature matrix plasticity.	Bend tests completed. Tensile specimens have been machined. However, the first specimen broke in the grip section in the machine when the technician was getting it ready for testing. The pressure was probaly too high. The testing of the other specimens has been suspended until the cause is determined.
Develop processing techniques for fabricating EMCs.	18 bend bars were infiltrated and melt infiltrated with either Si or SiGe. About 12 specimens were not completely melt infiltrated since the process needs to be optimized.
Evaluate mechanical properties of EMCs and demonstrate self-healing capabilities.	Four-point room temperature bend test has been completed. Three-point bend test to pre-crack the specimens have been completed. These specimens are being oxidized prior to testing. The length of time required to oxidize the secimens is being optimized. Four-point bend tests are underway at 1327^0 C.

Next Steps

a) Complete tensile tests of monolithic specimens after resolving the gripping problem (Table 1).
b) Complete oxidation studies on the pre-cracked bend specimens to identify the total time required for developing a suitable oxide layer in the pre-cracked specimens.
c) Oxidize all pre-cracked specimens at 1327^0 C.
d) Complete bend testing of oxidized pre-cracked and pristine specimens at 1327^0 C to evaluate the plasticity and self-healing properties of the EMCs.
e) Write and submit NASA report to NARI.
f) Submit Phase II proposal. This has been approved for FY12-13 funding.
g) The work will continue under Phase II funding.

Current TRL: 2

Applicable NASA Programs/Projects

Development of SiC/SiC CMCs for combustor liner, vane and blade applications is a major thrust of several ARMD projects (Aero Science, Fixed Wing, Rotary Wing, Environmental Responsible Aviation and Supersonics). In addition, several aircraft engine companies are aggressively pursuing the development of this materials technology. It is expected that a successful demonstration of the present concepts would be supported by an ARMD project especially there is great interest to develop CMCs for 1755 K (2700° F) applications.

Publications and Patent Applications

A provisional patent entitled "High Temperature Lightweight Self-Healing Ceramic Composites for Aircraft Engine Applications" has been filed based on technology disclosure LEW-18964-1. Technical papers and NASA reports will be written and submitted for publication after receiving management approval in the next few months.

Awards & Honors related to Seedling Research

Proposal for Phase II funding was accepted and will be funded during FY 12-13.

