# 3D Periodic and Interpenetrating Tungsten–Silicon Oxycarbide Nanocomposites Designed for Mechanical Robustness

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**ABSTRACT:** Metal-ceramic nanocomposites exhibit exceptional mechanical properties with a combination of high strength, toughness, and hardness that are not achievable in monolithic metals or ceramics, which make them valuable for applications in fields such as the aerospace and automotive industries. In this study, interpenetrating nanocomposites of three-dimensionally ordered macroporous (3DOM) tungsten-silicon oxycarbide (W-SiOC) were prepared, and their mechanical properties were investigated. In these nanocomposites, the crystalline tungsten and amorphous silicon oxycarbide phases both form continuous and interpenetrating networks, with some discrete free carbon nanodomains. The W-SiOC material inherits the periodic structure from its 3DOM W matrix, and this



periodic structure can be maintained up to 1000 °C. In situ SEM micropillar compression tests demonstrated that the 3DOM W–SiOC material could sustain a maximum average stress of 1.1 GPa, a factor of 22 greater than that of the 3DOM W matrix, resulting in a specific strength of 640 MPa/(Mg/m<sup>3</sup>) at 30 °C. Deformation behavior of the developed 3DOM nanocomposite in a wide temperature range (30-575 °C) was investigated. The deformation mode of 3DOM W–SiOC exhibited a transition from fracture-dominated deformation at low temperatures to plastic deformation above 425 °C.

**KEYWORDS:** High-temperature mechanical behavior, strength, three-dimensionally ordered macroporous material, interpenetrating metal—ceramic composite, micropillar compression

## 1. INTRODUCTION

Advanced ceramic materials provide enhanced thermal stability, high hardness, and good chemical/oxidation resistance.<sup>1</sup> They are attractive for many high-performance applications in the automotive and aerospace industries, defense, and energy generation (fuel cells, thermoelectric generators, and nuclear reactors).<sup>2–4</sup> However, lacking a method of energy dissipation similar to that found in metals (plastic deformation), ceramics have poor flaw tolerance, making their failure unpredictable under high mechanical loads or in thermal-cyclic environments.

A breakthrough toward expanding the application range of ceramics was the development of metal–ceramic composites. The incorporation of metals into ceramics enhances the toughness and flaw tolerance of the overall materials through local plastic deformation and mechanical decoupling of the phases during fracture. For example, metal–matrix composites (MMCs) are a well-known and already commercialized type of metal–ceramic composites. Another relatively new class of metal–ceramic composites is interpenetrating composites (IPCs) that consist of three-dimensionally interpenetrating matrices of metal and ceramic phases.<sup>5</sup> One major advantage of IPCs is that they provide an opportunity for achieving the full functionality of different phases because these are all continuous throughout the structure.<sup>6,7</sup> IPCs are also good

candidate materials when isotropic mechanical/physical properties are desired.  $^{1,7}$ 

In addition to tuning the compositions, introducing size effects is another efficient way to improve the mechanical properties of materials.<sup>8</sup> The "smaller is stronger" paradigm has been observed in both single-component materials and composites.<sup>8-12</sup> For nanocomposites, especially, an interfacedriven strengthening paradigm occurs. The abundant interfaces between components in nanocomposites enhance their mechanical properties by acting as sources, sinks, barriers, or storage sites for dislocations active in the metal phase.<sup>17</sup> Additionally, the mechanical response of the composite can be tuned by controlling the degree of bonding between the phases. Strong interfacial bonding is shown to increase the toughness of MMCs with an isotropic microstructure,<sup>15–17</sup> while weak bonding is preferred in many brittle matrix, fiberreinforced composites to allow for mechanical decoupling between the fiber and the matrix.<sup>18,19</sup>

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Metal-ceramic nanocomposites are traditionally synthesized by mixing the precursors and then converting them into nanocomposites under high pressures or at high temperatures.<sup>20,21</sup> One drawback of these synthetic routes is the lack of control over the microstructures. One route, powder metallurgy, lacks synthetic control of structural features, resulting in stochastic distributions of pore and grain sizes and configurations, which are crucial details influencing the mechanical properties. Multilayer metal-ceramic nanocomposites are a relatively new but well-studied type of metal-ceramic nanocomposites.<sup>11,14,22</sup> Their microstructures can be controlled rather precisely with a layer thickness less than 5 nm through physical vapor deposition.<sup>11</sup> However, these materials have anisotropic properties, which limit their range of application. In this context, well-designed isotropic microstructures are desired for further development of metalceramic nanocomposites that can potentially enhance the overall mechanical properties of the materials and provide more opportunity to study the relationships between the nanoscopic structures and macroscopic mechanical properties of metal-ceramic nanocomposites.

Here, we introduce a novel method to fabricate metalceramic nano-IPCs with a periodic structure. In this method, three-dimensionally ordered macroporous (3DOM) materials are used to control the architecture of the IPC. 3DOM materials are porous solids that feature a highly ordered, fully interconnected, and periodic porous structure with uniform pore sizes, typically a few hundred nanometers in diameter.<sup>23,24</sup> 3DOM materials have been extensively studied, and they have been created in a wide variety of compositions,<sup>25,26</sup> such as carbon, ceramics (SiO<sub>2</sub>, MgO, Cr<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>), metals, and metal alloys (W, WMo, Mn<sub>3</sub>Co<sub>7</sub>, Ni<sub>x</sub>Co<sub>1-x</sub>).<sup>27,28</sup> The mechanical properties of 3DOM materials have drawn attention recently. Having ordered and periodic structures with nanosized ligaments, 3DOM materials in certain compositions have exhibited high strength.<sup>29-32</sup> For example, Pikul et al. demonstrated that 3DOM Ni with skeletal grains having a size of  $\sim 15$  nm has a yield strength that exceeds that of bulk Ni by a factor of more than 4 because the ligaments become nanostructured.<sup>29</sup> When a 3DOM material is used as the scaffold, another component can be introduced into the interconnected voids to form an IPC type nanocomposite. By varying the combinations of the materials, enhanced mechanical properties, such as higher yield strength and better thermal stability, are expected in the synthesized nanocomposites. In the present work, we demonstrate a synthetic approach to fabricate the metal-ceramic nano-IPC material with 3DOM W ligaments infiltrated with a polymer-derived SiOC ceramic phase.

