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# Analyzing the effect of composition, density, and the morphology of the "free" carbon phase on elastic moduli in silicon oxycarbide ceramics

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ARTICLE INFO	A B S T R A C T
<i>Keywords:</i> Silicon oxycarbide Free carbon morphology Elastic properties Molecular dynamics	We perform atomistic simulations to model structures and calculate elastic properties of silicon oxycarbide ce- ramics. We explore individual parameters – composition, density, carbon content – to disentangle mutual de- pendencies that are difficult to separate in experimental studies. Each parameter is studied through dynamic simulations at finite temperatures for a wide range of temperatures. With multi-million atom models in simu- lation boxes as large as 40 nm, we reveal a hitherto "hidden" parameter: the morphology of the "free" carbon phase. Embedding, distribution, and interconnection of the carbon phase inside the amorphous matrix of SiCO severely impact the material's mechanical properties. As a consequence, we call for the development of new characterization techniques that will quantify the morphology of carbon in this and similar systems.

#### 1. Introduction

Silicon oxycarbide (SiCO) ceramics have attracted much interest over the last decades [1]. They exhibit remarkable structural stability and chemical durability [2,3], oxidation resistance [4,5], and unusual creep resistance [6-8]. There are a variety of potential applications for SiCO ceramics, including usage as anode material in Li-ion batterieigis [9,10], as heating elements for pencil-type glow plugs [11], and as coatings [12]. The properties and structural characteristics of SiCO ceramics depend on the precursor materials and processing conditions, particularly on the maximum temperature reached during the pyrolysis step of the precursor-to-ceramic conversion process. Pyrolysis temperatures must reach around 1273 K to yield a single-phase amorphous SiC<sub>x</sub>O<sub>y</sub> [13]. Meanwhile, pyrolysis between 1273 K and 1723 K results in phase separation of the amorphous SiCO ceramic into crystalline SiC and amorphous SiO<sub>2</sub> [14,15]. Furthermore, if the composition of the amorphous SiCO displays excess carbon besides SiC and SiO<sub>2</sub>, then a "free" carbon phase C<sub>free</sub>, with carbon bonding (almost) exclusively to carbon, forms. The resulting composition is  $SiC_xO_y = (y/2)SiO_2 + (1 - y/2)SiC + (1 (x + y/2-1)C_{free}$ . However, the nanostructure of the amorphous SiCO is not yet fully known. To explain the viscoelastic behavior of SiCO [8] along with its unusual high-temperature creep resistance [6-8], Scarmi et al. [8] proposed a model in which an interconnected graphene network sequesters silica domains. Otherwise, exceeding a pyrolysis temperature of 1723 K usually results in amorphous SiO2 and SiC nanocrystals encased by turbostratic carbon [14].

Multiple studies addressed the origin and structural evolution of the excess carbon phase [16,17] A detailed summary of current understanding is presented in a recent review [18]. For pyrolysis temperatures lower than 1073 K, excess carbon has only begun to segregate and is amorphous, hydrogenated, and still dispersed in the ceramic matrix [19]. Increasing pyrolysis temperatures to 1073–1273 K results in a "free" carbon phase described as 2–3 layers thick turbostratic carbon saturated with hydrogen at the periphery [20]. Pyrolysis temperatures higher than 1273–1473 K eliminate hydrogen from peripheral carbons and yield extended carbon layers. Above pyrolysis temperatures of 1673 K, the excess carbon phase forms graphite nanocrystallites or an entangled network of single- or multi-layered graphene [18].

The mechanical properties of SiCO have been studied at ambient and elevated temperatures. Rouxel et al. were among the first to explore the high-temperature behavior of SiCO glasses [21]. They proposed that the Young's modulus of SiCO can be calculated using a simple rule of mixture using volume fractions of constituent phases. Since graphite has lower elastic moduli than SiC and SiO<sub>2</sub>, it is generally inferred that SiCO with high free carbon content displays low moduli when compared to SiCO with low free carbon content – provided that the ratio SiC to SiO<sub>2</sub> is comparable. This trend appears to be supported by a recent study by Sorarù et al., who synthesized SiCO glasses with varying amounts of free carbon and provided a thorough comparative study of Young's modulus and hardness [22]. The impact of the pyrolysis temperature on