List of Figures

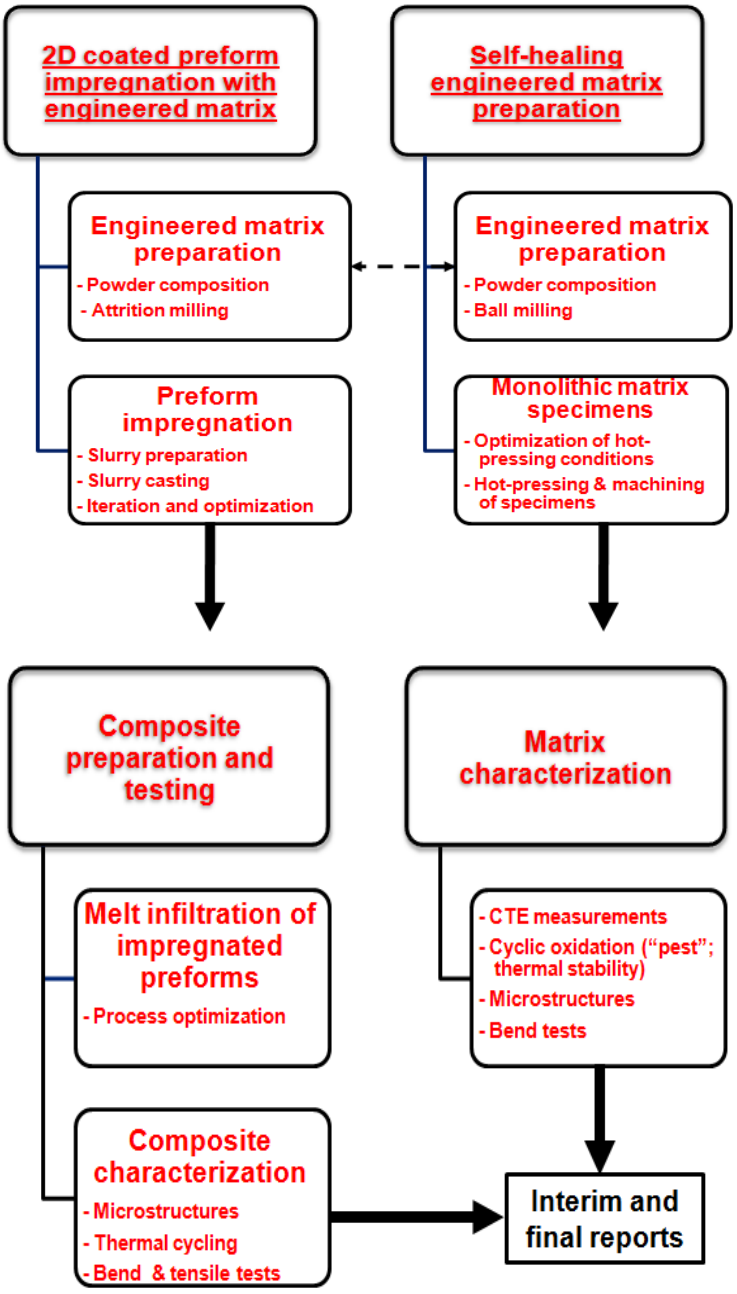


Figure 1. Work plan for EMC development.

Fig. 2 (a)

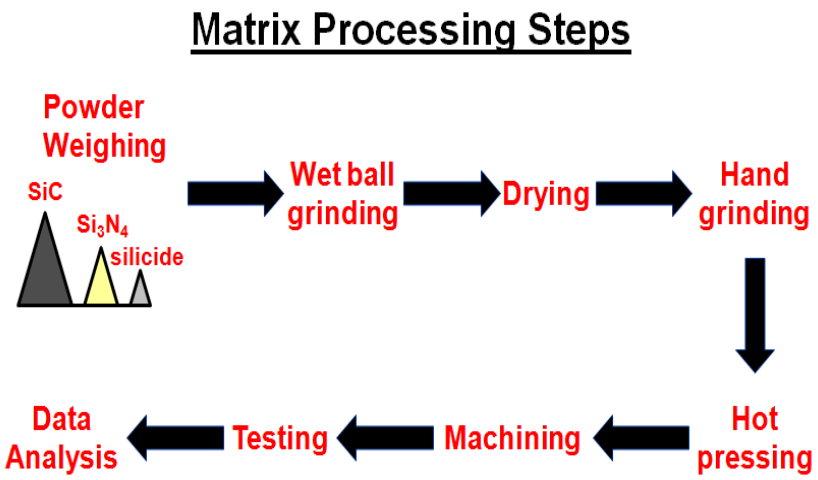


Fig. 2 (b)

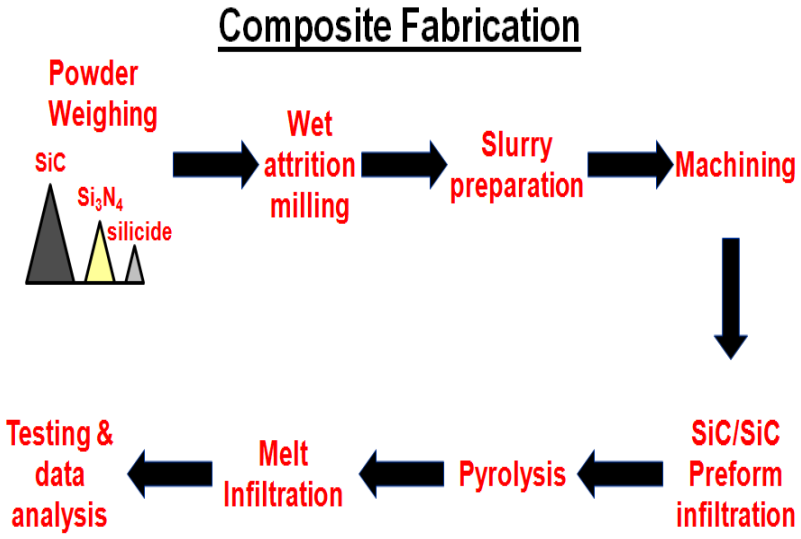
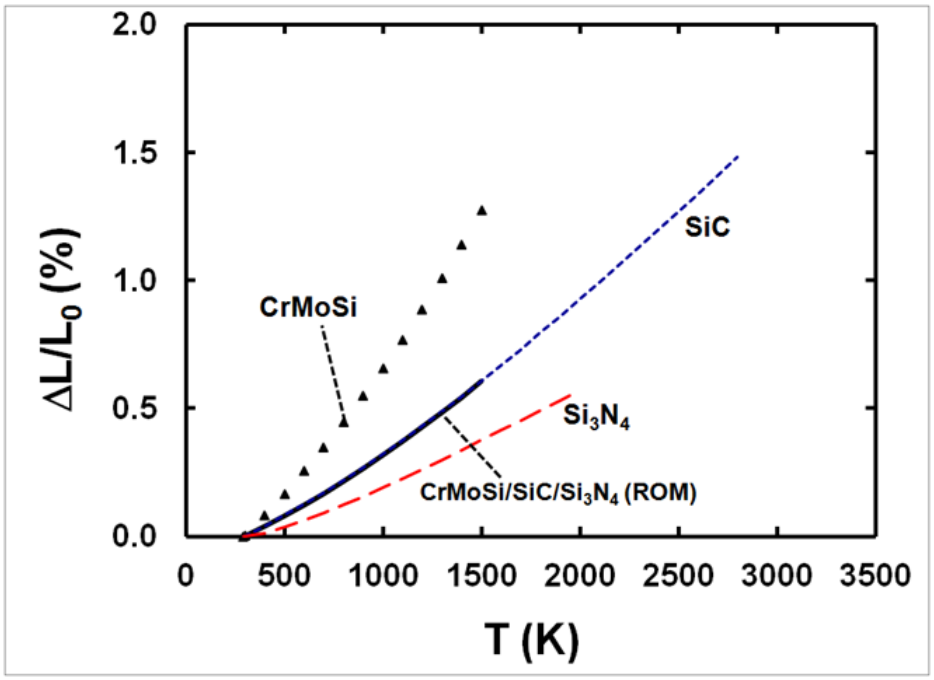