Tungsten, a body-centered cubic metal, was selected in part because it undergoes a brittle–ductile transition (BDT) in the temperature range 100–200 °C.<sup>33</sup> Notably, large increases in deformability have been observed in 3DOM W when the temperature was increased to 225 °C.<sup>30</sup> This behavior facilitates mechanical characterization when both phases are brittle at room temperature as well as when the tungsten exhibits increased plasticity at moderately elevated temperatures. SiOC polymer-derived ceramics (PDCs) are widely studied given their flexibility (compared to other ceramicprocessing methods) in the preparation of ceramic composites, fibers, and net-shaped monolithic components.<sup>34,35</sup> The liquid precursors can be cured in the temperature range 200–400 °C to form soft (Young's Modulus (*E*) < 1 GPa) polymers. Upon further heating, the organic-to-inorganic conversion (pyrolysis) produces an amorphous ceramic with increased stiffness ( $E \approx$ 150 GPa)<sup>36</sup> containing fine-scale (typically nanometers to micrometers) porosity generated during the escape of gaseous hydrocarbons during pyrolysis.<sup>37</sup> The as-pyrolyzed material is understood to have a nano-domain structure comprising Si-O-based regions surrounded by turbostratic or graphitic carbon.<sup>38</sup> Heat-treatment temperatures above 1200 °C are typically required to crystallize the SiOC. In addition to its processability, recent work has shown that mesoporous SiOC can sustain significant, recoverable elastic strains and ductilelike deformation.<sup>39</sup> The hypothesis underpinning this work is that the integration of the ordered 3DOM W and porous SiOC will produce a resilient IPC-type nanocomposite suitable for extreme conditions, such as high temperatures, pressures, and radiation fluxes. One such example is the divertor of a fusion reactor, where tungsten alloys are already employed, due in part to a tungsten's low degree of sputtering and low erosion at high temperatures.<sup>40</sup>

To prepare the nanocomposite, hereafter referred to as 3DOM W-SiOC, the 3DOM W scaffold was first synthesized through colloidal crystal templating.28,41 This scaffold was infiltrated with the preceramic polymer precursor SMP-10, a polycarbosilane, and pyrolyzed, yielding a SiOC ceramic phase in the voids of 3DOM W. The 3DOM W-SiOC material consisted of continuous phases of crystalline tungsten and amorphous silicon oxycarbide with some discrete free carbon. The 3DOM nanocomposite material featured a highly periodic structure, which remained thermally stable up to 1000 °C. Mechanical properties of the 3DOM W-SiOC material were investigated using micropillar compression tests in the temperature range from 30 to 575 °C. 3DOM W-SiOC showed a maximum stress of 1.1 GPa at 30 °C, a factor of 22 greater than the 3DOM W matrix alone. The deformation mode of the material exhibited a transition above 425 °C from fracture-dominated deformation to plastic deformation.

#### 2. EXPERIMENTAL SECTION

**2.1. Materials.** The following chemicals were used as-received: 2,2'-azobis(2-methylpropionamidine) (>99%), methyl methacrylate (99.9%), tungsten monocrystalline powder (>99.9%, 0.6–1  $\mu$ m sizes) from Aldrich Chemical Company; glacial acetic acid (ACS grade) from VWR International; hydrogen peroxide (certified ACS, 30%), tetrahydrofuran (THF, certified ACS) from Fisher Chemical; methanol (ACS reagent grade, >99.8%), potassium bromide (FT-IR grade, ≥99% trace metals basis) from Sigma-Aldrich; StarPCS SMP-10, a commercially available allylhydridopolycarbosilane polymer, from Starfire Systems, Inc; PELCO high-temperature carbon paste from Ted Pella, Inc; hydrogen gas (industrial grade) and argon gas (ultrahigh-purity/zero grade) from Matheson.

**2.2.** Synthesis of 3DOM W–SiOC Nanocomposites. Synthesis of Polymethyl Methacrylate Colloidal Crystal Templates. Polymethyl methacrylate (PMMA) spheres with average diameters of 397  $\pm$  4 nm were synthesized by emulsifier-free emulsion polymerization following established methods.<sup>42</sup> The PMMA spheres were then assembled into colloidal crystals in the form of thin films by convective self-assembly, following a previously reported method.<sup>30</sup> The detailed steps for assembling the PMMA colloidal crystal films are provided in the Supporting Information.