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Fig. 1. Models of  $Si_2CO_2 + C_{free}$  (24,576 atoms) generated at  $T_{max} = 4000$  K with a. density = 1.4 g/cm<sup>3</sup> and b. = 2.2 g/cm. Models from a. and b. shown without Si and O atoms and only C atoms with c. = 1.4 g/cm<sup>3</sup> and b. = 2.2 g/cm. C content  $C_{free}$ :Si = 0.5, density,  $T_{max} = 4000$  K. Si atoms are blue, O atoms are red, and C atoms are black.

mechanical properties is also of interest for ceramic matrix composites (CMCs) that use a SiCO matrix and/or SiCO fibers embedded into a ceramic matrix [23,24].

In contrast to many experimental studies, only a few computational investigations relate to SiCO. Early on, we used density functional theory (DFT) and ab initio molecular dynamics to investigate structure and elastic moduli of amorphous SiCO [25]. Subsequent work addressed interfacial bonding between glassy SiCO and the free carbon phase [26]. Further atomistic simulations with empirical potentials investigated some temperature-dependency of mechanical properties [27,28].

In this study, we focus on the elastic properties of amorphous SiCO, including different amounts of "free" carbon,  $C_{free}$ . We perform atomistic simulations using an empirical potential to investigate how elastic moduli depend on various parameters, namely composition of the amorphous SiCO glass matrix, density,  $C_{free}$  content, and the particular morphology the  $C_{free}$  attains. We also study the temperature dependency of moduli. Significant computer resources facilitate us to examine each parameter individually, enabling us to disentangle dependencies that are difficult to separate in experimental studies. Anticipating our results, we show that – for the same composition and density – the impact of carbon morphology on mechanical properties is considerable.

#### 2. Method

In previous work, we generated SiCO models using an approach based on the Wooten, Winer, and Waire (WWW) algorithm and optimized these models within density functional theory (DFT) [25,26]. While DFT calculations are highly accurate, they are also computationally expensive, thus limiting the size of models and the extent of simulations. Calculations using the Tersoff potential, an empirical bond-order potential, are much faster than DFT calculations, and models can routinely be as large as millions of atoms. Simulations can extend for microseconds if needed. Models generated with the Tersoff potential, on the other side, display structural imperfections. Nevertheless, the Tersoff potential reproduces mechanical properties adequately [27,28], even though the specific parametrization of the potential in some cases does impact the magnitude of trends [29].

Throughout this work, we perform molecular dynamics simulations implemented in the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [30]. Interactions are described via the Tersoff potential [31,32]. Si-Si, Si-C, and C-C interactions are parameterized by Tersoff [31-33]. Si-O interactions are parameterized by Munetoh et al. [34]. Similar to previous studies, we treat interactions between O atoms or between C and O as repulsive only, based on spectroscopic evidence [2]. We generate SiCO models through a melt-quench process: randomly positioned Si, C, and O atoms are heated from 0 K to temperature T<sub>max</sub> at a rate of 10 K/ps. For the critical parameter T<sub>max</sub>, we choose temperatures between 2000 and 8000 K. At  $T_{max}$ , the system is equilibrated for 200 ps and then cooled to 300 K at a rate of 10 K/ps. All simulations are done at constant volume to fix density. We performed additional simulations using different equilibration times and cooling rates. Overall, we find that carbon morphology in models is almost completely determined through T<sub>max</sub>. Longer equilibration times, we tested up to 100 ns at T<sub>max</sub>, have some impact. However, changes that occur when increasing  $T_{\text{max}}$  by just 50 K are similar to an extension of equilibration time by a factor of 20-100. A slower cooling rate, e.g. 1



Fig. 2. (Left) Shear modulus and (right) Young's modulus vs. density for models with content  $C_{free}$ :Si = 1 and composition Si<sub>5</sub>CO<sub>8</sub> + 5  $C_{free}$ , SiO<sub>2</sub> +  $C_{free}$ , and Si<sub>2</sub>CO<sub>2</sub> + 2  $C_{free}$  generated at  $T_{max}$  = 3000 K. Elastic constants are calculated in triplicate for each of 3 independently generated models. Error bars (if larger than the symbol used) represent standard error. Simulations are done at 300 K. Lines are provided to guide the eye.

