Hierarchical Coupling of Molecular Dynamics and Micromechanics to Predict the Elastic Properties of Three-Phase and Four-Phase Silicon Carbide Composites

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The results obtained from previously conducted molecular dynamics analysis of silicon carbide (α-SiC (6H, 4H, & 2H-SiC), β-SiC (3C SiC)), silicon and boron nitride, were utilized as inputs in the MAC/GMC micromechanics software to model and evaluate the elastic properties of three-phase SiC/BN/SiC and four-phase SiC/BN/Si/SiC composites. This method of analysis eliminates the need for back-calculation of the apparent properties of the base constituents from the measured ceramic matrix composites properties. The multiscale models are validated against the available data in literature.

I. Introduction

In the search for materials that can tolerate substantial stresses at hotter temperatures, applications such as jet and rocket engines, and space vehicles that must be able to withstand extremely harsh environment during the reentry, engineers have been devising tough, lightweight composites made of silicon carbide fibers, embedded in a ceramic material. Silicon carbide can withstand 2,000 °C and this materials serves as a source of hope for tomorrow's engines that will need higher operating temperatures since hotter engines are more fuel-efficient, produce more thrust and can carry larger loads (the key operating factors for spacecraft and advanced aircraft). In addition to heat engines and structural applications, silicon carbide (SiC) is a very promising semiconductor material for high-temperature, high-frequency and high-power optoelectronic devices. Ceramic matrix composites (CMCs) can be generally described as a material system comprised of fibers or particles embedded within a ceramic matrix. For example, silicon carbide/silicon carbide (SiC/SiC) composites contain coated SiC fibers and a SiC matrix. Of particular interest for high temperature applications are SiC/SiC CMCs that utilize a fiber coating composed of boron nitride (BN) [1-3].

SiC can exist in several crystalline phases including α-SiC (6H, 4H, and 2H SiC), β-SiC (3C) and as an amorphous material (a-SiC) [4-7]. The BN coating contains amorphous BN (a-BN) with a small volume fraction of layered hexagonal BN (h-BN) [8-9]. Finally, some unreacted silicon (Si) from processing exists in a crystalline (c-Si) or amorphous structure (a-Si). The molecular structure of the phases within the fiber, matrix, and coating influence the thermo-mechanical behavior of the composite and can be controlled through a combination of material processing methods including chemical vapor infiltration, melt infiltration, and polymer impregnation and pyrolysis [10, 11].

Previous work examined the influence of micromechanics idealization (GMC and HFGMC), for both ordered and disordered microstructures, on the unidirectional and laminated composite effective properties, proportional limit stress (PLS) and fatigue life for a typical ceramic matrix composite with weak interface [12,13]. They also determined

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the influence of ordered and disordered microstructures on the effective properties and fatigue life of graphite/epoxy polymer matrix composites (PMCs) at low fiber volume fractions in the context of assessing the advantages/limitations of the micromechanics idealization available within the general synergistic, multiscale-modeling framework for composites.

Because of flexibility in the arrangement of the different phases within a given constituent, in addition to the morphology of the constituents themselves within the composite (fibers and coating within the matrix), it may be possible to design SiC/SiC composites to meet specific performance requirements. Validated numerical simulations can be utilized during the material design process, effectively widening the available design space and allowing for exploration of novel microstructures at a relatively low expense and rapid throughput compared to physical material production and testing. To achieve this, accurate data for the thermo-mechanical properties of the basic phases of the constituent materials in the composite must first be obtained through experimentation or simulation at nanoscale. Ref. [14] has done the preliminary work towards establishing a multiscale modeling framework to enable a link between molecular structure of the materials phases, the arrangement of the phases in the constituents, and the morphology of the constituents in the composite to the performance of the composite material. The focus of the current work is to develop micromechanics models at higher length scales for the analysis of unidirectional SiC/SiC CMCs. The established and validated molecular dynamics (MD) data for the mechanical properties of different possible material phases in a SiC/SiC composite were utilized in this study for the micro-mechanical analysis of three-phase SiC/BN/SiC and four-phase SiC/BN/Si/SiC composites [14]. These material constituent phases include α-SiC (6H, 4H, and 2H SiC) as the matrix, β-SiC (3C) as the fibers, amorphous BN (a-BN) as a coating or interface, and the embedded crystalline Si in the matrix phase. The numerical predictions of the elastic properties of the CMCs are validated against experimental and numerical data available in the existing literature.