Synthesis of 3DOM W. 3DOM W was synthesized following a previously reported method: a water/methanol solution (4:1 in volume) of 1 M acetylated peroxotungstic acid was used to infiltrate the PMMA colloidal crystal template, followed by heat treatment under H<sub>2</sub> (2 °C/min to 310 °C, dwelling at 310 °C for 2 h, then 5 °C/min to 800 °C, and dwelling at 800 °C for 1 h).<sup>30,41</sup> The PMMA template was removed during the heat treatment and 3DOM W was

formed. The 3DOM W product was in the form of thin, strip-like pieces with a flat surface. The pieces had lateral dimensions ranging from 50 to 200  $\mu$ m, with thicknesses between 5 and 20  $\mu$ m. The detailed steps for fabricating the 3DOM W material are provided in the Supporting Information.

Synthesis of 3DOM W-SiOC. 3DOM W pieces were infiltrated with the SMP-10 preceramic precursor, and the mixture was placed in a Schlenk flask. Dynamic vacuum (200-500 torr) was applied to promote the infiltration of SMP-10 into the voids of 3DOM W. The infiltrated 3DOM W was then pyrolyzed under Ar (2 °C/min to 800 °C with no dwell time) to form the 3DOM W-SiOC material during pyrolysis. More detailed steps for fabricating the 3DOM W-SiOC material are provided in the Supporting Information. For multiple infiltrations, 50 vol % SMP-10/50 vol % THF was used as the precursor for the second and third infiltration steps; 30 vol % SMP-10/70 vol % THF was used as the precursor for the fourth and fifth infiltration steps. The composite materials were pyrolyzed following each infiltration step (2 °C/min to 800 °C under Ar with no dwell time before allowing the furnace to cool). Some of the 3DOM W-SiOC materials were heated further to monitor structural and compositional changes at high temperatures (1 °C/min to either 1000 °C or 1300 °C with no dwell time after reaching 800 °C nor any dwell time before allowing the furnace to cool).

2.3. Characterization. Fourier transform infrared (FT-IR) spectra were obtained in both attenuated total reflectance (ATR) and transmission modes. The ATR-IR spectra were obtained using a Bruker Alpha-P Platinum FT-IR spectrometer equipped with a Platinum ATR sampling module hosting a diamond crystal (single bounce). The transmission IR spectra were obtained using a Nicolet Magna 760 IR spectrometer, using KBr pellets of the sample (mass ratio of sample/KBr = 1:100. Raman spectroscopy was performed using a WITec Alpha300R confocal Raman microscope with 532.0 nm laser radiation, and the scattering was detected using a DV401 CCD thermoelectrically cooled detector. Nitrogen sorption experiments were performed on a Quantachrome Autosorb-iQ2 analyzer using an ultrahigh-purity-grade nitrogen adsorptive. All samples were degassed under dynamic vacuum (0.003 mTorr) at 120 °C for 12 h before analyses. Brunauer-Emmett-Teller surface areas were evaluated from the adsorption isotherms in the relative pressure range of 0.01-0.20. Pore size distributions were obtained from nitrogen isotherms using nonlocal density functional theory methods included in Quantachrome software and assuming nitrogen adsorption at 77 K in slit-shaped carbonaceous pores. Powder X-ray diffraction patterns were collected using a PANalytical X'Pert Pro diffractometer. X-rays were generated with a Co anode (K $\alpha$  radiation,  $\lambda$  = 1.789 Å) operating at a 45 kV accelerating voltage and a 40 mA emission current. Scanning electron microscopy (SEM) was performed using a JEOL-6500 field emission scanning electron microscope with an accelerating voltage of 5.0 kV. The fast-Fouriertransform (FFT) image analysis was performed via the Gatan Microscopy Suite (GMS) software. SEM combined with energydispersive X-ray spectroscopy (SEM-EDS) was conducted using a JEOL JXA-8900 electron probe microanalyzer equipped with an UltraDry-SDD detector and operating with an accelerating voltage of 10.0-15.0 kV. All samples were coated with a 50 Å platinum film prior to SEM imaging. Transmission electron microscopy (TEM) images were obtained using an FEI Tecnai T12 transmission electron microscope with an accelerating voltage of 120 kV and a LaB<sub>6</sub> filament. Samples were sonicated for 5 min in ethanol and then deposited onto carbon film-coated copper grids, and the solvent was allowed to evaporate under ambient conditions.

**2.4.** Nanoindentation. Preparation of the Specimen. The fabricated 3DOM W–SiOC pieces were transferred and mounted onto a steel AFM disk using PELCO high-temperature carbon paste. The specimen was then cured at 90 °C for 3 h and 270 °C for another 3 h (5 °C/min from 90 to 270 °C). Micropillars with a diameter of approximately 10  $\mu$ m and an aspect ratio of 2 were produced via an annular milling protocol in an FEI Quanta 200 3D DualBeam focused ion beam (FIB) scanning electron microscope using gradually reducing diameter annuli at an accelerating voltage of 30 kV and a

beam current of 5 nA. Final smoothing annuli were performed with a lower beam current of 1 nA to reduce taper and remove re-deposited material to more clearly see the ligament structure for obtaining inplane strain maps of the deformed pillar during loading. Examples of these pillars are shown in Figure 4a,c,e,g.

Micropillar Compression. Samples were compressed in situ in a FEI Helios G4 UX dual beam FIB/SEM using a Hysitron PI88 Picoindenter (Bruker Nanosurfaces, Minneapolis, MN) equipped with an XR high-load transducer and a 20  $\mu$ m diameter diamond flat punch tip with a 60° cone angle. Pillars were compressed in displacement control at applied displacement rates of 10 nm/s corresponding to initial strain rates of approximately  $5 \times 10^{-4} \text{ s}^{-1}$ . After 1  $\mu$ m of displacement, a partial unload was performed to obtain the pillar stiffness. Both the sample and the indenter tip were heated to each testing temperature (30, 225, 425, and 575 °C) and allowed to thermally equilibrate for at least 30 min prior to compression testing. The data were corrected for the load-cell drift, substrate compliance, and contact-point corrections, which are described in detail in the Supporting Information. Stresses were calculated by dividing the load by the cross-sectional area of the top of the pillar, and strains were calculated as indenter displacement divided by the pillar height. The relative energies absorbed during deformation were calculated using the area under the stress-strain curve calculated via the Matlab trapz function, a trapezoidal numerical integration algorithm.