Figure 2. Schematic flow charts showing the steps in the fabrication of the (a) engineered matrix and (b) self-healing engineered matrix composites.



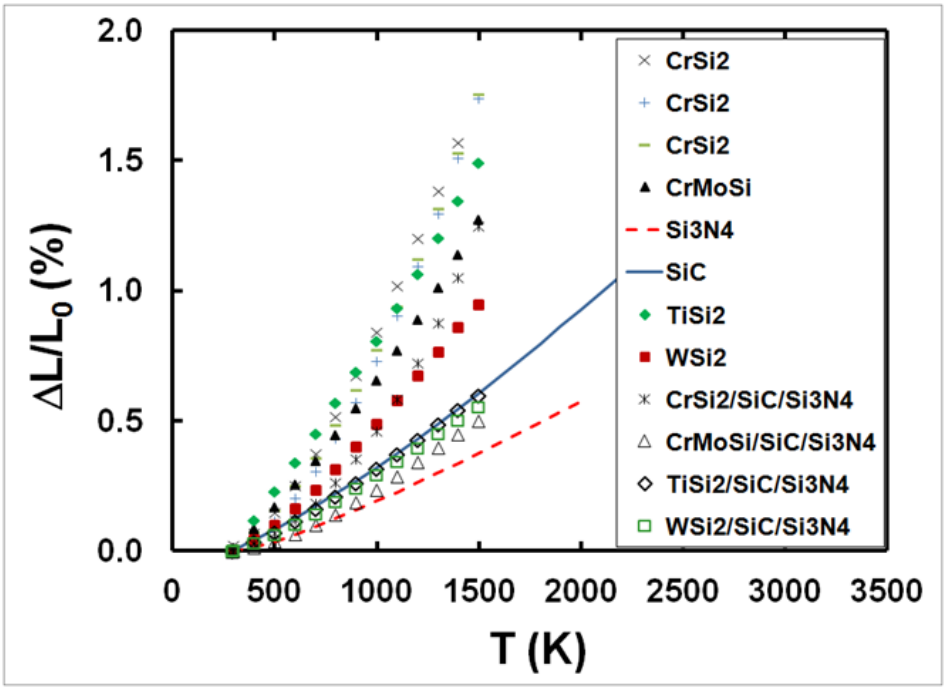


Figure 3. (a) Comparison of the predicted values of thermal strains for a CrMoSi/SiC/Si_3N_4 engineered matrix with those for SiC and Si_3N_4 as a function of absolute temperature. (b) Measured values of CTE for several engineered showing proof-of-concept.