K/ps, does not change the morphology of carbon segregations but reduces the fraction of local defects in the final structure. Most importantly, it has a negligible impact on mechanical properties. Throughout our simulations, we use a time step of 1 fs to integrate the equations of motion.

In this study, we explore the impact of compositions and densities on the mechanical properties of SiCO. Addressing the composition of the stoichiometric SiCO glass matrix, we model three different compositions: SiO<sub>2</sub>, Si<sub>5</sub>CO<sub>8</sub> (=SiC<sub>0.2</sub>O<sub>0.8</sub>), and Si<sub>2</sub>CO<sub>2</sub> (=SiC<sub>0.5</sub>O). This reflects 0, 20, and 50 mol-% SiC content, respectively. For each glass composition, we then build models with four different free carbon contents by adding as many C atoms as to achieve a ratio of Cfree:Si of 0.5, 1, 2, and 3. Thus,  $Si_5CO_8$  with  $C_{free}$  corresponding to a ratio  $C_{free}:Si = 2$  has the composition Si\_5CO\_8:10  $\cdot C_{free} = Si_5C_{11}O_8.$  Overall, this yields  $3 \cdot 4 = 12$  different compositions that we explore. Structures for each composition are then generated at five different densities (1.4–2.2  $g/cm^3$ ). Furthermore, we generate models of each system for five different  $T_{\text{max}}$ , 2000, 3000, 4000, 6000, and 8000 K, to examine various free carbon morphologies. Finally, we generate three independent models by choosing different initial random numbers for each set of model parameters (glass composition, Cfree content, density, Tmax). In total, this yields (3.4).5.5.3 = 900 models.

When developing models for this study, we realized that the simulation box size can constrain the morphology of the free carbon phase. This is particularly important for models with high carbon content and for models that display segregation. Modeling structural features of a particular dimension requires a simulation at a significantly larger length scale. For our study, models with a simulation box size between 7 and 10 nm are necessary to develop extended nano-sized carbon networks. Consequently, the models we generate contain between 24,000 and 50,000 atoms in cubic boxes with side lengths between 7 and 10 nm. Fig. 1 shows two models of  $Si_2CO_2 + C_{free}$  (24,576 atoms) with different densities. For each model, we display once all atoms (Fig. 1 a, b) and then the C atoms only (Fig. 1 c, d). Subsequent models' figures will display the C atoms only to highlight characteristics of carbon morphology. For consistency checks and to explore the impact of periodic boundary conditions, we modeled one composition,  $Si_5CO_8 + 10$ C<sub>free</sub>, with a density of 2.2 g/cm<sup>3</sup> in 8-fold and 64-fold sizes following the same simulation protocol as described above. The largest model, thus, comprises 2.52 million atoms and has a box length of  $\sim$ 40 nm. We find through this scaling analysis that, albeit some subtle differences emerge and will be discussed, our choice of models is sufficient for exploring mechanical properties.

After model generation, we compute the elastic constants c<sub>ii</sub> of each model through dynamic simulations at temperatures from 100 to 2000 K [35]. Temperatures for dynamic simulations of moduli are not to be confused with T<sub>max</sub>, the temperature used for generating a particular model. For each model, 13 short simulations are performed: one for the initial state, six positive deformations, and six negative deformations. The first simulation is done to determine the initial state of the structure without deformation by equilibrating at a target temperature. During the other 12 simulations, models are deformed by 0.5% in a selected direction and equilibrated at the target temperature for 1.0 ps. Subsequently, simulation at the target temperature is done for 0.3 ps in which the stress tensor is sampled in ten equal intervals from 0.2 ps to 0.3 ps and the ten samples are averaged together at 0.3 ps. The time-averaged stress tensor is then used to determine the elastic constants. The results of positive and negative deformations are averaged for each elastic constant. Application of the Voigt-Reuss-Hill approximation [36–38] to the calculated elastic constants yields values for bulk modulus,  $B_0$ , shear modulus, G, and Young's modulus, E. Using this method, we calculate the bulk modulus of cubic SiC to be 225 GPa at 300 K, which agrees with the value reported by Tersoff (220 GPa) [32].