SEM images of the micropillar side wall were analyzed using digital image correlation (DIC) to obtain in-plane strain maps. These images were recorded from in situ videos at an angle approximately 20° from the normal. In DIC, the relative displacements of smaller regions within the deformed specimen are found with respect to a reference (undeformed) image. The features inherent to the 3DOM structure provided the pattern needed for the DIC algorithm to monitor deformation of the micropillar sidewall with the applied load. Videos recorded during the in situ compression of the 3DOM structure were separated into individual frames. To shorten the processing time, every third frame was used without additional image post-processing. DIC analysis was performed using an open-source software (Ncorr).<sup>43</sup> The applied subset radius was 30 nm, and the strain radius was 100 nm. The strain ( $\varepsilon_{yy}$ ) along the loading direction was obtained at different loading stages.

#### 3. RESULTS AND DISCUSSION

3.1. Synthesis of 3DOM W-SiOC Materials. The procedures for synthesizing the 3DOM W-SiOC materials are shown in Figure 1. A PMMA colloidal crystal template was first fabricated through convective self-assembly. 3DOM W was then synthesized by infiltrating the template with a tungsten precursor, followed by thermal reduction and template removal under a hydrogen atmosphere, resulting in the formation of 3DOM W in the body-centered cubic  $\alpha$ -W form (Figure S1a). Major cracks occurred naturally in the PMMA templates during the convective self-assembly process, where longitudinal cracks formed because of the tensile forces generated during water evaporation, and transverse cracks formed at the boundaries of wet and dry regimes as the water level decreased.<sup>44</sup> These cracks broke the colloidal crystals into individual strips (Figure S2b), which meant that the final 3DOM W products were also individual strips (Figure 2a). A single strip of 3DOM W had well-defined and periodic 3DOM regions (Figure 2b) with window openings of ~226 nm between adjacent cages and ligament widths of ~30 nm (Figure 2c).

3DOM W-SiOC was synthesized by infiltrating the interconnected void space of 3DOM W with polycarbosilane SMP-10, a preceramic polymeric precursor, followed by heat treatment under Ar. SMP-10 does not contain any oxygen, so theoretically it condenses and forms SiC during heat



**Figure 1.** Scheme summarizing the synthetic steps for fabricating 3DOM W–SiOC materials. PMMA spheres were first packed into colloidal crystals via convective self-assembly. The resulting PMMA colloidal crystals were used as a sacrificial template to fabricate 3DOM W materials. An SMP-10 polymeric precursor was then introduced into the voids of 3DOM W and pyrolyzed to form SiOC. The schematic of the final 3DOM W–SiOC material is based on the results of multiple characterization methods, which will be discussed in the following text.

treatment.<sup>37</sup> However, the oxygen was very difficult to avoid during the pyrolysis, which resulted in the formation of SiOC instead of SiC as the final ceramic phase (Figure S3). Although not as hard as SiC, SiOC materials have superior oxidation and corrosion resistance, especially at high temperatures. A detailed compositional analysis of the 3DOM W–SiOC is discussed in the next section.

The 3DOM W-SiOC nanocomposite maintained the 3DOM structure (Figure 2d,e), with the SiOC component present inside the pores of 3DOM W in the form of granular particles (Figure 2e,f). Differently sized voids were present throughout the SiOC phase. The textural mesopores in SiOC shown in the TEM image (Figure 2f) were likely caused by the volume shrinkage during the conversion of the liquid SMP-10 precursor to the solid SiOC phase. Extensive volume shrinkage has been observed in the preparation of polymer-derived ceramics using preceramic polymer precursors. Typically, the volume shrinkage can exceed 50% and sometimes reaches up to 80% for certain types of polymer precursors.<sup>45,46</sup> Differently sized pores and cracks are usually generated during the volume shrinkage. Additionally, some larger voids were observed in our material (Figure 2d). In addition to the influence of volume shrinkage, the formation of these large voids was possibly also due to incomplete SMP-10 precursor infiltration into certain regions of the porous tungsten scaffold prior to pyrolysis.

Given that denser materials could have better mechanical properties, multiple infiltrations of SMP-10, followed by pyrolysis were performed, in an attempt to introduce more SiOC into the system. However, on the basis of SEM images, no obvious improvement in pore filling was observed even after five cycles (each cycle refers to one-time infiltration, followed by pyrolysis, Figure S4). The evolution of the pore structure during multiple infiltrations was followed by N<sub>2</sub> physisorption analysis (Figure S5). 3DOM W-SiOC produced after one infiltration cycle (3DOM W-SiOC-1cycle) had a surface area (88  $m^2/g$ ) and a pore volume (0.11  $cm^3/g$ ) similar to 3DOM W-SiOC obtained after three infiltration cycles (3DOM W-SiOC-3cycles, 81 m<sup>2</sup>/g, 0.10 cm<sup>3</sup>/g). Additionally, 3DOM W-SiOC-1cycle and 3DOM W-SiOC-3cycles both possessed pores with similar diameters centered around 4 nm, indicating that multiple infiltrations did not introduce



# 3DOM W 3DOM W–SiOC



**Figure 2.** SEM (a–e) and TEM (f) images of 3DOM W (a–c) and 3DOM W–SiOC (d–f) materials at different magnifications. The positions of some W ligaments, the introduced SiOC, and some larger voids are marked in (d). Textural mesopores can be observed between the SiOC particles in (f). The FFT image as an inset in (b) was generated based on the selected area (10  $\mu$ m × 10  $\mu$ m) outlined by dashed lines; it confirms the periodicity of the 3DOM W structure in the viewing plane.

more precursor material. Therefore, 3DOM W–SiOC-1cycle was used for subsequent mechanical measurements.

