

Supplementary Information for

Nanoporosity-Driven Deformation of Additively Manufactured Nano-Architected Metals

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Supplementary Note 1. Structural geometry characterizations of 3D metallic Ni nano-architectures.

Figs. 1D, G and J show the CAD model constructed according to the feature dimensions measured from pre-mortem SEM micrograph of each specimen for the purpose of structural relative density estimation. The influence of the elliptical voxel shape of the TPL laser beam on the resolved feature aspect ratio in the octahedral nanolattice is taken into account: the beam is assumed to be elliptical; both the major (Z-axis) length, a , and minor (X or Y-axis) length, b , are measured at ~ 10 beams; the characteristic feature size for the nanolattice specimen is then estimated as $d \sim \sqrt{ab}$. For the shell-based nano-architectures, the influence of the elliptical TPL laser voxel shape is insignificant; thus, the wall-thickness, t , is measured at 10 locations, and the characteristic feature size for the specimen is then estimated as $d \sim \bar{t}$.

As such, it is determined that: $d_{\text{octahedral}}$ varied between 163 and 445 nm with $\bar{\rho} \sim 26.6 \pm 3.4\%$; $d_{\text{Schwarz-P}}$ varied between 114 and 231 nm with $\bar{\rho} \sim 26.6 \pm 5.8\%$; and $d_{\text{spinodal-like}}$ varied between 102 and 506 nm with $\bar{\rho} \sim 33.3 \pm 5.1\%$. These d values fall within the diameter range of nanoHIAM-Ni nanopillars that have been examined by the authors in their recent work for detailed nanomechanical characterizations, thus enabling physics-informed modeling of the mechanical behavior of these nano-architectures at the next structural hierarchy.

Note that Fig. 1A shows the true 3D representation of the two-photon lithography laser line trace in the DeScribe software (version 2.5.4) using the as-designed, i.e., as-printed feature dimensions. While Figs. 1B-J shows a zoom-in version comparison of the CAD model references (Figs. 1D, G and J) and the respective as-fabricated features (Figs. 1C, F and I). The main deviation and root causes of the as-fabricated vs. the as-designed are:

1. Two photon lithography voxel: the two photon lithography laser has a focusing size smaller in X-Y plan and taller in Z-direction, causing the smallest as-printed features to be elongated in Z-direction.
2. Absolute dimension: overall linear shrinkage to 10-20% of as-printed dimension, depending on Ni infusion solution concentration.
3. Feature (beam and wall) aspect ratio: depending on calcination/reduction pressure, temperature, and duration, the bulk dimension and local feature dimension shrinkage could have different contributions as a result of varying atom diffusion kinetics under varying conditions.

Overall, it is commonly observed that the as-fabricated features may have increased aspect ratio and relative density than the design.

Supplementary Note 2. In situ nano-compression experiment.

Stress-strain response, deformation behavior, and failure

Fig. 2A presents the characteristic engineering stress-strain responses of the beam-based octahedral nanolattices, with representative *in situ* snapshots in insets Fig. 2B. Irrespective of the characteristic feature dimension, d , the octahedral lattices experienced similar deformation stages during compression. Contact establishment was immediate, suggested by the stable longitudinal modulus starting from the onset of loading. The subsequent small strain bursts $\lesssim 1\%$ and ones $\lesssim 10\%$ were attributed to premature failure and densification of the sacrificial base support and bottom layer(s) immediately adjacent to the base, as manifested by the difference between snapshots Figs. 2B, $d \sim 163$ nm ((1)-(2)), $d \sim 185$ nm ((1)-(2)), and $d \sim 445$ nm ((1)-(2)). Note that the largest nanolattice ($d \sim 445$ nm), between (2)-(3), experienced additional strain burst equivalent to the height of two and one lattice layers, respectively, due to the premature collapse of the bottom layers which are tapered in geometry due to shrinkage mismatch during fabrication, leading to their lesser load-bearing capability in comparison to the upper intact layers. The ultimate lattice failure, indicated with the cross symbol, occurred via catastrophic global collapse and densification of the nanolattice layers, amounting to a total strain of ~ 40 -50%, as in $d \sim 163$ nm ((2)-(3)), $d \sim 185$ nm ((2)-(3)), and $d \sim 445$ nm ((3)-(4)). The ultimate failure mode was consistently observed across the feature dimension range ~ 150 -500 nm and attributed to materials failure, meaning the load-bearing features in each repeating unit cell have reached their critical strength limit. The corresponding nominal stress level is then defined as the ultimate compressive strength of the nanolattice. Minimal recovery strain was observed upon unloading. Despite the similar deformation characters, the lattice strength was considerably higher at smaller d – approximately 10-time increase from $d \sim 445$ nm decreasing to $d \sim 163$ nm (Fig. 2B).

Fig. 2C presents the stress-strain responses of the shell-based Schwarz-P nanolattices, whose early deformation behaviors qualitatively resemble those of the beam-based octahedral counterparts (Figs. 2D, $d \sim 225$ nm ((1)-(2)), $d \sim 192$ nm ((1)-(2)), and $d \sim 143$ nm ((1)-(2))). Upon larger compressive strain, the majority of the Schwarz-P nanolattices, represented by the dark and light grey curves, exhibit the dominant failure mode of catastrophic global collapse attributed to materials failure, consistent with the octahedral nanolattices (Figs. 2D, $d \sim 225$ nm ((2)-(3)) and $d \sim 192$ nm ((2)-(3))). Curiously, the yellow curve demonstrates an alternative failure mode, which is less catastrophic – wall buckling propagates gradually layer-by-layer (Figs. 2D, $d \sim 143$ nm ((2)-(4))), followed by densification past a cumulative compressive strain of 0.6. The layer-by-layer buckling initiated from the top layer where the as-fabricated unit cells exhibit geometric distortion and pre-existing crack openings, suggesting a structural failure route occurring at lower stress level premature to meeting the materials failure criterion. Despite the similar shell wall aspect ratios between the specimens in Figs. 2D, $d \sim 192$ nm and $d \sim 143$ nm, their absence and presence of structural imperfections exemplifies the universal competition between material failure versus structural failure at the nanoscale.