#### 3. Results and discussion

#### 3.1. Impact of density

We start our investigation of the elastic properties of SiCO by comparing models with identical chemical compositions but different densities. Hence, in a system with the same glass composition and content Cfree:Si, we only vary the volume of the simulation box. Furthermore, we compare only data for models generated using the same T<sub>max</sub>. Comparison is also made only for data attained using the same simulation temperature during dynamic simulations of moduli. Results are shown in Fig. 2 for three selected compositions. In general, we find that the elastic response of SiO<sub>2</sub> and SiCO is aligned with predictions of elastic medium theory: more dense models exhibit higher elastic moduli [39]. Similar trends were computed previously for stoichiometric SiCO glass using DFT calculations [25]. In fact, Colombo et al. observed that Young's modulus increased with increasing density for SiCO ceramic foams [40]. Without quantifying dependencies in greater detail, we find that the slope of the relation moduli versus density depends on the composition of the glass phase, T<sub>max</sub> used for



Fig. 3. (a) Shear modulus and (b) Young's modulus for models with C content  $C_{free}$ :Si = 0.5, density  $\rho = 2.2 \text{ g/cm}^3$ , and composition SiO<sub>2</sub> + 0.5  $C_{free}$ , Si<sub>5</sub>CO<sub>8</sub> + 2.5  $C_{free}$ , and Si<sub>2</sub>CO<sub>2</sub> +  $C_{free}$  generated using  $T_{max} = 4000$  K. Elastic constants are calculated in triplicate for each of 3 independently generated models. Error bars represent standard error. Lines are provided to guide the eye.

model construction, and the temperature used for the dynamic simulation of elastic moduli.

#### 3.2. Impact of glass composition

We next assess the impact of the composition of the glass matrix in SiCO on its elastic properties. Thus, for models comprising the same free carbon content  $C_{free}$ :Si and density  $\rho$ , and generated using the same  $T_{max}$ , we analyze the dependency of elastic moduli on the composition of the glass matrix. In Fig. 3, we show the temperature dependency of moduli (between 100 K and 2000 K) for models with a free carbon content  $C_{free}$ : Si = 0.5. Before discussing the trend, we note that the error margin increases significantly at higher temperatures. This error margin is considerably reduced in large models, as shown below.

We observe that the higher the SiC content in the glass, the higher the elastic moduli. This trend is found for all combinations of C content, density, and  $T_{max}$ , albeit to a different extent in each case. The result is

hardly surprising, given that both amorphous and crystalline SiC [41, 42] have higher elastic moduli than most amorphous and crystalline forms of SiO<sub>2</sub> [43,44]. The glass matrix of SiCO can be regarded as a solid solution of both components. For models of glassy SiCO without free carbon, this trend was previously reported based on DFT calculations, albeit for much smaller models [25].

Experimentally, SiCO samples with very low amounts of excess carbon (SiC<sub>0.31</sub>O<sub>1.39</sub> + 0.07 C) have been synthesized and measured to have Young's modulus between 90 and 100 GPa [45]. The Young's moduli of SiCO samples with higher amounts of free carbon (12 – 54 wt % C<sub>free</sub>) are 77 – 108 GPa [22]. Under high load, the Young's modulus of SiCO with composition SiC<sub>0.8</sub>O<sub>1.6</sub> has been measured at 180 ± 30 GPa [46]. Our computed values of Young's modulus for the selected SiCO compositions fall within experimental ranges. However, elastic moduli for the Si<sub>2</sub>CO<sub>2</sub> + C<sub>free</sub> are higher due to the high SiC content in the SiCO glass.

We observe that elastic moduli decrease with increasing simulation



Fig. 4. A. Shear mofdulus and b. Young's modulus vs free carbon content,  $C_{free}$ :Si ratio *n*, for models of Si<sub>5</sub>CO<sub>8</sub> + 5*n*C<sub>free</sub>, SiO<sub>2</sub> + *n*C<sub>free</sub>, Si<sub>2</sub>CO<sub>2</sub> + 2*n*C<sub>free</sub> generated at T<sub>max</sub> = 3000 K with  $\rho = 2.2 \text{ g/cm}^3$ . C content C<sub>free</sub>:Si *n*, density  $\rho = 2.2 \text{ g/cm}^3$ , T<sub>max</sub> = 3000 K. Elastic constants are calculated in triplicate for each of 3 independently generated models. Error bars (if larger than the symbol) represent standard error. Simulations are done at 300 K. Lines are provided to guide the eye.