**3.2. Composition and Structure of 3DOM W–SiOC.** The empirical composition of the 3DOM W–SiOC nanocomposite was determined to be  $W_{0.42}Si_{1.0}C_{1.8}O_{0.56}$  by SEM-EDS analysis (Figure S3 and Table S1). To further investigate the phases of the 3DOM W–SiOC material, selected area electron diffraction (SAED) (Figure 3) and powder XRD patterns (Figure S1a) were obtained. The major crystalline phase was identified to be  $\alpha$ -W by both techniques. When the 3DOM W region was excluded from the selected area (Figure 3c), no evidence for crystalline SiC or SiO<sub>2</sub> phases was observed in the SAED pattern, suggesting the presence of an amorphous SiOC phase.

Additional diffraction spots in one of the SAED patterns (Figure 3a) were ascribed to W<sub>2</sub>C (*Pbcn*, typically denoted  $\beta$ or  $\beta'$ -W<sub>2</sub>C). Equivalent reflections were not present in the XRD pattern (Figure S1a), likely due to the low mass percentage of the W<sub>2</sub>C phase in the overall 3DOM W–SiOC material. As elaborated in the Supporting Information, this

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Figure 3. TEM images and the corresponding SAED patterns of the 3DOM W–SiOC material. Three different areas were selected. Areas (a) and (b) included the 3DOM W ligaments and the internal SiOC phase. Area (c) was selected to avoid any 3DOM W region.

 $W_2C$  is likely a metastable phase attributed to a transient reaction between "free carbon" in the ceramic phase and the nanosized W ligaments in some localized areas (Figures S1b and S6). Free carbon has been an important consideration in the research field of PDCs.<sup>34,47</sup> It is formed as a result of phase separation when the polymeric precursor is processed at elevated temperatures. Free carbon usually exists in the form of nanocrystalline graphitic domains.<sup>47</sup> The free carbon formed during the processing of polymeric precursors can suppress further crystallization and phase separation in the PDC materials at higher temperatures by acting as a diffusion barrier.<sup>48,49</sup> However, free carbon can also compromise the strength and hardness of PDC materials.<sup>50</sup>

To confirm the possible presence of free carbon in the 3DOM W-SiOC materials, Raman spectroscopy was applied as a local and short-range probing tool. Multiple random areas of 3DOM W-SiOC were selected for the measurement (Figure S7). The characteristic D-band (around 1355 cm<sup>-1</sup>; only active with disorder in graphitic sheets and from edge regions) and G-band (around 1580 cm<sup>-1</sup>, originates from all sp<sup>2</sup> carbon sites) for carbon were observed in the 3DOM W-SiOC samples.<sup>51</sup> The intensities of the D- and G-bands varied at different areas, indicating that free carbon nanodomains were distributed non-uniformly throughout the 3DOM W-SiOC material (Figure S7a). The lateral size  $(L_a)$  of free carbon nanodomains (nanocrystalline graphite) in the 3DOM W-SiOC material was determined to be about 1.0 nm based on the Raman spectrum with the most distinguished D- and Gbands (Figure S7b). Additionally, the appearance of W-C

vibration peaks in some Raman spectra confirmed the formation of  $WC_x$  species in certain localized regions.

The relative content of free carbon present in the 3DOM W–SiOC was estimated based on the empirical formula  $(W_{0.42}Si_{1.0}C_{1.8}O_{0.56})$  derived from SEM-EDS (Figure S3). The formula of a stoichiometric SiOC material is  $SiO_{2(1-x)}C_{x'}$  in which a tetravalent carbon atom can be replaced by two divalent oxygen atoms. Whenever free carbon is generated inside the SiOC material, the composition becomes  $SiO_{2(1-x)}C_x + yC$ .<sup>52</sup> Therefore, the approximate composition of the 3DOM W–SiOC material can be resolved into 0.42W +  $Si_{1.0}O_{0.56}C_{0.72} + 1.1C$ .

To better understand the phase composition of the 3DOM W-SiOC nanocomposite, we investigated the state of the oxygen in this material. The possibility of oxygen-containing crystalline phases such as WO<sub>3</sub> and SiO<sub>2</sub> was excluded by both long-range (XRD, Figure S1a) and local (SAED, Figure 3; Raman, Figure S7b) characterization techniques. FT-IR spectroscopy provided more information about the bonding environment of the oxygen atoms in 3DOM W-SiOC (Figure S8). The dominant peaks in the ATR-IR spectrum for cured SMP-10 disappeared in the ATR-IR spectra of pyrolyzed SMP-10 and 3DOM W-SiOC, indicating the completion of the polymer-to-ceramic conversion process at 800 °C.<sup>49,53</sup> Instead, remarkably increased intensities below 1100 cm<sup>-1</sup> were observed in the ATR-IR spectra of pyrolyzed SMP-10 and 3DOM W-SiOC, corresponding to Si-C vibrations (centered at ~800 cm<sup>-1</sup>) in both materials.<sup>49,54</sup> Higher resolution transmission IR spectra (inset of Figure S8) revealed extra

peaks for 3DOM W–SiOC corresponding to Si–O–Si (1100 and 468 cm<sup>-1</sup>) and Si–C (801 cm<sup>-1</sup>) vibrations that were not present in the spectrum of pyrolyzed SMP-10.<sup>49,54,55</sup> Therefore, the bonding environment of oxygen in the 3DOM W–SiOC involved mainly Si–O–Si units.