Fig. 2E presents the stress-strain responses of the non-periodic spinodal-like architecture, demonstrating similar signatures of rapid contact establishment and catastrophic collapse as the

periodic nanolattice counterparts. The dark and light green curves (Figs. 2F, $d \sim 242$ nm and $d \sim 410$ nm) represent the materials failure-dictated nano-architecture response, showing $\sim$ linear loading up to $\sim 10\%$ compressive strain uniformly distributed throughout the nano-architecture (Figs. 2F, $d \sim 242$ nm (①-②) and $d \sim 410$ nm (①-②)), then catastrophic collapse by $\sim 60\%$ strain via full fracture of the nano-architecture shells (Figs. 2F, $d \sim 242$ nm (②-③) and $d \sim 410$ nm (②-③)), and finally minimal recovery upon unloading. On the other hand, the grey curve represents the structural failure-dictated failure via gradual shell wall buckling and densification (Figs. 2F, $d \sim 110$ nm (②-⑤)), similar to the Schwarz-P nanolattice specimen in Fig. 2D, $d \sim 143$ nm. Note that the specimens that experienced such premature structural failure are excluded from the following analysis of the size-dependent lattice strengths, so that only specimens that experienced materials failure are considered for a clear correlation between the nano-architecture strengths and the building block material strengths.

Weibull modulus fitting from experimental results

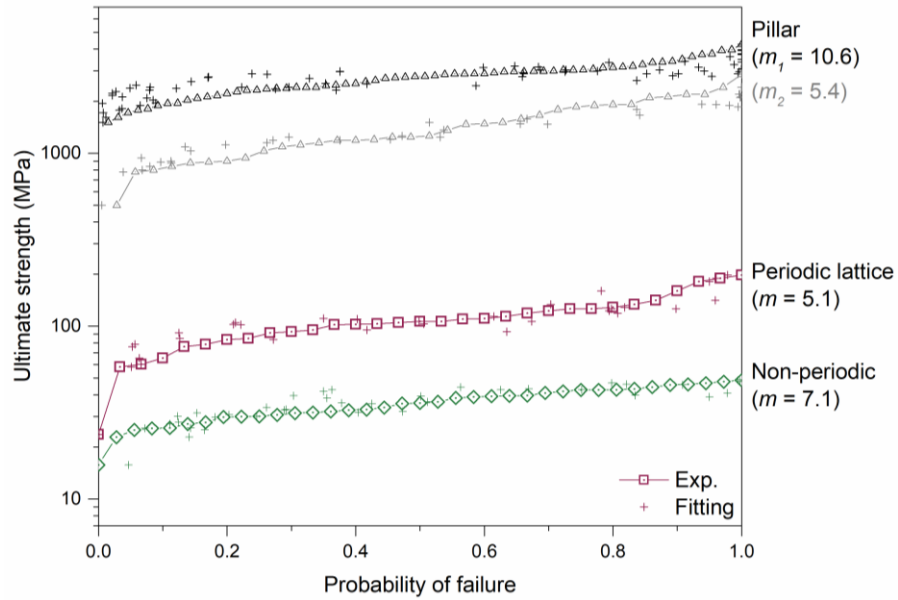
Considering the potentially finite number of representative element contained in each nanoscale specimen, we adapted the expression for the failure probability based on the precursor-to-Weibull (PWBL) distribution discussed by Bernal⁽¹⁾ to the present experimentally measured ultimate strengths of Ni nanopillar and nano-architectures under compression:

$$P_{fj} = 1 - \left(1 - \left(\frac{\sigma_j}{\sigma_0}\right)^m\right)^{N_j}$$

where:

- (i) P_{fj} is the failure probability of pillar #j;
- (ii) σ_j is the yield strength of pillar #j measured by the experiment;
- (iii) σ_0 is the distribution parameter for characteristic stress;
- (iv) m is the distribution parameter for Weibull modulus;
- (v) N_j is the number of representative elements in pillar #j: we consider the volume defect-mediated failure mechanism. Thus, we take a 3D representative element and V_0 as the distribution parameter for the size (i.e., volume) of the element; therefore, $N_j = V_j/V_0$ with V_j approximated as the cylindrical volume for nanopillar #j or as the nominal volume of the architectures equaling the product of the bulk width cubed with the structural relative density. We performed least-square fitting for nanopillars (regime 1 of $\beta \sim 0.2$: $N = 65$; regime 2 of $\beta \sim 2.0$: $N = 35$), periodic nanoarchitectures ($N = 31$), and non-periodic nano-architectures ($N = 37$), separately, where the experimental value of $P_f(\sigma)$ is approximated by the proportion of tested specimens in each category whose yield strength was $< \sigma$. Results are summarized in Supplementary Table 1 and Supplementary Fig. 1.

Supplementary Table 1. PWBL least-square fitting results.			
	$V_0^{1/3}$ (nm)	σ_0 (MPa)	m
Nanopillar (regime 1)	1.6E1	5.2E3	10.6
Nanopillar (regime 2)	0.7E1	11.9E3	5.4
Periodic nano- architecture	1.1E2	3.4E2	5.1
Non-periodic nano- architecture	1.7E3	5.4E1	7.1



Supplementary Figure 1. Precursor-to-Weibull (PWBL) distribution analysis of ultimate strengths in pillar and nanolattices. The Weibull parameters (m) were fitted to the experimental data.

Supplementary Note 3. Gamma distribution fitting of the porosity distribution at lattice nodal region.

As shown in Fig. 3, concentrated porosity is observed at the nodal junction area in octahedral nanolattices and the porosity distribution can be approximated by a gamma function with feature dimension (d) dependent shape parameter (k) and scale parameter (θ). Based on the observation on the experimental and fitted distribution functions for three nanolattices with increasing d (Fig. 3D), the mean porosity ($k\theta$) and k of the distribution function increases steadily with d , suggesting the existence of larger porosity at nodal junction areas while the change in θ is less significant especially for nanolattice with larger d . Thus, for the interpolation of gamma function parameters for any given d , θ is chosen to keep at constant values of 0.02 while k is determined from the linear interpolation of the mean porosity ($k\theta$) as a function of d . The fitted gamma distribution is further adopted in the finite element analysis to assign the porosity-based material properties in the nodal elements (Supplementary Fig. 4D).

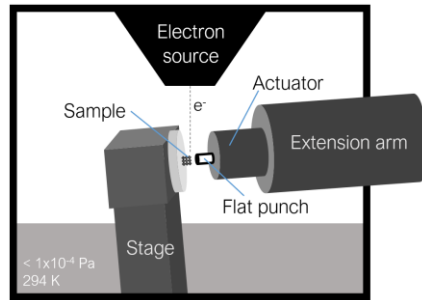
Supplementary Note 4. Stress distribution in unit cell of spinodal-like architecture.