Fig. 5. a. Shear modulus and b. Young's modulus of  $Si_5CO_8 + 10 C_{free}$  models (39,360 atoms, a=7.9 nm, 2.2 g/cm<sup>3</sup>) generated at  $T_{max} = 4000$  K. C content  $C_{free}$ :Si = 0.5, 1, 2, 3, density  $\rho = 2.2$  g/cm<sup>3</sup>,  $T_{max} = 4000$  K. Elastic constants are calculated in triplicate for each of 3 independently generated models. Error bars represent standard error. Lines are provided to guide the eye.

temperature for the selected SiCO compositions. Generally, elastic properties of materials decrease with increasing temperature [47,48]. However, SiO<sub>2</sub> glass displays a peculiar anomalous behavior since its moduli tend to increase with increasing temperature [49,50]. Interestingly, experimental studies [21,51,52] indicate a similar increase of Young's modulus of SiCO glass with increasing temperature. However, these studies measured the Young's modulus of fully phase-separated SiCO glass, which consists of crystalline SiC, Cfree (if excess carbon present), and a glassy SiO<sub>2</sub>-rich matrix [14]. Of the three phases in phase-separated SiCO glass, only SiO2 exhibits anomalous elastic behavior [49,50], likely the consequence of a hypothetical amorphous-amorphous transformation [53,54]. Stabler et al. [51] suggests that the glassy SiO2-rich matrix dominates the temperature dependence of Young's modulus in SiCO glass-ceramics. Our SiCO models are not fully phase separated and do not exhibit a glassy SiO<sub>2</sub>-rich matrix; thus, there is no anomalous behavior, and generally, Young's modulus decreases with increasing temperature.

#### 3.3. Impact of free carbon content

We then investigate models with different free carbon content Cfree: Si, while keeping the model density and composition of the glass matrix identical. Results of shear modulus G and Young's modulus E for a series of such models generated at the same  $T_{max}$  are shown in Fig. 4. We find that elastic moduli increase as the free carbon content increases as long as other parameters remain constant. The relation between modulus and carbon content appears approximately linear within the range of compositions studied here. These results seem to contradict recent experimental studies by Sorarù et al. [22]. The authors concluded that Young's modulus of SiCO ceramics decreases with increasing Cfree content. We note, however, that the densities of the investigated samples decreased with increasing Cfree content. Therefore, their Cfree content is strongly correlated to density, and the impact of one variable cannot be distinguished from the effects of the other. As we pointed out in the preceding section, decreasing density causes decreasing moduli, and the apparent disagreement can be remedied this way.

To gain further insight into the impact of the free carbon on a modulus *M*, we seek the contribution of the carbon phase to moduli of the compound models. We analyze this through a simple mixing model:  $M_{\text{SiCO:Cfree}} = x_{\text{SiCO}} * M_{\text{SiCO}} + x_{\text{Cfree}} * M_{\text{Cfree}} (x_i \text{ is the mass fraction of glass and free carbon phase), into which we insert moduli for the SiCO glass to extract moduli of the carbon phase. To obtain moduli <math>M_{\text{SiCO}}$  of SiCO glass

phases, we extrapolate the data shown in Fig. 4 to zero Cfree content. For SiO<sub>2</sub> this procedure yields  $B_0 = 64$  GPa, G = 37 GPa, and E = 89 GPa. (each  $\pm$  2 GPa) Performing simulations for pure SiO<sub>2</sub> (24,600 atoms,  $T_{max}$ =2000 K,  $\rho = 2.2$  g/cm<sup>3</sup>) under conditions similar to those used for SiCO:C<sub>free</sub> models, we find  $B_0 = 58$  GPa, G = 34 GPa, E = 85 GPa (each  $\pm$  2 GPa). These results are well aligned with the extrapolation towards zero C content. We note that the computed bulk modulus for SiO<sub>2</sub> glass is considerably higher than experimentally reported ( $B_0 \approx 36$  GPa, [49]). A similar extrapolation analysis yields B, G, and E of 66, 36, and 91 GPA, respectively, for Si<sub>5</sub>CO<sub>8</sub>. For Si<sub>2</sub>CO<sub>2</sub>, we obtain 84, 50, and 125 GPa for B, G, and E, respectively. We then insert the extrapolated data into the mixing model and apply it to the data shown in Fig. 4. The (hypothetical) moduli  $M_{\rm Cfree}$  of the carbon phase are obtained through best fits. We obtain reasonable agreement for a bulk modulus of the carbon phase  $B_{\text{Cfree}}$  between 90 and 111 GPa, a shear modulus  $G_{\text{Cfree}}$  within 70 – 93 GPa, and a Young's modulus  $E_{Cfree}$  between 200 and 250 GPa. Note that these values are extracted under the assumption of a mixing model based on mass fraction. The moduli extracted from the compound models can then be compared to data computed through simulations of a large model of graphite:  $B\,=55$  GPa,  $G\,=87$  GPa, and  $E\,=171$  (all  $\pm$  1 GPa). We also simulated (glass-free) models of a morphous carbon along the same protocol and received B = 166 GPa, G = 176 GPa, and E = 390 GPa (all  $\pm 1$  GPa) – in agreement with recently reported values [55]. We find that – within a simple mixing model – the free carbon phase's impact on a compound model's elastic moduli is larger than expected from mixing graphite but smaller than expected by mixing pure amorphous carbon to glassy SiCO. Overall, its impact falls between contributions expected from adding graphite or amorphous carbon.