The thermal stability of the 3DOM W-SiOC composite was also investigated. At 1000 °C, the material maintained its 3DOM structure (Figure S9a) and  $\alpha$ -W was still the only crystalline phase observed in the XRD pattern (Figure S1a). However, more intense peaks corresponding to W-C vibrations were observed in the Raman spectrum (Figure S7b), suggesting the formation of more  $WC_x$  species (either WC or  $W_2C$ ) at localized areas. Additionally, the lateral size of free carbon nanodomains increased from 1.0 to 1.3 nm on the basis of the calculated  $I_{\rm D}/I_{\rm G}$  ratios. This result indicated the growth of free carbon at an elevated temperature, possibly due to the continuing phase separation in the amorphous SiOC. At an even higher temperature of 1300 °C, the periodic 3DOM structure was destroyed, and an irregular, bicontinuous poresolid structure formed as a result of sintering (Figure S9b). Raman spectra collected at random areas to examine the possibility of further reaction between W (or  $WC_r$ ) and SiOC showed peaks corresponding to both W-Si and W-C vibrations, suggesting the formation of WSi<sub>x</sub> and WC<sub>x</sub> at 1300 °C (Figure S10).  $^{56-58}$  Strong carbon signals (D- and Gbands) were observed in some areas but not in others, which was likely caused by extensive phase separation or the loss of carbon (converted into CO) at this high temperature. Additionally, the lateral size of the free carbon nanodomains increased to 2.3 nm.

**3.3. Thermomechanical Properties of 3DOM W–SiOC.** Micro- and nano-scale mechanical measurements are wellsuited for probing the mechanical behavior of materials where size limitations prohibit bulk testing. Thus, micropillars of 3DOM W–SiOC were compressed at temperatures ranging from 30 to 575 °C. Representative images of pillars before compression and after deformation at each temperature can be seen in Figure 4. There is a clear change in deformation morphology as the temperature is increased. At 30 °C (Figure 4b), the material fails catastrophically at 1.1 GPa (Figure 5a). In this case, a flaw on the surface of the pillar provides a stress concentration, which allows a crack to propagate along the entirety of the pillar, and the material fails in a brittle manner.

In a previous study, a distinct increase in deformability of 3DOM W without any ceramic filler was seen at 225 °C.<sup>30</sup> However, compression of 3DOM W-SiOC did not show this behavior. Instead, a crack quickly propagated along the plane of maximum shear (Figure 4d), similar to the 30 °C case. The increased achieved strain (Figure 5b) implies some increased plasticity but not enough to prevent the material from failing by abrupt crack propagation arising from local stress fluctuations, exacerbated by partial misalignment that adds bending stresses. In contrast, enhanced deformability was observed at 425 °C (Figure 4f), where large strains were accommodated in the deformation process. The main failure mode was not via catastrophic cracking as it was in the two lower-temperature cases. Instead, the structure widened significantly toward the bottom of the pillar, indicating significant plasticity of at least one phase. A similar morphology was observed at 575 °C (Figure 4h), where the pillar widened significantly during deformation. In this case, however, the pillar widened at the top of the pillar rather than



**Figure 4.** SEM images of 3DOM W–SiOC pillars before deformation (left) and after compression (right) at (a,b) 30 °C; (c,d) 225 °C; (e, f) 425 °C; and (g,h) 575 °C. The major deformation mode changes from fracture-dominated at low temperatures to plastic-deformation-dominated at higher temperatures.



**Figure 5.** (a) Stress-strain curves for the compression of 3DOM W-SiOC at 30 °C and 3DOM W from ref 30. (b) Stress-strain curves for the compression of 3DOM W-SiOC at all temperatures. Stresses decrease and strains increase with increasing temperature.

the bottom, clearly changing the area in contact with the indenter tip during deformation.

Representative engineering stress–strain curves for 3DOM W–SiOC at 30 °C and 3DOM W at room temperature can be seen in Figure 5a.<sup>30</sup> As previously reported, 3DOM W begins to fail at approximately 50 MPa macroscopic stress, whereas 3DOM W–SiOC can support stresses as high as 1.1 GPa, a factor of 22 greater than 3DOM W. The absolute stresses endured by 3DOM W–SiOC are significantly greater than those in 3DOM W, as expected for a higher-density material, especially when the second composite phase is a stiff material such as SiOC. However, 3DOM W–SiOC only deforms to a maximum of approximately 10% strain prior to catastrophic failure, whereas 3DOM W achieved strains of greater than 15%

without catastrophic failure. Despite the distinct difference in the macroscopic behavior, it is useful to compare the relative area under the stress-strain curve for each of these cases. The area under the stress-strain curve is a measure of the total energy absorbed during the deformation process. The ratio of the energy of deformation of 3DOM W-SiOC at 30 °C to that of 3DOM W at room temperature was approximately 10.5. 3DOM W-SiOC requires approximately 10.5 times more energy to deform than pure 3DOM W. As previously noted, however, at 30 °C, 3DOM W-SiOC displays limited plasticity prior to catastrophic failure, limiting its use as an energyabsorptive material at that temperature.