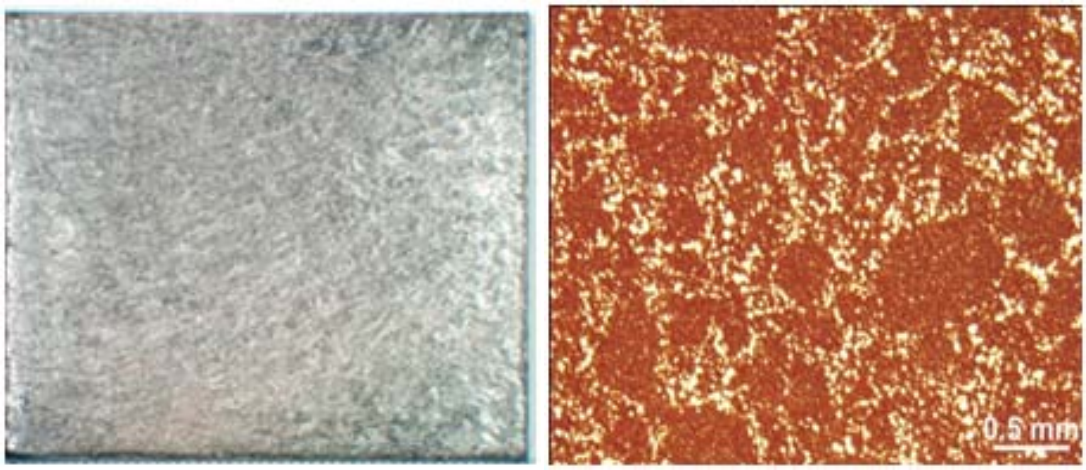


Figure 4. (a) Photograph of a 50 x 50 mm hot-pressed CrMoSi/SiC/Si_3N_4 plate. (b) Microstructure of hot-pressed CrMoSi/ SiC/Si_3N_4 .

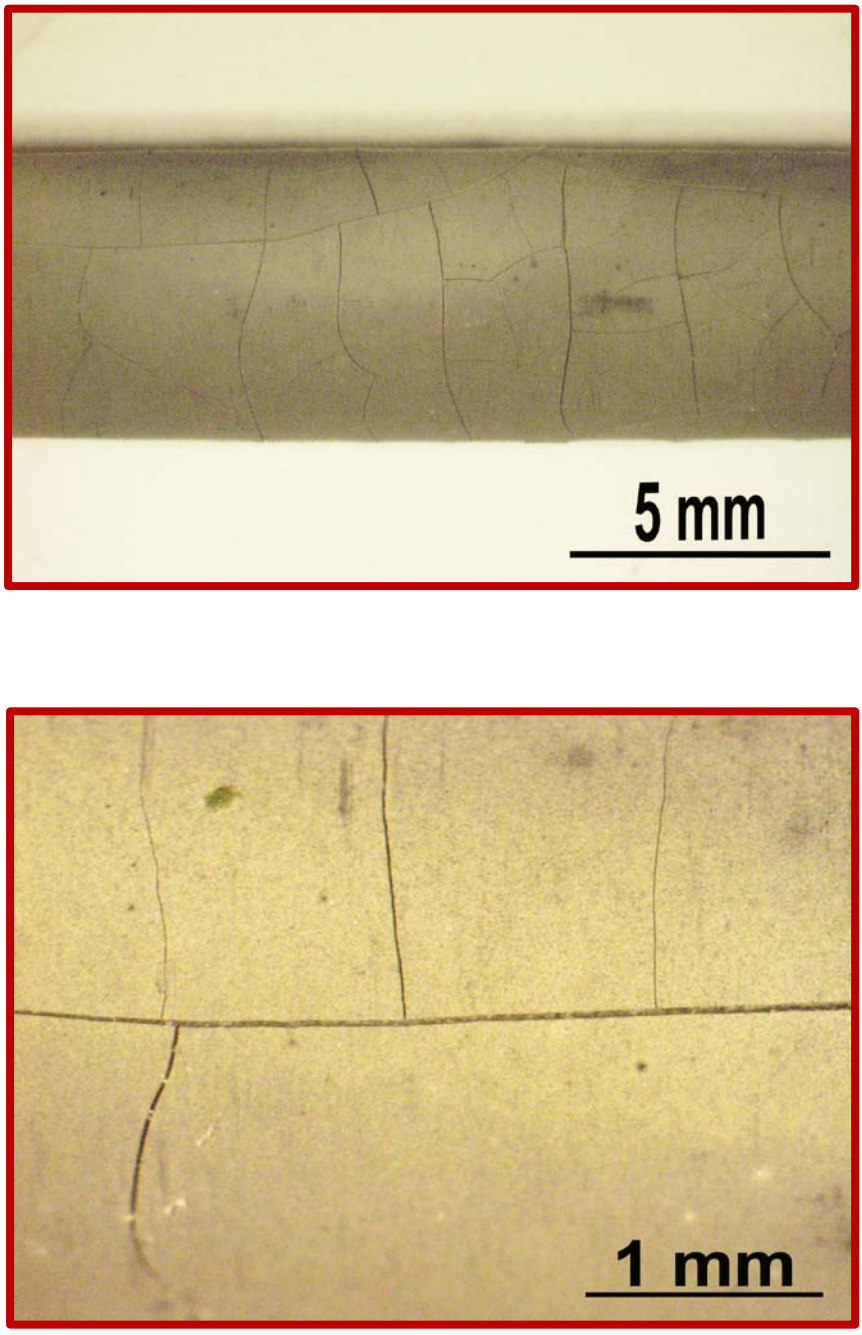


Figure 5. Macrograph of the surface of a $MoSi_2/SiC/Si_3N_4$ CTE specimen showing extensive cracks after three thermal cycles.