Increasing the simulation temperature at which elastic moduli are computed, we find that all moduli decrease with increasing temperature. This is shown in Fig. 5 for shear modulus and Young's modulus of selected models of SiCO (compare Fig. 3 as well). The trend holds regardless of the amount of free carbon, as simulation temperature does not change the impact of free carbon on elastic properties. Models with higher free carbon content generally have higher shear and Young's modulus for any given temperature in the investigated range. Increasing the carbon content from  $C_{\rm free}$ :Si ratio = 0.5 to  $C_{\rm free}$ :Si ratio = 3 results in almost doubling shear and Young's modulus.

#### 3.4. Impact of carbon morphology

The most striking result we found in our investigation is the impact of



Fig. 6.  $Si_5CO_8 + 10 C_{free}$  models (39,360 atoms; a=7.9 nm; 2.2 g/cm<sup>3</sup>) generated at a.  $T_{max}$ =2000 K, b.  $T_{max}$ =4000 K, c.  $T_{max}$ =6000 K, d.  $T_{max}$ =8000 K. C content  $C_{free}$ :Si = 2, density  $\rho$  = 2.2 g/cm<sup>3</sup>. Only C atoms (black) are shown.



**Fig. 7.** Young's modulus plotted as a function of  $T_{max}$  used in model generation. Si<sub>5</sub>CO<sub>8</sub> + 5*n*C<sub>free</sub> models with  $\rho = 2.2$  g/cm<sup>3</sup> and C<sub>free</sub>:Si = *n*, with *n* = 0.5, 1, 2, and 3. Elastic constants are calculated in triplicate for each of 3 independently generated models. Error bars represent standard error. Simulations are done at 300 K. Lines are provided to guide the eye.

the morphology of free carbon on elastic properties. Different carbon morphologies can be attained by using different maximum temperatures  $T_{max}$  during structure generation while keeping all other parameters (composition, density) identical. For instance, generating a structure at  $T_{max} = 2000$  K yields a model with small groups of carbon atoms,

including C<sub>6</sub>-rings (like benzene) and short chains, see Fig. 6a. The groups are dispersed and isolated within the surrounding glass matrix. Thus, the carbon structure is not extended, and C-C bonds do not form a continuous path throughout the model. Increasing  $T_{\text{max}}$  to 4000 K yields an extended C-C bond network with continuous paths connecting almost all C atoms. Only a minor portion of C atoms remain isolated. Indeed, most C atoms are three-connected (sp<sup>2</sup>-like) and found within six-membered carbon rings, like aromatic carbon segregations (Fig. 6b). The network is best characterized as "sheet-like". Notably, small amounts of SiCO glass phase separate the curved 2D sheets of carbon from each other. Generating the structure at an even higher T<sub>max</sub> (6000 K or 8000 K) results in the formation of predominantly tubular networks (Fig. 6c and d). Details of this "genesis" of the carbon structure within SiCO and how it depends on composition, heating rate, and other simulation parameters will be given elsewhere. Note that all models shown in Fig. 6 have the same composition and density.