Stress-strain curves for 3DOM W-SiOC at 30, 225, 425, and 575 °C can be seen in Figure 5b. As expected, the maximum stress decreases and ductility increases with increasing temperature. As previously discussed, pillars failed catastrophically at approximately 10% strain at 30 °C. Only minimal increases in ductility were observed at 225 °C, where maximum strains were on the order of 12%. However, the maximum stresses were already significantly decreased, dropping from 1.1 to 0.8 GPa. A further increase of the temperature to 425 °C resulted in distinctly different behavior, where deviation from linear-elastic behavior was observed at only 0.3 GPa, followed by an increase in stress, likely due to densification, and achieving large strains, up to 25% prior to unloading, twice of that observed at 225 °C. Similar behavior was observed at 575 °C, where deviation from linear-elastic behavior was observed at 0.1 GPa, and maximum stresses were only approximately 0.2 GPa at large ( $\sim$ 30%) strains after significant geometric hardening and densification, stemming from the tapered pillar geometry.<sup>5</sup>

An analysis of the area under the stress-strain curve, such as was performed to compare 3DOM W-SiOC to 3DOM W, makes it clear that the composite requiring the most mechanical work for deformation is 3DOM W-SiOC at 425 °C. On average, it absorbed 1.52× more energy than at 30 °C, 1.79× more than at 225 °C, 2.38× more than at 575 °C, and 15.9× more than 3DOM W at room temperature. At low temperatures (<225 °C), only limited strain can be applied before failure, resulting in low ductility and low energy absorption. As the temperature is increased, ductility increases, but the stresses required to deform the material at 575 °C result in lower overall energy absorption. However, in contrast to the low-temperature cases, this energy is stored in the material via plastic deformation and potential densification.

The stresses achieved at room temperature are not unexpected. Studies of tungsten nanofoams with ligament sizes of 25 nm have shown flow strengths of 1.1 GPa at room temperature with 49% relative density. The reported flow stress correlates fairly well with the 1.1 GPa maximum stress observed at 30 °C in this study if one considers that the tungsten ligaments in our study are similar (30 nm) but surrounded by an additional coating of a brittle material (SiOC) between the ligaments. With similar relative densities and grain sizes, the tungsten ligaments should yield at similar stresses. Earlier studies of the fracture toughness of the SiOC tested at room temperature found the value to be  $K_{\rm IC} \sim 0.73 - 0.99$  MPa m<sup>1/2</sup>.<sup>60</sup> We hypothesize that the low fracture toughness of the infiltrated SiOC along with the native flaw population give rise to local stress changes that are sufficient to overcome the low fracture toughness of SiOC. More extensive modeling may be needed to relate the macroscopic failure

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stress to the local tensile stress for Mode I failure or local shear stress for a Mode II failure.

Notably, the 1.1 GPa failure strength represents a very high specific strength. Normalizing the strength by the density (1.73 g/cm<sup>3</sup>, see the Supporting Information), the specific strength is 640 MPa/(Mg/m<sup>3</sup>) at 30 °C. This specific strength is significantly higher than those reported for other porous materials such as 3DOM W (52 MPa/(Mg/m<sup>3</sup>)),<sup>30</sup> 3DOM nickel (220 MPa/(Mg/m<sup>3</sup>)),<sup>29</sup> nanoporous tungsten (120–250 MPa/(Mg/m<sup>3</sup>)),<sup>62</sup> and 3DOM SiO<sub>2</sub>/TiO<sub>2</sub> composites (125–460 MPa/(Mg/m<sup>3</sup>)).<sup>32</sup> In fact, the specific strength of 3DOM W–SiOC remains high even at high temperatures, decreasing to 460 MPa/(Mg/m<sup>3</sup>) at 225 °C, 170 MPa/(Mg/m<sup>3</sup>) at 425 °C, and 58 MPa/(Mg/m<sup>3</sup>) by 575 °C. These same points can be found on the Ashby map of strength and density in Figure 6, where higher specific strength materials are located



**Figure 6.** Ashby map showing the relationship between the strength and the density using data from ref 61. CRFP: carbon-fiber-reinforced polymer. Data points: 3DOM W–SiOC (squares, from black to green: increasing temperature, this study), NP W (triangles, from black to green: increasing relative density),  $^{62}$  SiO<sub>2</sub>/TiO<sub>2</sub> inverse opals (IO) (circles, from black to green: increasing TiO<sub>2</sub> thickness),  $^{32}$  nickel IO (star),  $^{29}$  3DOM W (X).  $^{30}$ 

toward the upper-left of the diagram. The specific strengths of 3DOM W–SiOC at 30 and 225 °C are similar to that of carbon fiber-reinforced polymers. However, 3DOM W–SiOC is able to withstand significantly higher temperatures than a polymer-based composite while still retaining high specific strength. 2D strain maps of the strain along the loading direction at 30 and 575 °C are shown in Figure 7. At 30 °C (Figure 7a), local strains are relatively low prior to failure, as was observed in the stress–strain curve, which assumes uniform strain. The local strain distribution is qualitatively the same at 225 °C (Figure S12a). However, at 425 °C (Figure



**Figure 7.** Maps of the strain  $(\varepsilon_{yy})$  along the loading direction during the compression of 3DOM W–SiOC micropillars at (a) 30 and (b) 575 °C. Strains are fairly homogeneous at 30 °C, whereas horizontal bands of constant strain (compaction bands) are present at 575 °C, indicating a behavior similar to that of a low-density solid.