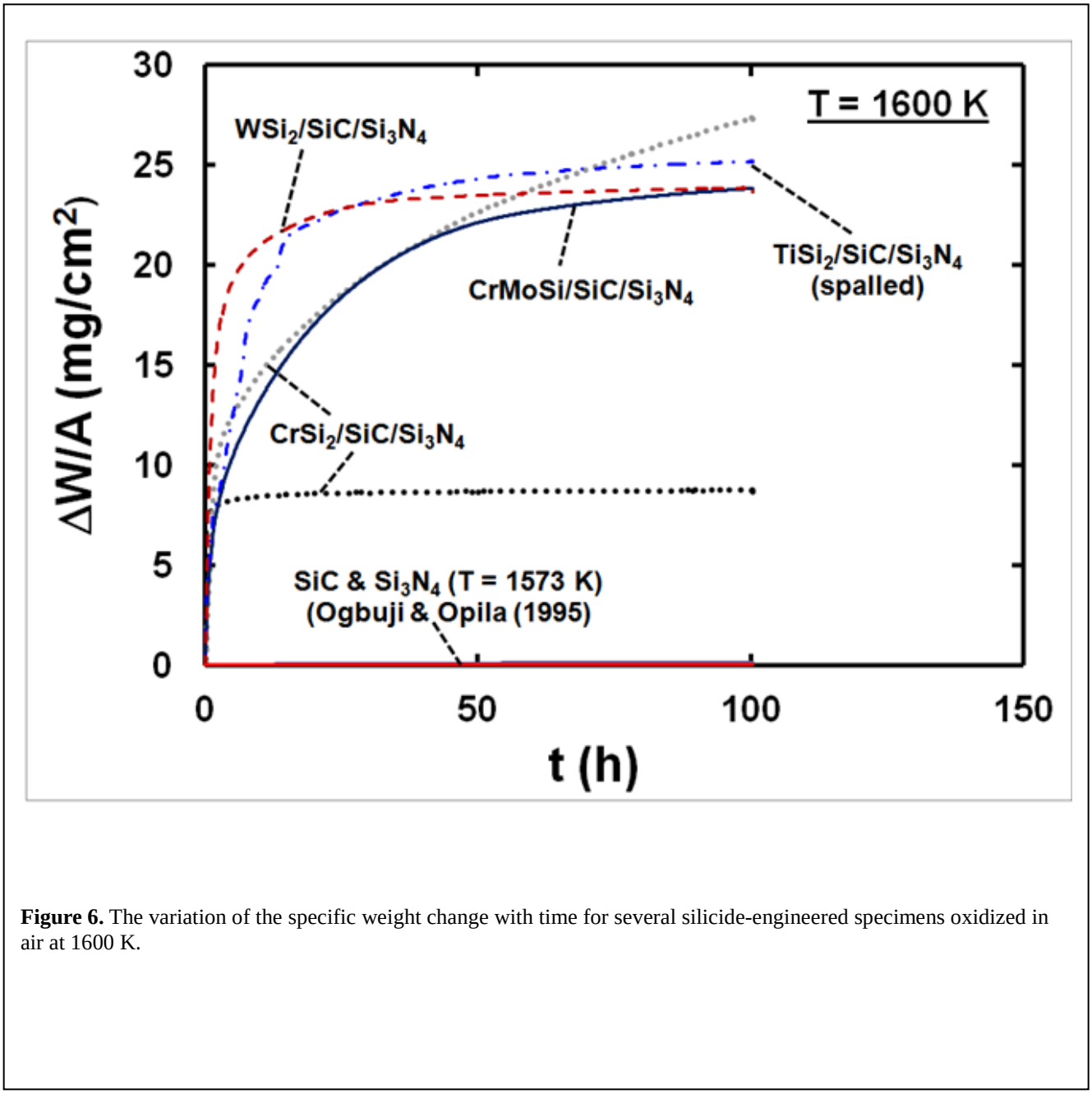
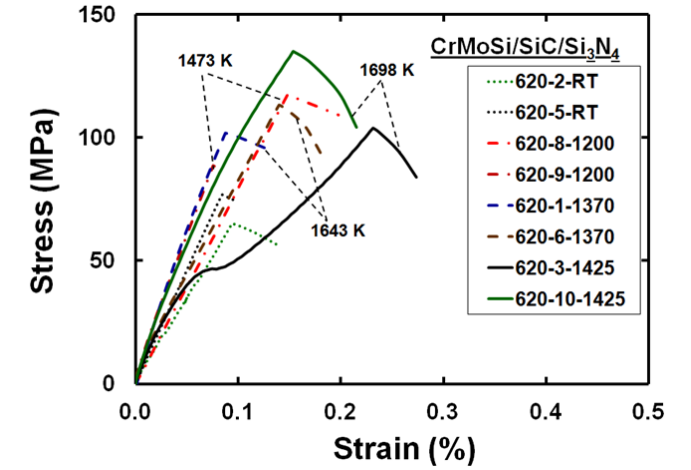
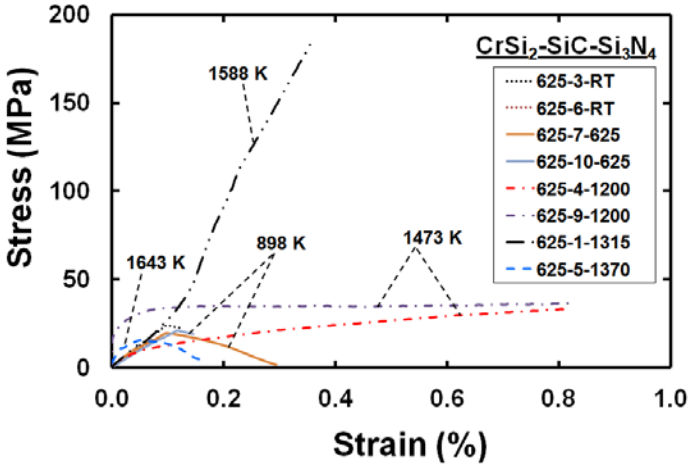