II. Micromechanics Model for Three-phase SiC/BN/SiC and Four-phase SiC/BN/Si/SiC Composites

Micromechanics analysis can be used to predict the effective response of heterogeneous materials at the continuum scale, and the properties of the constituents can be determined from simulations at the lower, atomistic scales. In this study, continuum-level predictions were obtained using the generalized method of cells (GMC) micromechanics theory, where the input data for the continuum scale were output results from the MD data produced by Refs. [14-17]. The generalized method of cells for continuous (or discontinuous) fibrous composites utilizes a repeating unit cell (RUC) representing the periodic material microstructure which can consist of an arbitrary number of phases necessary to accurately model the composite material. For technical details on the mathematical homogenization and localization steps within GMC, the reader is referred to Ref. [17].

The micromechanics analysis establishes the overall (macroscopic) behavior of the multi-phase composite and is expressed as a constitutive relation between the average stress and strain, in conjunction with the effective elastic stiffness. The semi-analytical procedure is computationally efficient and provides solutions on the order of seconds. The GMC is implemented with the MAC/GMC software package, developed by the NASA Glenn Research Center [18]. The software was used to execute the micromechanical analysis, utilizing the corresponding properties of the micro-constituents of composites in the MAC/GMC analysis to simulate the three-phase SiC/BN/SiC and four-phase SiC/BN/Si/SiC composites.

Previous work established several MD models to predict the elastic stiffness properties of several different phases of SiC, BN, and Si [14]. The advantage of using simulation to predict the properties of the base conditions of the composite are numerous. Conducting simulations at lower lengths scales avoids the need to back-calculate or calibrate the properties of the constituents against composite data. Such calibrations typically lead to data sets that are non-unique. In addition, the results from the subsequent micromechanics models are correlations, rather than true predictions, and do not offer any insight into the accuracy of the models for validation. Moreover, experiments at the lower length scales can be costly and time consuming, and also contain a degree of uncertainty and scatter [19-22]. The properties of the subcells in the different constituents (SiC fiber, BN coating, free Si, and SiC matrix) of the CMC RUCs were taken from the average values reported in Ref. 14 and are presented in Tables 1-3. The SiC fibers and matrix contain a combination of different SiC phases, but the exact phase-composition is difficult to determine. As an initial approximation, it is assumed that the fiber is composed of β-SiC and the matrix is α-SiC. Different combinations of α-SiC and amorphous boron nitride were used as matrix and interface, respectively with β-SiC fibers, in order to obtain bounds on the properties of the ceramic matrix composite.

Table 1. Elastic response of SiC [14].

Property	α (6H)	α (4H)	α (2H)	β (3C)
E_x (GPa)	543.1900	608.5120	437.9240	340.0000
E_y (GPa)	539.9330	529.7060	585.5070	343.2800
E_z (GPa)	617.9660	652.6440	600.6640	325.4000
G_{xy} (GPa)	252.4010	263.2470	147.6260	195.7470
G_{xz} (GPa)	225.7890	225.4510	165.2300	203.0700
G_{yz} (GPa)	218.7930	225.4360	225.5010	181.9890
ν_{xy}	0.2290	0.2117	0.2013	0.2558
ν_{xz}	0.0812	0.1048	0.0878	0.2442
ν_{yz}	0.0961	0.0798	0.0745	0.2546

Table 2. Elastic response of a-BN [14].