Further analysis was performed to understand the effects of the geometric factors including the local curvature and shell thickness on the heterogeneous stress distribution in the spinodal-like unit cells (Figs. 4A-C and Supplementary Fig. 6). The stress of one thousand randomly picked material points on the surface of the unit cell was extracted from FE simulations and plotted against their local curvature and shell thickness in Supplementary Fig. 7. No strong correlation was observed between the stress field and these local geometric factors suggesting that the stress field in the spinodal-like unit cells cannot be solely determined by the local structure but is also affected by the complex surrounding microstructures. This is further confirmed by our machine learning analysis using TensorFlow 2.16.0(2) where a neural network with 64x64x1 dense layers and ReLU activation functions was trained to learn the distribution of the stress field of the unit. The neural network could not correctly predict the stress field with only inputs of the local geometry parameters, i.e., curvature and shell thickness (Supplementary Fig. 8A) suggesting a lack of key knowledge in the input information. With the additional inputs of nodal coordinates, the neural network with the same structure started to develop the ability to predict the stress field (Supplementary Fig. 8B). These analyses further demonstrate the non-local features of the heterogeneous stress field in the spinodal-like unit cells leading to potentially more complex fracture behavior.

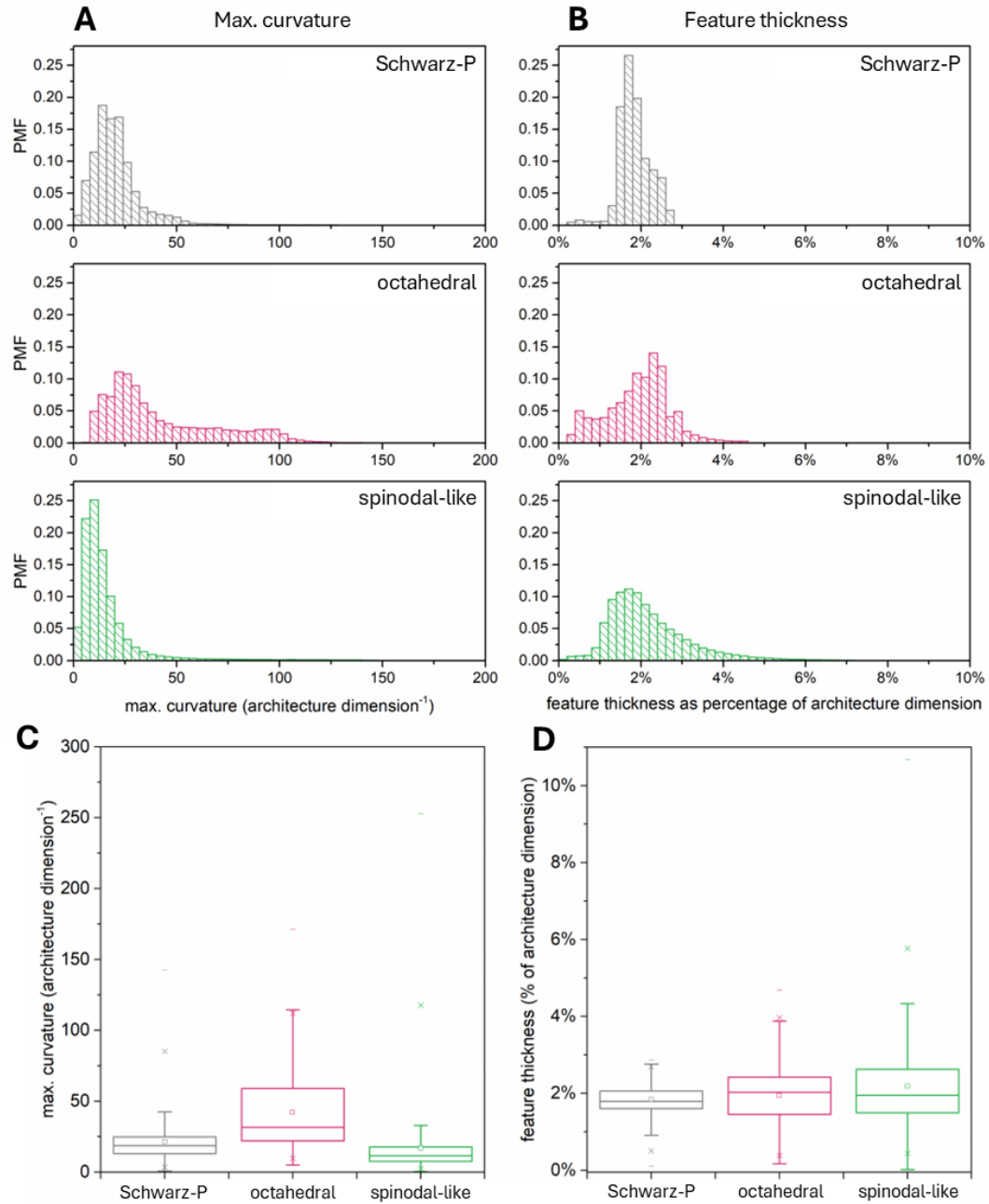
Supplementary Note 5. Comparison of different material models in the FE analysis of the ultimate strength of octahedral nanolattices.

Two material models were used in this work to demonstrate the capability of utilizing the building block information to predict the mechanical response of the nanoarchitecture. The baseline material properties for Ni were extracted from the compression stress-strain curve of the nanopillar with a diameter of 145 nm, and the yield strength was determined to be 3 GPa. When this value was used in both the homogeneous degradation model and the porosity-based model for the evaluation of the ultimate strength of the nanolattice, the scaling factors obtained from both models match the experimental results (Supplementary Fig. 9), while the porosity-based model yields lower values of the ultimate strength. The lower strength from the porosity-based model is attributed to strong degradation at nodal elements with large porosity, as sampled from the gamma distribution (Fig. 3D). The porosity-based model can match both the scaling factor and values of the experimental data with a scaled yield strength, which can be interpreted as the reference strength of defect-free nanocrystalline material.