We then computed elastic moduli for these models with identical composition, carbon content, and density but different carbon morphology (as directed via  $T_{max}$ ). Results, exemplified for structures with glass composition  $Si_5CO_8$  and different amounts of free carbon, are presented in Fig. 7. The data shows that elastic moduli in SiCO structures can vary by up to 25% only by changing the morphology of the carbon segregation. The impact of morphology is more pronounced the higher the carbon content is. At low free carbon content,  $C_{free}$ : Si = 0.5, only minor differences in moduli appear; thus, the amorphous glass matrix dominates elastic properties. Conversely, at high free carbon content,  $C_{free}$ :Si = 3, the impact of free carbon morphology is substantial, with up to 25% difference (136 GPa vs. 172 GPa for C:Si=2; 157 GPa vs. 200 GPa for C:Si=3). Therefore, at high  $C_{free}$  content – when a contribution of carbon to mechanical properties is more substantial – the spatial distribution of carbon and its morphology within the compound



**Fig. 8.** Young's modulus vs. simulation temperature for models of  $Si_5CO_8 + 5nC_{free}$  generated at  $T_{max}$  between 2000 K and 8000 K with a. n = 0.5, b. n = 1.0, c. n = 2.0, d. n = 3.0 where  $n = C_{free}$ . Si. density  $\rho = 2.2$  g/cm<sup>3</sup>. Elastic constants are calculated in triplicate for each of 3 independently generated models. Error bars represent standard error. Lines are provided to guide the eye.

is essential. Overall, we find that amorphous SiCO – with identical composition and density – exhibits significant variation in its mechanical properties depending on the extent and morphology of carbon segregations.

Our results highlight that caution must be applied when using a "rule-of-mixture" to estimate or analyze properties in SiCO compound systems. Rouxel et al.[21] followed such an approach when comparing elastic properties of SiCO with a volume-weighted sum of elastic properties of constituent phases. Such an approach will yield only a rough approximation since it neglects a possible impact of the morphology of the phases. Our calculations predict that the morphology of the free carbon phase does have a significant effect on elastic properties. Therefore, even when model composition and density are identical, a simple rule-of-mixture may not be sufficient in estimating the elastic properties of SiCO.

We also investigated the temperature dependence of elastic properties of models with different carbon morphology, see Fig. 8. Consistent with the results shown above, we find that the moduli of SiCO generally decrease with increasing temperature. At low free carbon content, here  $C_{free}$ :Si = 0.5, elastic properties decrease by 10 – 40% when comparing data obtained at 300 K to that computed at 2000 K. At high free carbon content,  $C_{free}$ :Si = 3, elastic properties decrease between 20% and 40% within the investigated temperature range. There is a subtle impact of carbon morphology, identified through  $T_{max}$  (the temperature at which models have been generated), on the "consistency" or "thermal stability" of elastic moduli. Models generated at  $T_{max}=6000$  K and 8000 K have more consistent elastic properties and tend to decrease less at higher temperatures than models generated at  $T_{max}=2000$  K, 3000 K, and 4000 K.

#### 3.5. Finite-size effects

Our final investigation addresses the size of models used in this study. The initial series of our models had a characteristic unit cell extension (box dimension) of 10 nm and contained 24,000–50,000 atoms, depending on composition. A close look at the tubular segregations emerging for  $T_{max}$  of 6000 K and 8000 K, see Fig. 6c and d, shows that these segregations have diameters of about 2 nm and 4 nm, respectively. Since these fall well into the size of the simulation cell, the periodic boundary conditions are likely to impact structure generation and property calculations. To investigate such finite-size effects, we considered the composition  $Si_5CO_8 + 10 C_{free}$  with a density of 2.2 g/ cm<sup>3</sup> and generated 8 times and 64 times larger models. These comprise simulation box dimensions of approximately 20 nm and 40 nm, respectively. Three different series of 20 nm models and one series of 40 nm models were generated. We maintained all procedural



a.

b.

Fig. 9.  $Si_5CO_8 + 10 C_{free}$  with  $C_{free}$ : Si = 2 and density  $\rho = 2.2 \text{ g/cm}^3$ ) generated at a.  $T_{max} = 6000 \text{ K}$  and b.  $T_{max} = 8000 \text{ K}$ . The models comprise about 2.5 million atoms within a simulation box of approximately 40 nm.