Figure 6. The variation of the specific weight change with time for several silicide-engineered specimens oxidized in air at 1600 K.





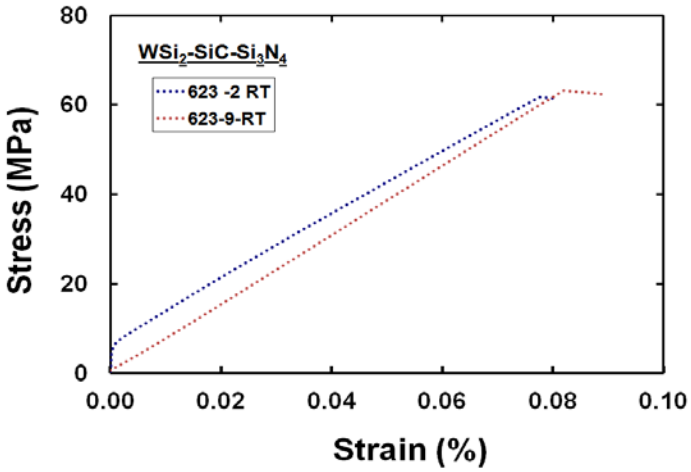


Figure 7. Bend stress-strain data for $CrMoSi-SiC-Si_3N_4$, $CrSi_2-SiC-Si_3N_4$ and $WSi_2-SiC-Si_3N_4$ specimens tested at room temperature, 1473, 1643 and 1698 K. The $WSi_2-SiC-Si_3N_4$ underwent catastrophic oxidation during heat-up to high temperatures.