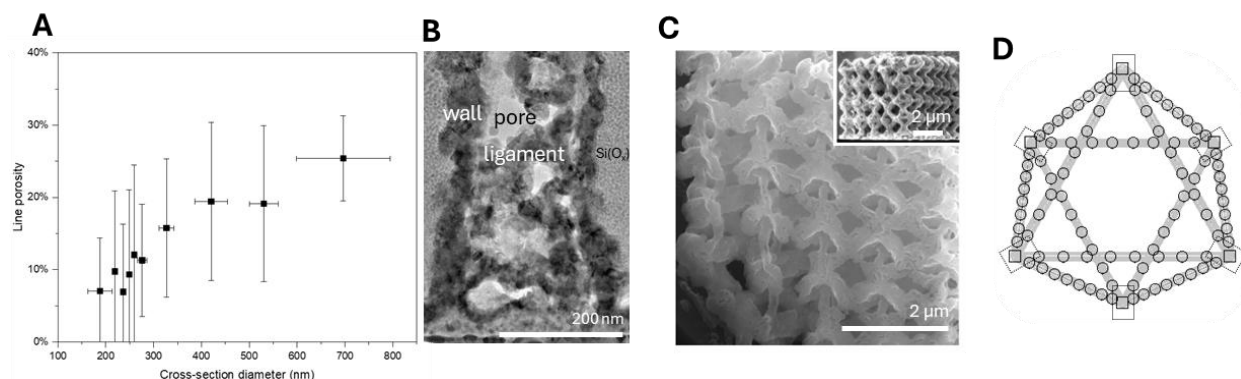
The major difference between the homogeneous model and the porosity-based model is that the latter considers the real porosity distribution and the associated local material fracture in the nanoarchitectures. The typical stress-strain curves of nanolattices with different feature dimensions and relative densities simulated with both models are presented in Supplementary Fig. 10, which clearly demonstrates a prolonged non-linear region prior to the ultimate stress in the porosity-based model, resulting from the local damage at nodal elements with large porosity. As a consequence of the modeling of real porosity distribution, the porosity-based model predicts an increased magnitude of the scaling factor with larger feature dimensions (Supplementary Fig. 11), suggesting a stronger effect of the building block defects on the mechanical response of the nanoarchitecture.



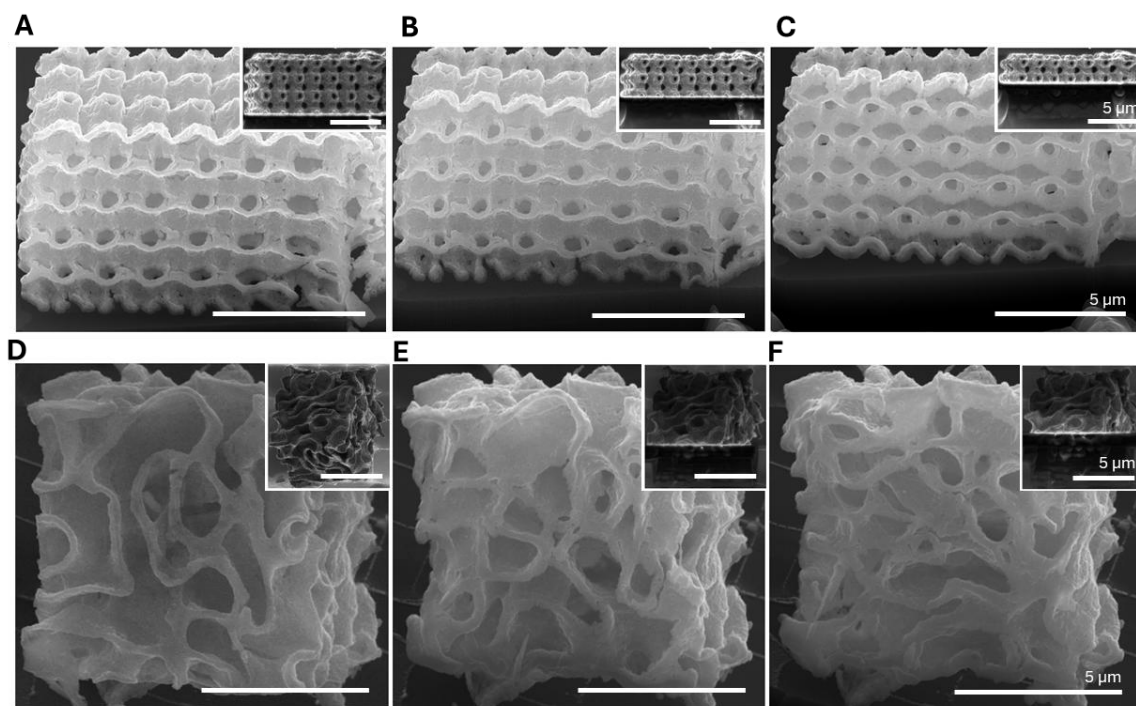
Supplementary Figure 2. Schematic of in situ compression using SEMentor.



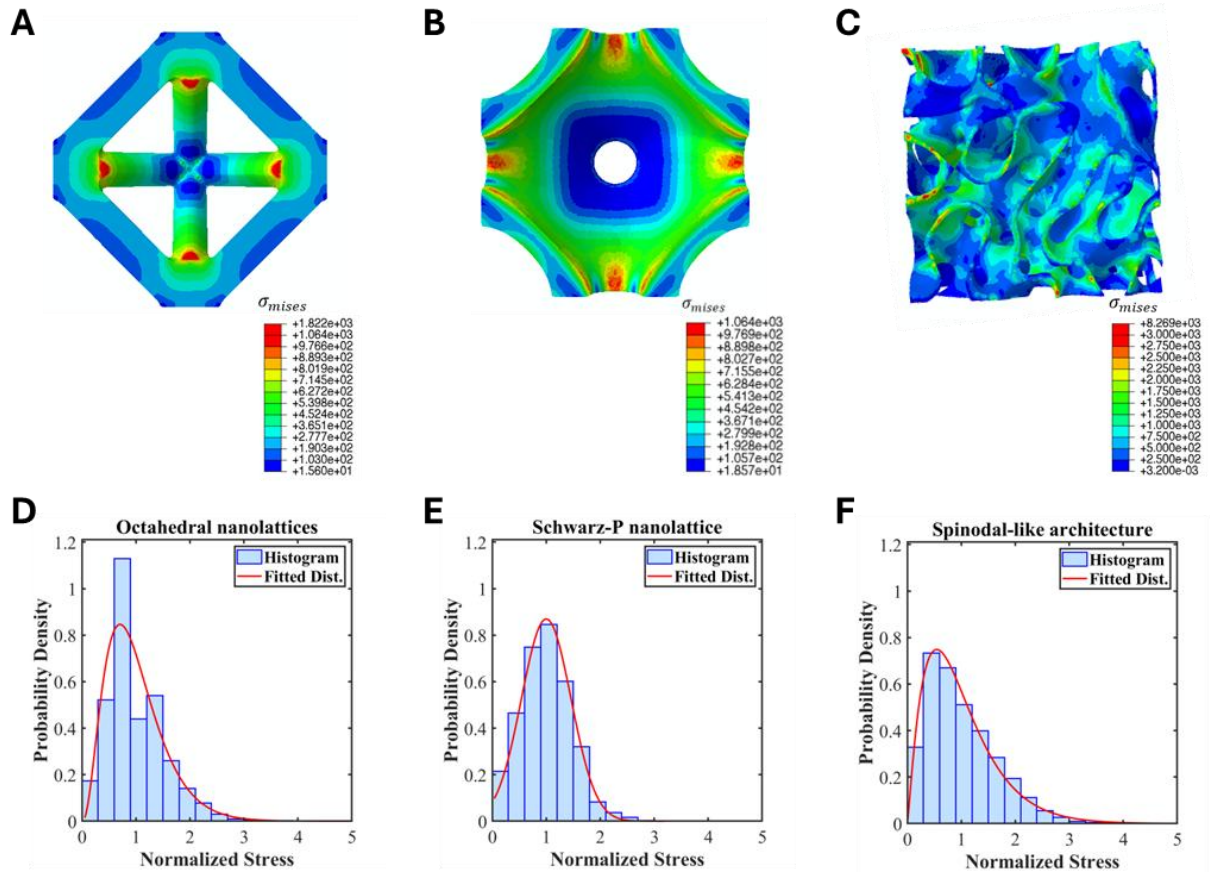
Supplementary Figure 3. Geometric properties of nanoarchitectures computed using experimentally measured parameters via SEM and subsequent CAD remodeling. Probability Mass Functions (PMFs) of (A) maximum curvature and (B) feature thickness in the three nanoarchitectures. The relative density is set equal 21.7% for the three nanoarchitectures used for this plot for fair comparison. The mean values and standard deviations of (C) maximum curvature and (D) feature thickness.