Fig. 10. Young's modulus of  $Si_5CO_8 + 10 C_{free}$  ( $C_{free}$ :Si = 2, density = 2.2 g/cm<sup>3</sup>) as a function of simulation temperature for models of different size attained at a.  $T_{max} = 2000$  K and b.  $T_{max} = 8000$  K. A unit cell of a 10 nm model contains 39,360 atoms, a 20 nm model contains 314,880 atoms, and a 40 nm model contains 2519,040 atoms. Three models each are generated for 10 and 20 nm, while only a single model is generated with a size of 40 nm. Elastic constant calculations for all models are done in triplicate. Error bars represent standard error. Lines are provided to guide the eye.

parameters, including heating rates, as outlined in the method section for these simulations. In Fig. 9, we show 40 nm models generated at  $T_{max}$ = 6000 K and 8000 K. The model obtained at  $T_{max}$  = 6000 K still resembles its smaller counterpart in carbon morphology. The same trend holds for models obtained at even lower temperatures. On the other side, the 40 nm model generated at  $T_{max}$  = 8000 K exhibits a 3D tubular network, which is different from the 2D tubular networks the smaller 10 nm models generated at the same  $T_{max}$  exhibit (see Fig. 6d).

We computed Young's moduli of Si<sub>5</sub>CO<sub>8</sub> + 10 C<sub>free</sub> models in three different sizes, 10, 20, and 40 nm, generated using T<sub>max</sub> = 2000 K and T<sub>max</sub> = 8000 K and compared them with each other, see Fig. 10. Young's moduli calculated for 20 nm and 40 nm models agree with data previously obtained for the 10 nm model. We corroborate the ~20% difference in Young's moduli between models with identical composition and density but generated at different T<sub>max</sub> (2000 K vs. 8000 K). Therefore, the impact of carbon morphology on elastic properties persists for models in larger simulation boxes. On the other side, a noticeable structural difference between the 10 nm and the larger models generated at T<sub>max</sub> = 8000 K relates to a 2D tubular network present in the former and 3D tubular networks found in the latter.

The most apparent benefit of simulating models of larger size emerges in simulations at elevated temperatures. The uncertainty obtained for data of a single model is much smaller, and the consistency between different models obtained through the same protocol is much higher. The data shown in Fig. 10 exemplifies this for a composition  $Si_5CO_8 + 10 C_{free}$ : above 500 K. Young's moduli of 10 nm models generated with  $T_{max} = 2000$  K exhibit substantial uncertainty. In contrast, 20 nm models provide consistent results and agree with the data of the 40 nm model. Trends are similar for models generated at  $T_{max} = 8000$  K, which exhibit larger carbon segregations. Young's moduli computed for the larger models carry smaller errors and are consistent with each other. However, while the larger size models exhibit higher fidelity, we notice that all trends observed for small models are found in larger models as well – with the latter corroborating the results of the former.

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#### 4. Conclusions

Using molecular dynamics simulations with the Tersoff potential, we calculate elastic properties of SiCO models with different glass

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compositions, densities,  $C_{free}$  content, and carbon morphology. We examine each parameter individually and disentangle dependencies that are difficult to separate in experimental studies. In general, our results align well with expectations and previous experimental observations. In particular, higher elastic moduli are found for models with higher SiC content in the SiCO glass and for models with higher density. Dynamic simulations at finite temperatures show that for any given composition of SiCO, the elastic moduli decrease with increasing temperature. Our results then indicate that – when maintaining the density of a system – increasing the amount of  $C_{free}$  yields higher elastic moduli. While this appears to contradict previous experimental results [22], we show that density variations dominate the underlying experimental data in this study.

Finally, we uncover a "hidden" parameter – the morphology of the  $C_{free}$  phase – that impacts the mechanical properties of SiCO. Models with identical composition and density but different morphology of the same amount of  $C_{free}$  exhibit different mechanical properties. In general, models with dispersed small fragments of  $C_{free}$  have lower moduli than models with extended networks or tubular segregations of  $C_{free}$ . The effect can reach up to 25% of the mechanical property for models comprising large amounts of "free" carbon. As a consequence, caution has to be exerted if a simple rule-of-mixture based on the composition or volume content is used to predict the mechanical properties of SiCO. At this time, we are not aware of any experimental method that can quantify the morphology of "free" carbon embedded in the amorphous matrix of SiCO. Hence, we term it "hidden" and direct approaches for experimental characterization need to be developed to attain quantitative measures.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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