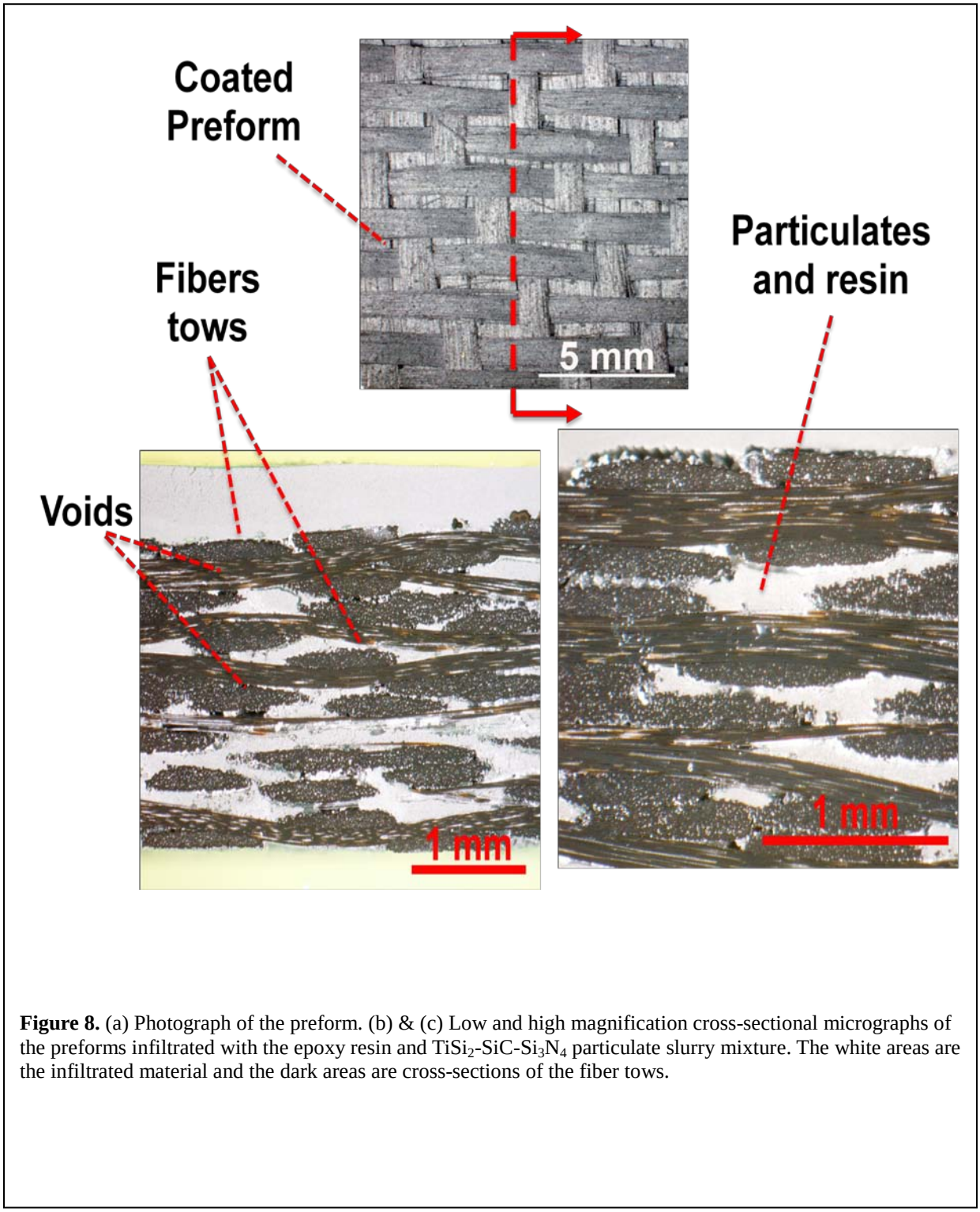


Figure 8. (a) Photograph of the preform. (b) & (c) Low and high magnification cross-sectional micrographs of the preforms infiltrated with the epoxy resin and $TiSi_2$-SiC-Si_3N_4 particulate slurry mixture. The white areas are the infiltrated material and the dark areas are cross-sections of the fiber tows.