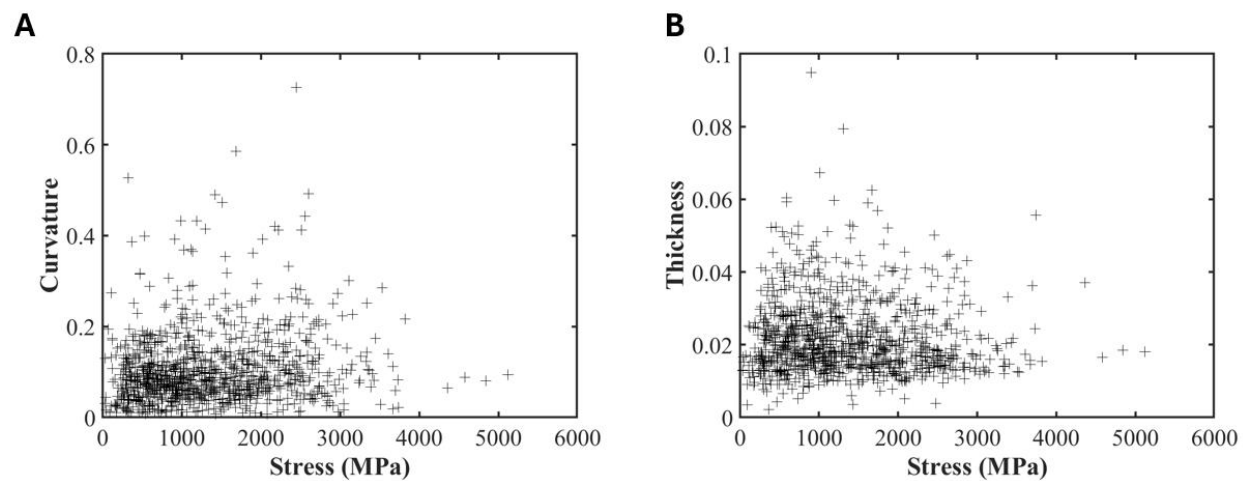
Supplementary Figure 4. Material-level porosity properties from nanoHIAM-Ni nanopillars to nanoarchitectures. Nanopillar porosity (A) distribution and (B) TEM micrograph, adapted with permission from Zhang and Li, et al. (3). Copyright 2023 American Chemical Society. (C) SEM micrograph of porosity concentration at nodal junctions in octahedral nanolattice corresponding to $d \sim 350$ nm in Fig. 3B; inset showing FIB micrograph of the top-down view. (D) A schematic view of finite-element partitioning for an octahedral unit cell, with circular and square symbols representing the vertices of the beam elements and the nodes of the lattice, respectively, and the boxed regions indicating near-node beam elements.



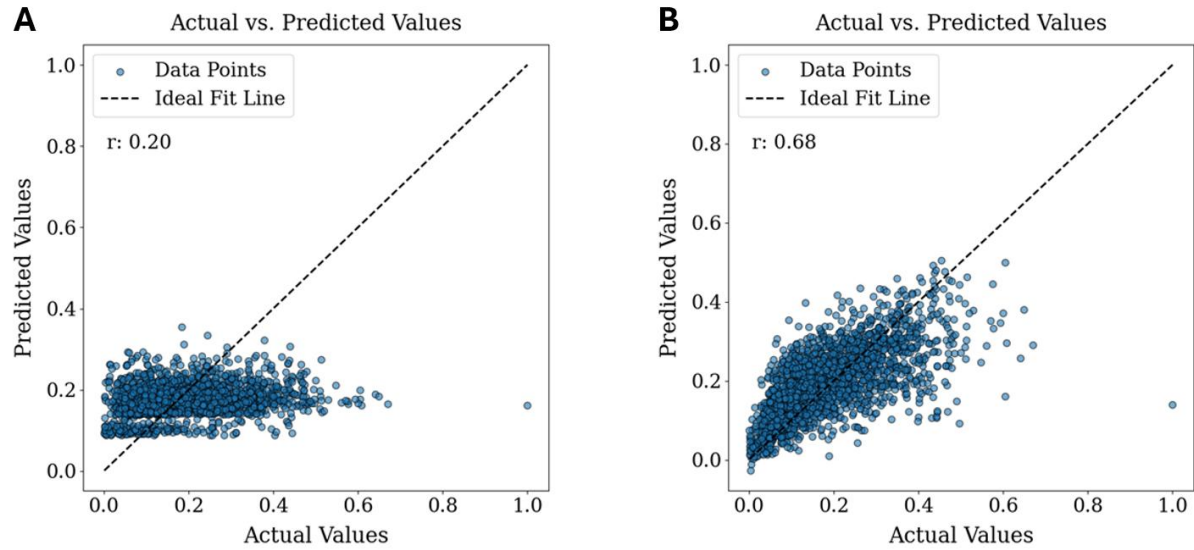
Supplementary Figure 5. Material porosity properties in Schwarz-P nanolattice and spinodal-like nanoarchitecture. (A-C) SEM micrographs of FIB-milled cross-sections of Schwarz-P nanolattice, insets show the Ga-ion FIB micrograph of the corresponding top-down view at three representative locations. (D-F) SEM micrographs of FIB-milled cross-sections of spinodal-like nanoarchitecture, insets show the Ga-ion FIB micrograph of the corresponding top-down view at three representative locations.