S12b) and 575 °C (Figure 7b), compaction (collapse) bands appear in the local strain maps, indicating that the material is behaving like a low-density solid at 425 °C and above.<sup>63</sup> Such banding occurs when the dominant failure mode is plastic hinge formation of the W ligaments and typically becomes less evident with decreasing porosity, usually completely disappearing at porosities around 70%.<sup>64,65</sup> Here, the porosity is therefore approximately 60% (see the Supporting Information) outside the conditions where compaction banding is commonly observed. This anomalous behavior poses two questions: (1) why do compaction bands show up only at higher temperatures? (2) Why do compaction bands show up in a low porosity material?

In our previous study of the compression of 3DOM W micropillars, compaction bands were observed at room temperature, whereas they were not observed in 3DOM W-SiOC until 425 °C in this study.<sup>30</sup> This indicates that at room temperature, the limiting deformation mode changes from bending-dominated ligament deformation in the case of an open-cell (3DOM W structure in the previous work) to the material-dependent fracture observed in the nanocomposite (3DOM W-SiOC). At low temperatures, the complex pore structure in the non-W phases and any surface anomalies contribute to stress concentrations, and local changes in the tensile or shear stresses eventually allow for the formation and propagation of unstable cracks. The low fracture toughness of the SiOC certainly exacerbates unstable cracking. At low temperatures, only relatively few slip systems are active in tungsten, making it difficult for the tungsten ligaments to plastically deform. In addition, one would need to consider the fact that the tungsten ligaments are surrounded by SiOC, which would also need to deform. However, the voids present in the as-synthesized material act as stress concentrators which allow the SiOC to easily fracture. At low temperatures, the tungsten ligaments are below or near the BDT temperature (BDTT) of 100–200  $^{\circ}C_{r}^{33}$  allowing a crack in the SiOC phase to continue through the tungsten ligament with relative ease. However, once the temperature is increased significantly beyond the BDTT of tungsten, these same types of cracks cannot propagate so easily through the tungsten. Instead, the tungsten ligaments yield under bending that results in the formation of a plastic hinge. The plastic hinge collapse causes compaction bands making the parent matrix, tungsten, the deciding factor in the material deformation. When a compaction band forms, the stress redistribution can subsequently cause the porous SiOC infiltrant to densify. The result of this behavior is a strong material (in terms of specific strength) even up to 575 °C with high deformability at temperatures above ~400 °C. Additionally, it can be compacted at higher temperatures, which could further increase the observed mechanical properties.<sup>6</sup>

## 4. CONCLUSIONS

We developed a novel method to fabricate interpenetrating metal-ceramic nanocomposites. Using 3DOM W as a scaffold, a liquid preceramic precursor SMP-10 was introduced into the pores of the 3DOM material, followed by condensation and pyrolysis to form the 3DOM W-SiOC material. This nanocomposite was composed of bicontinuous, periodic networks of crystalline  $\alpha$ -W and amorphous SiOC phases, also containing discrete free carbon nanodomains (nanocrystalline graphite) with a lateral size of ~1 nm. The 3DOM W-SiOC material had an overall porosity of ~58%, containing

textural mesopores and some remaining macropores within the SiOC phase due to incomplete SMP-10 infiltration into certain regions of the 3DOM W scaffold and volume shrinkage of the infiltrated SMP-10 during pyrolysis. The 3DOM W–SiOC material maintained its periodic structure up to 1000 °C. At 1300 °C, sintering degraded the 3DOM structure. At this high temperature, additional WSi<sub>x</sub> and WC<sub>x</sub> phases formed, and the free carbon grew in size (from 1.0 nm at 800 °C to 2.3 nm) due to continued phase separation. This fabrication method provides an opportunity for preparing different types of interpenetrating nanocomposites and achieving the full functionality of different phases or even obtaining synergistic effects.

Micropillar compression studies of 3DOM W-SiOC show stresses of up to 1.1 GPa achievable at 30 °C before brittle failure, a 20-fold increase in stress as compared to the unfilled 3DOM W. Failure was still primarily brittle up to 225 °C, whereas high strains and deformability were observed at 425 and 575 °C. Considering the energy under the stress-strain curve to be a measure of the energy absorbed during deformation, the maximum energy absorbed was measured at 425 °C. Compaction banding was observed at 425 and 575 °C, indicating that the material behaves as a low-density solid at these temperatures, which is likely linked to the porosity of the SiOC infiltrant. The high specific strength, as high as 640 MPa/ $(Mg/m^3)$ , along with high deformability at moderate temperatures, make this an ideal candidate material for hightemperature applications, as well as for future studies into the fundamentals of thermally activated deformation at the nanoscale. To obtain larger bulk composites of 3DOM W-SiOC, it may be possible to consolidate smaller domains of this well-ordered material through a fast sintering process, such as spark plasma sintering..

## ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c06894.

- Additional details on materials synthesis, methods for analysis of porosity and mechanical data corrections, SEM images, XRD patterns, elemental analyses, N<sub>2</sub> sorption data, IR and Raman spectra, and strain maps (PDF)
- In situ compression deformation process at 30  $^{\circ}$ C (MP4)
- In situ compression deformation process at 225  $^{\circ}$ C (MP4)
- In situ compression deformation process at 425  $^\circ C$  (MP4)
- In situ compression deformation process at 575  $^\circ \mathrm{C}$  (MP4)

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## Notes

The authors declare no competing financial interest.

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