Property	5-layered $\dot{\varepsilon}=10^7$/s
E_x (GPa)	46.3940
E_y (GPa)	46.7390
E_z (GPa)	56.4200
G_{xy}(GPa)	16.1680
ν_{xy}	0.2892
ν_{yx}	0.2974

Table 3. Elastic response of Si [14].

Property	Value
E_x (GPa)	145.0410
E_y (GPa)	141.8900
E_z (GPa)	143.6830
G_{xy} (GPa)	54.9106
G_{xz} (GPa)	55.3215
G_{yz} (GPa)	54.0125
ν_{xy}	0.3207
ν_{xz}	0.3109
ν_{yz}	0.3135

It should be noted that MAC/GMC has the ability to utilize many different micromechanics analysis models and RUC architectures for the CMC. Specific MAC/GMC commands are presented as `COMMAND` in this section. For this study, a user-defined architecture (`ARCHID=99`), was used to represent the RUCs for three-, and four-, phase CMC composites, displayed in Fig. 1 and 2, respectively. Figure 1 shows the RUC containing subcells of β-SiC fibers (blue), a-BN as the interphase (yellow), and α-SiC as the matrix phase (green) to simulate three-phase SiC/SiC composite. The four-phase RUC (Fig. 2) contains subcells of β-SiC fibers (blue), a-BN as the interphase (yellow), free Si that is embedded in matrix phase (sky blue) and α-SiC as the matrix phase (green) and was originally developed as part of previous work [23]. For both models, the fiber volume fraction was 0.25, and the ratio of interface thickness to fiber radius (`RITFR`) was 0.07. In these simulations, linear elastic constitutive model (`CMOD=6`) was used, the loading was strain control (`MOD=1`) with a strain magnitude of 2%.

III. Results and Discussions

The three and four-phase CMC comprising α-SiC structures, (6H SiC, 4H SiC, and 2H SiC), β–SiC (3C), a-BN, and Si were modeled using the GMC micromechanics theory. As stated before, the elastic moduli, shear moduli, and Poisson's ratios for each model were obtained using the MAC/GMC software. The predicted mechanical properties for the three-phase SiC/BN/SiC and four-phase SiC/BN/Si/SiC composites are documented in Tables 4 and 5, respectively. It can be seen from the data in these tables that different combination of the phases of crystalline α-SiC (6H, 4H and 2H) and a-BN (obtained from different layers of h-BN), given a fixed volume fraction of β-SiC fibers (0.25), resulted in a range of CMC properties. The results show that the structural properties of the modeled CMCs depend substantially on the crystallinity of the matrix. The properties varied with different structures of α-SiC but did not exhibit any significant change with a-BN for either CMC composite.

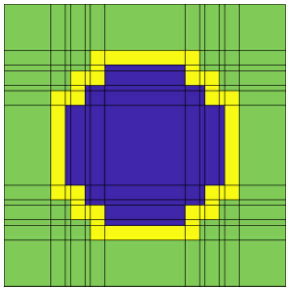

Fig. 1. The RUC architecture for a 3-phase CMC, blue=SiC fiber, yellow=BN interface and green=SiC matrix.

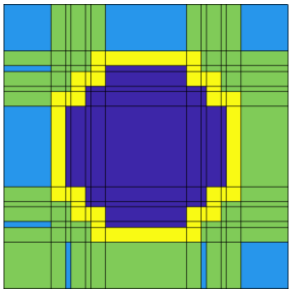

Fig. 2. The RUC architecture for a 4-phase CMC, blue=SiC fiber, yellow=BN interface, sky blue=free Si, and green=SiC matrix [23].

Table 4. The properties for the three-phase composites when β–SiC is fiber, α-SiC (6H, 4H, or 2H) is the matrix and a-BN is the interface.