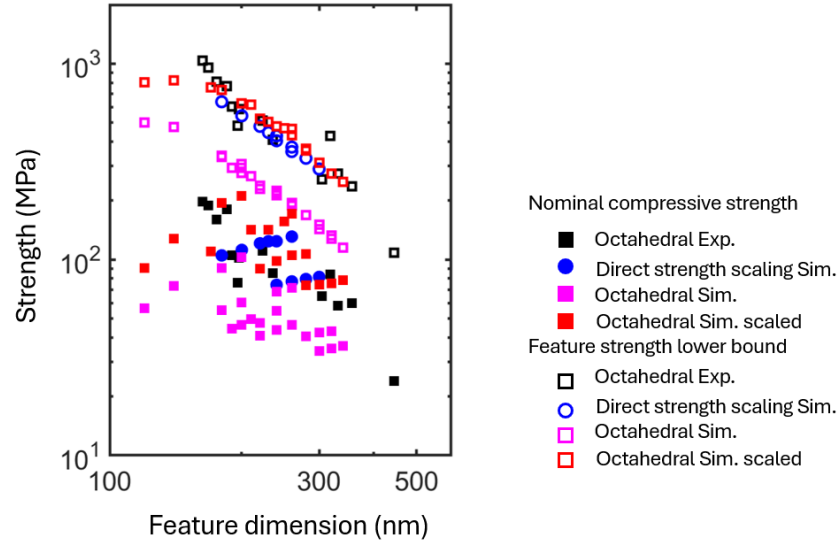
Supplementary Figure 6. Analysis of stress distribution in nanoarchitectures. Cross-sectional view of the stress concentration in (A) Octahedral nanolattice, (B) Schwarz-P nanolattice, and (C) Spinodal-like architecture, corresponding to main Fig. 4A-C. Statistical distribution of mises stress in (D) Octahedral nanolattice, (E) Schwarz-P nanolattice, and (F) Spinodal-like architecture .



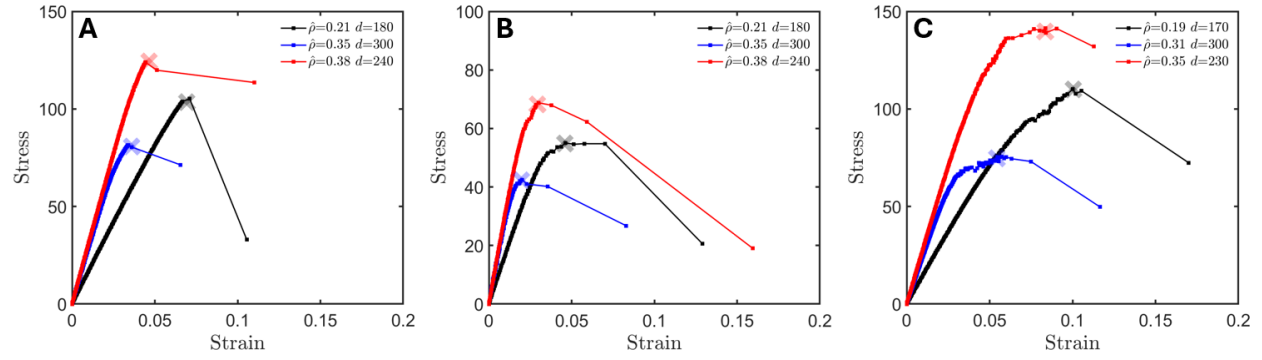
Supplementary Figure 7. Correlation between the stress distribution with geometric factors in Spinodal-like architecture. (A) stress-curvature plot. (B) stress-thickness plot.



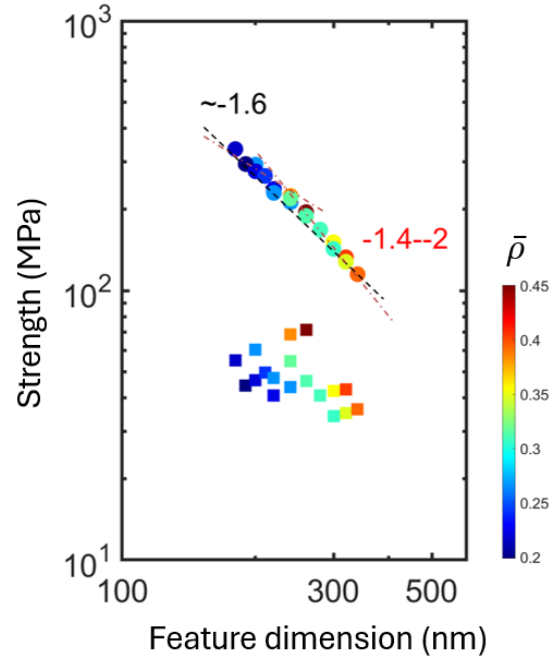
Supplementary Figure 8. Neural network (NN) training results for the prediction of stress distribution in Spinodal-like architecture. NN prediction of stress distribution corresponding to Supplementary Figure 7 with (A) only curvature and thickness as inputs and (B) additional information of node coordinates.