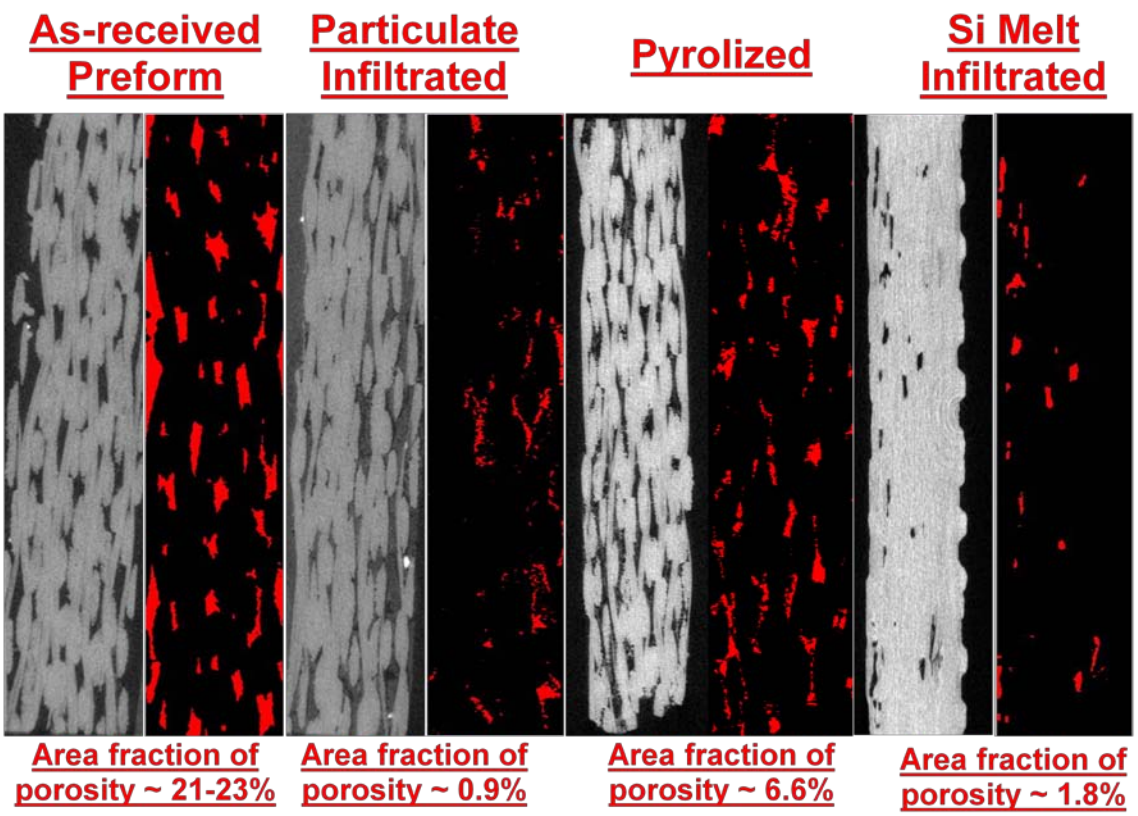


Figure 9. CT scans of the cross-sections. (a) As-received preform; (b) epoxy-particulate infiltrated preform; (c) pyrolized composite; and (d) silicon melt-infiltrated composite. The x-ray images are on the left and the corresponding threshold images used for determining void volume fraction are shown in red and black are to their right. The porosity appear as dark regions in the x-ray images and red in the threshold images.

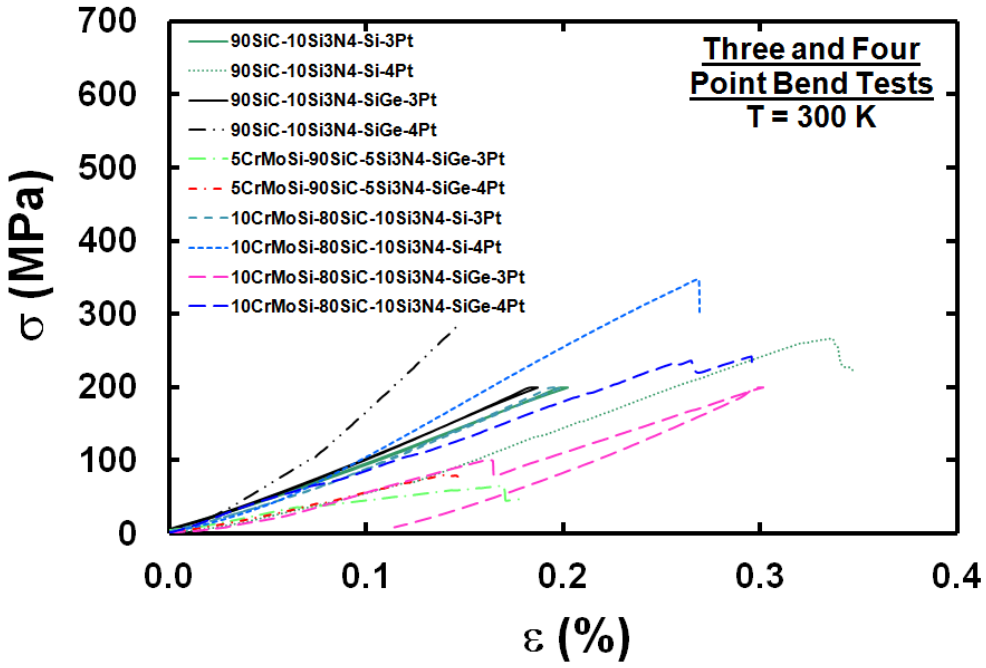


Figure 10. Room temperature three and four-point bend tests for several EMCs. The three-point bend tests were used for pre-cracking the specimens and they were unloaded after crack development.