Properties	2H	4H	6H
E_{11} (GPa)	363.750	467.040	427.010
ν_{12}	0.217	0.2259	0.2300
ν_{13}	0.2174	0.2259	0.230
E_{22} (GPa)	352.160	328.420	332.650
ν_{23}	0.2050	0.218	0.218
E_{33} (GPa)	352.160	328.420	332.650
G_{23} (GPa)	108.860	103.930	104.650
G_{13} (GPa)	104.750	156.630	151.880
G_{12} (GPa)	104.750	156.630	151.880

Table 5. The properties for the four-phase composites when β–SiC is fiber, α-SiC (6H, 4H, or 2H) embedded with free Si is matrix and a-BN is the interface.

Properties	2H	4H	6H
E_{11} (GPa)	308.570	380.050	352.310
ν_{12}	0.2412	0.247	0.2502
ν_{13}	0.2407	0.247	0.2499
E_{22} (GPa)	247.560	239.210	240.500
ν_{23}	0.2795	0.289	0.2873
E_{33} (GPa)	248.130	239.600	240.920
G_{23} (GPa)	84.983	82.758	83.084
G_{13} (GPa)	85.647	112.890	110.470
G_{12} (GPa)	85.333	111.200	108.950

Furthermore, comparing the data in Table 4 to Table 5, the CMC properties are influenced by the presence of free Si. The Young's and shear moduli for the four-phase model are generally lower than that of three-phase model, while the Poisson's ratios for the four-phase are higher. This shows that the stiffness of the CMC matrix is compromised when there is free Si in the microstructure of the matrix. In Ref. [4], the fiber and matrix properties were back-calculated, while the coating properties were assumed to match the experimental axial stiffness of 327 GPa obtained from a heat-treated, cross-ply CMC laminate. However, the results in this current work represent true predictions of the composite properties. It can be seen here that the 3-phase model over predicts the axial stiffness E11 (363.4 – 467.0 GPa), while the 4-phase model bounds the axial stiffness value (308.2 – 380.1 GPa). Similarly, the Young's modulus in the transverse direction E22 and the computed shear modulus is as shown in Table 6 and compared with Ref. 4. The predictions of E22 from three-phase and four-phase models are slightly higher than Ref. [4], and the four-phase model exhibits the most accurate results. The shear modulus G12 from Ref. [4] falls within the range of the predicted values for the four-phase model but lower than that of three-phase model. Thus, it can be concluded that the addition of free-Si to the micromechanics model improved the accuracy of the effective stiffness predictions. Otherwise, the stiffness of the matrix must be artificially reduced to represent a homogenized SiC matrix containing the free Si, and the model is no longer predictive.

Table 6. The range of predicted data as compared with Ref. 4.

Properties	3-phase	4-phase	Ref. 4
E_{11} (GPa)	363.75 - 467	308.57 - 380.05	327
E_{22} (GPa)	328.42 - 352.16	239.21 - 247.56	216
G_{12} (GPa)	104.75 - 156.63	85.33 - 111.20	90

IV. Conclusion

MAC/GMC was used to predict the mechanical properties of three-phase and four-phase CMC SiC composites. The microstructures of the constituents in the SiC/SiC composites contain a variety of different phases comprising crystalline α-(6H, 4H, and 2H) and β-SiC (3C), amorphous BN, and free silicon (Si). Different microstructures of crystalline α-(6H, 4H, and 2H) and amorphous BN obtained from different layers of h-BN were utilized with fixed volume fractions of β-SiC fiber and free Si. The properties of the constituents were obtained from MD simulations that were conducted as part of previous work. The current predictions of the constituent and composite were in good agreement with the available data in literature and serve as validation for the micromechanics and MD methods used. The predictions showed that the modeled properties of CMC composites heavily depend on the microstructural constituents of the matrix, and indicate that explicit modeling of the free Si is likely needed for accurate predictions. As such, the model can be used to quickly assess the amount of free Si in a CMC product, and/or determine the amount of free Si needed to meet particular performance requirements.

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