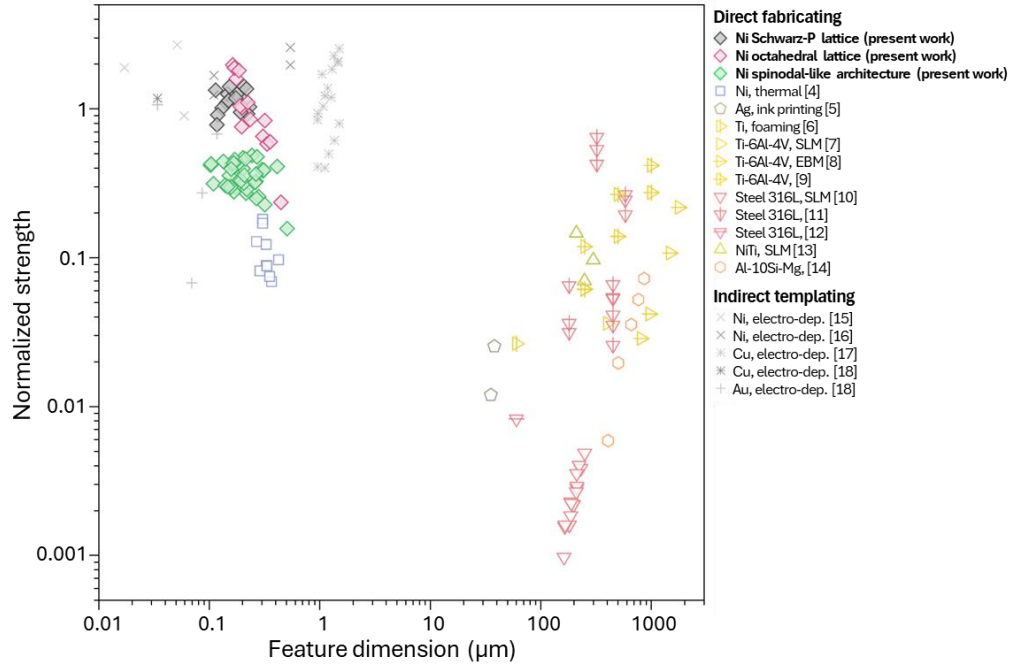
Supplementary Figure 9. Size dependence of the simulated lattice strengths with different degradation models. Simulation results of the compressive strength of octahedral nanolattices with three types of degradation models (a direct strength-scaling model, a nanoporosity-based model, and a nanoporosity-based model with scaled material parameters), as well as the calculated lower-bound feature strength, are compared with the experimental results.



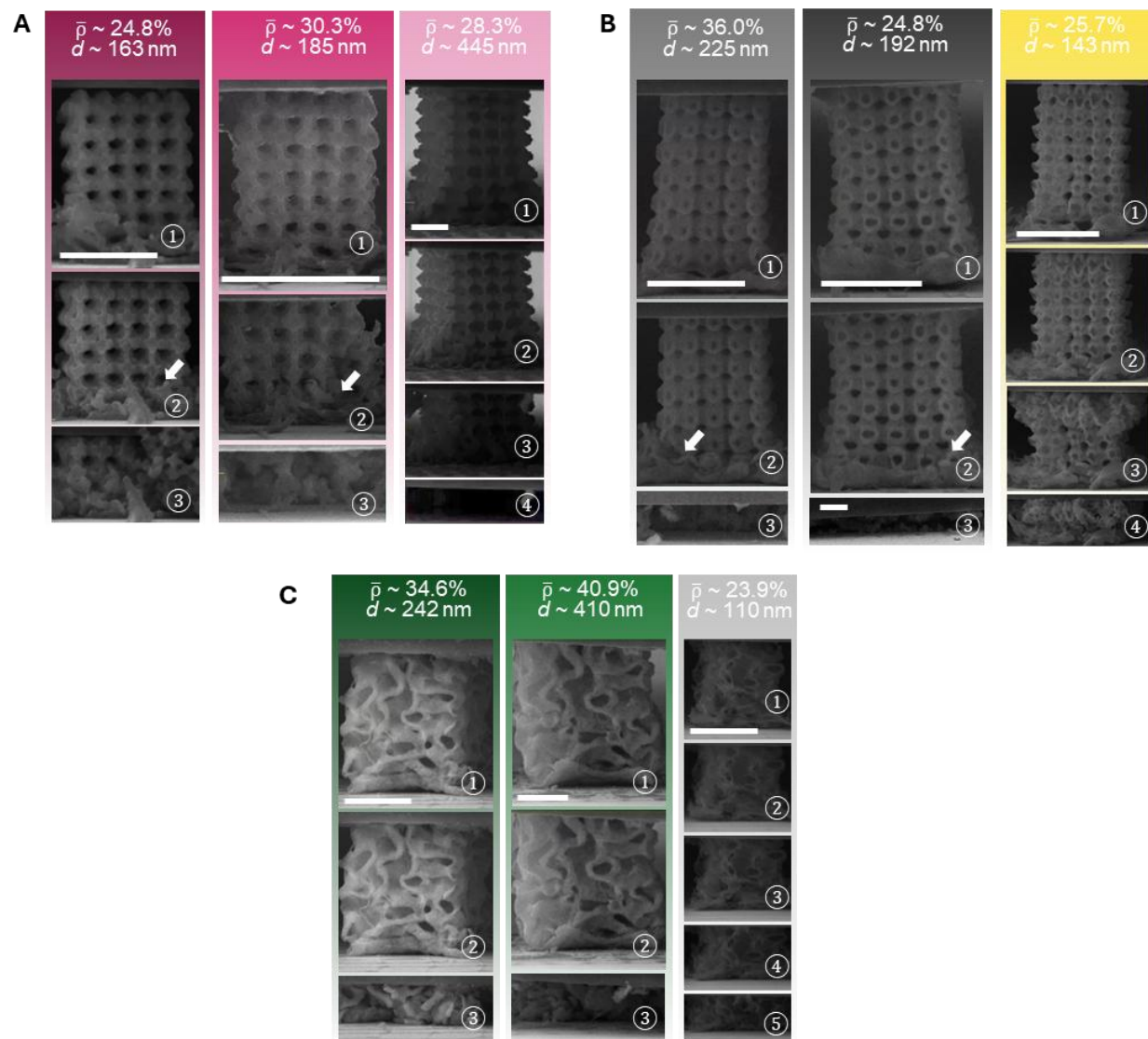
Supplementary Figure 10. Typical stress-strain curves from finite element simulations (FEM) of beam-element models. FEM simulation results of 6x6x4 beam-based octahedral nanolattices with (A) homogenized reduction model. (B) nanoporosity based model. (C) nanoporosity based model with scaled material parameters.



Supplementary Figure 11. Size-dependence of the simulated lattice strengths using the porosity distribution-based degradation model. The simulation results of compressive strength were obtained for octahedral nanolattices with relative density, $\bar{\rho} \sim 20\text{--}40\%$ and feature dimension $\sim 180\text{--}340$ nm. The overall scaling factor is ~ -1.6 , while a stronger size dependence is observed with increasing feature dimension, as demonstrated by the variation of the scaling factor from -1.4 to -2.0 .



Supplementary Figure 12. Normalized strength as a function of feature dimensions. Results from the present study are compared with data from prior studies, as shown in Fig. 5A. The normalized strength is calculated by dividing the strength of the nanolattices by the typical yield strength of the corresponding bulk material. The yield strengths used for the calculation are 100 MPa (Ni), 205 MPa (Steel 316L), 827 MPa (Ti-6Al-4V), 240 MPa (Al-Si10-Mg), 50 MPa (Ag), 130 MPa (Cu), 100 MPa (Au), 483 MPa (Ti), and 300 MPa (NiTi).



Supplementary Figure 13. Enlarged snapshots from in situ compression of nano-architectures. SEM snapshots of (A) octahedral nanolattices, (B) Schwarz-P nanolattices, and (C) spinodal-like architectures, corresponding to main Fig. 2.

Supplementary References

1. R. A. Bernal, On the application of Weibull statistics for describing strength of micro and nanostructures. *Mech. Mater.* **162**, 104057 (2021).
2. M. Abadi, A. Agarwal, P. Barham, E. Brevdo, Z. Chen, C. Citro, G. S. Corrado, A. Davis, J. Dean, M. Devin, S. Ghemawat, I. Goodfellow, A. Harp, G. Irving, M. Isard, Y. Jia, R. Jozefowicz, L. Kaiser, M. Kudlur, J. Levenberg, D. Mane, R. Monga, S. Moore, D. Murray, C. Olah, M. Schuster, J. Shlens, B. Steiner, I. Sutskever, K. Talwar, P. Tucker, V. Vanhoucke, V. Vasudevan, F. Viegas, O. Vinyals, P. Warden, M. Wattenberg, M. Wicke, Y. Yu, X. Zheng, TensorFlow: Large-Scale Machine Learning on Heterogeneous Distributed Systems. arXiv arXiv:1603.04467 [Preprint] (2016). <https://doi.org/10.48550/arXiv.1603.04467>.
3. W. Zhang, Z. Li, R. Dang, T. T. Tran, R. A. Gallivan, H. Gao, J. R. Greer, Suppressed Size Effect in Nanopillars with Hierarchical Microstructures Enabled by Nanoscale Additive Manufacturing. *Nano Lett.* **23**, 8162–8170 (2023).
4. A. Vyatskikh, S. Delalande, A. Kudo, X. Zhang, C. M. Portela, J. R. Greer, Additive manufacturing of 3D nano-architected metals. *Nat. Commun.* **9**, 593 (2018).
5. M. S. Saleh, C. Hu, R. Panat, Three-dimensional microarchitected materials and devices using nanoparticle assembly by pointwise spatial printing. *Sci. Adv.* **3**, e1601986 (2017).
6. K. Kato, A. Yamamoto, S. Ochiai, Y. Daigo, T. Isobe, S. Matano, K. Omori, Cell Proliferation, Corrosion Resistance and Mechanical Properties of Novel Titanium Foam with Sheet Shape. *Mater. Trans.* **53**, 724–732 (2012).
7. V. J. Challis, X. Xu, L. C. Zhang, A. P. Roberts, J. F. Grotowski, T. B. Sercombe, High specific strength and stiffness structures produced using selective laser melting. *Mater. Des.* **63**, 783–788 (2014).
8. E. Hernández-Nava, C. J. Smith, F. Derguti, S. Tammas-Williams, F. Leonard, P. J. Withers, I. Todd, R. Goodall, The effect of defects on the mechanical response of Ti-6Al-4V cubic lattice structures fabricated by electron beam melting. *Acta Mater.* **108**, 279–292 (2016).
9. C. N. Kelly, J. Francovich, S. Julmi, D. Safranski, R. E. Guldberg, H. J. Maier, K. Gall, Fatigue behavior of As-built selective laser melted titanium scaffolds with sheet-based gyroid microarchitecture for bone tissue engineering. *Acta Biomater.* **94**, 610–626 (2019).
10. S. Tsopanos, R. A. W. Mines, S. McKown, Y. Shen, W. J. Cantwell, W. Brooks, C. J. Sutcliffe, The Influence of Processing Parameters on the Mechanical Properties of Selectively Laser Melted Stainless Steel Microlattice Structures. *J. Manuf. Sci. Eng.* **132** (2010).
11. M. Simoes, J. A. Harris, S. Ghouse, P. A. Hooper, G. J. McShane, Process parameter sensitivity of the energy absorbing properties of additively manufactured metallic cellular materials. *Mater. Des.* **224**, 111398 (2022).
12. K. Kato, A. Yamamoto, S. Ochiai, M. Wada, Y. Daigo, K. Kita, K. Omori, Cytocompatibility and mechanical properties of novel porous 316L stainless steel. *Mater. Sci. Eng. C* **33**, 2736–2743 (2013).

13. M. Speirs, B. Van Hooreweder, J. Van Humbeeck, J.-P. Kruth, Fatigue behaviour of NiTi shape memory alloy scaffolds produced by SLM, a unit cell design comparison. *J. Mech. Behav. Biomed. Mater.* **70**, 53–59 (2017).
14. C. Yan, L. Hao, A. Hussein, S. L. Bubb, P. Young, D. Raymont, Evaluation of light-weight AlSi10Mg periodic cellular lattice structures fabricated via direct metal laser sintering. *J. Mater. Process. Technol.* **214**, 856–864 (2014).
15. J. H. Pikul, S. Özerinç, B. Liu, R. Zhang, P. V. Braun, V. S. Deshpande, W. P. King, High strength metallic wood from nanostructured nickel inverse opal materials. *Sci. Rep.* **9**, 719 (2019).
16. R. Ramachandramoorthy, M. Mieszala, C. V. Manzano, X. Maeder, J. Michler, L. Philippe, Dual-templated electrodeposition and characterization of regular metallic foam based microarchitectures. *Appl. Mater. Today* **20**, 100667 (2020).
17. X. W. Gu, Julia. R. Greer, Ultra-strong architected Cu meso-lattices. *Extreme Mech. Lett.* **2**, 7–14 (2015).
18. H. Cheng, X. Zhu, X. Cheng, P. Cai, J. Liu, H. Yao, L. Zhang, J. Duan, Mechanical metamaterials made of freestanding quasi-BCC nanolattices of gold and copper with ultra-high energy absorption capacity. *Nat. Commun.* **14**, 1243 (2023).