

Scalable fabrication and mechanical behaviour of hierarchical porous nickel networks

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HIGHLIGHTS

- Scalable alloying–dealloying route for two-level and three-level hierarchical Ni networks.
- Bulk three-level hierarchical nanoporous Ni is achieved with ligament sizes down to 13 nm.
- Three-level hierarchical nanoporous Ni networks exhibit nearly three orders of magnitude higher specific surface area than that of pristine Ni foam.
- New scaling law predicts the stiffness of hierarchical porous metallic networks.

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ABSTRACT

As the demand for light-weight structural and functional materials grows, the fabrication of hierarchical, high-performance micro- and nano-architectures becomes increasingly important. Here, we present a scalable alloying–dealloying strategy to fabricate porous metal with two- and three-level hierarchical networks (2 L-/3L-HN). By exploiting the vapour pressure difference between Ni and Zn, vapour phase alloying of Ni foam with Zn, followed by vapour phase dealloying of the resulting γ -Zn₈₄Ni₁₆ foam, generates a second hierarchical level, producing 2L-HN Ni or 2L-HN β -Zn₅₀Ni₅₀. Re-alloying 2L-HN β -Zn₅₀Ni₅₀ to 2L-HN γ -Zn₈₄Ni₁₆ via vapour phase alloying while preserving its hierarchical architecture enables chemical dealloying to create a third level of hierarchy at the nanoscale, producing 3L-HN Ni with significantly increased specific surface area. A novel scaling law is proposed to predict the mechanical properties of these hierarchical porous metallic networks as a function of solid fraction, and its validity is supported by compression tests on 2L-HN Ni with varying densities. This work establishes a scalable and versatile route for fabricating multiscale porous metallic networks with light-weight, tunable mechanical performance and high surface area.

1. Introduction

Nanoporous metals have shown a wide range of promising applications in catalysis [1], actuation [2,3], sensing [4–6] or energy storage and conversion [7–10], primarily due to their high specific surface area. More recently, hierarchical nanoporous metals have attracted increasing attention [11–13], owing to their multiscale pore architecture. In these materials, larger pores at the upper hierarchical level facilitate rapid ion transport and enhance charging kinetics, while smaller pores at the lower hierarchical level provide an increased specific surface area [14].

Hierarchical structures are widespread in nature, such as bone [15], nacre [16] and enamel [17], where their complex, multi-level architectures give rise to exceptional mechanical properties. Inspired by these natural examples, hierarchical nanoscale metallic materials are expected to achieve superior mechanical performance in addition to enhanced functional properties. Notably, the well-known “the smaller, the stronger” effect in metallic materials [18–20], in which reducing structural dimensions can significantly increase strength further emphasises the importance of nanoscale architecture for mechanical properties, not solely for increasing surface area. Recent advances in additive man-

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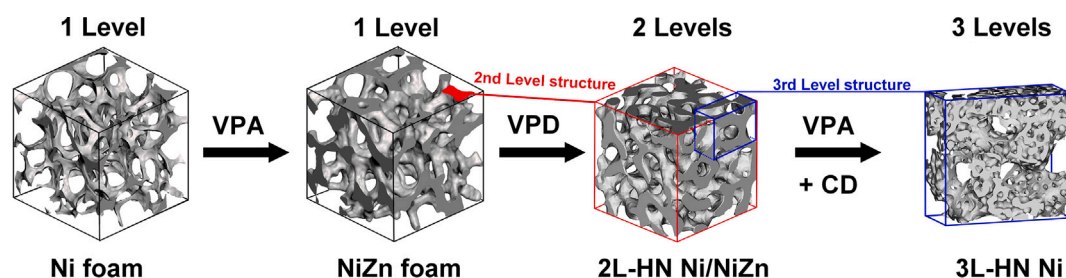


Fig. 1. Schematic illustration of the production process for two-level and three-level hierarchical porous Ni networks. Starting with a pristine Ni foam (left), vapour phase alloying (VPA) with Zn leads to an NiZn alloy foam (middle left). This structure forms the macroporous network at the highest hierarchical level and is preserved throughout subsequent preparation steps. Vapour-phase dealloying (VPD) of the NiZn alloy foam introduces an additional, finer porous network within the foam struts, as highlighted in the red inset (middle right), resulting in a two-level hierarchical porous network (2L-HN) of Ni or NiZn alloy. A subsequent VPA step on the 2L-HN NiZn alloy followed by chemical dealloying (CD) generates a third, finest porous network, as shown in the blue magnified inset (right), producing a three-level hierarchical porous network (3L-HN) of Ni. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

ufacturing have enabled the fabrication of three-dimensional nanoarchitected metals, which exhibit strengths comparable to, or even exceeding, those of their bulk counterparts [21]. However, scaling such nanoarchitected metallic materials to macroscopic dimensions while preserving their structural integrity and mechanical performance remains a significant challenge.

Dealloying has been demonstrated as one effective approach to achieve the scalable fabrication of mechanically robust hierarchical nanoporous gold with two levels of nested-network hierarchy [22–24]. Macro-compression tests revealed enhanced strength due to nanoscale struts and the hierarchical structure. It is predicted that incorporating a third hierarchical level could further enhance mechanical performance. However, the experimental realisation of bulk nanoporous metals with a three-level hierarchical network (HN) has so far been limited to Au and its mechanical properties have not been reported. Zhu et al. 3D-printed an Ag-Au lattice structure using direct ink writing followed by sintering and dealloying processes to form the second and third hierarchical levels [25]. Shi et al. used vapour phase alloying (VPA)-vapour phase dealloying (VPD) to create a macroporous $\text{Ag}_{95}\text{Au}_5$ foam followed by two-step electrochemical dealloying to create two additional hierarchical levels [26].

For the fabrication of cost-efficient HN metals, Ni foam (NF) is one of the most widely used precursors. Most studies have focused on fabricating materials to improve the functional properties while keeping the structural rigidity of the pristine metal foam intact. This is typically achieved by modifying only the surface region of the struts using different alloying-dealloying methods or deposition techniques [27–41]. For instance, Shi et al. combined VPA using Zn with different dealloying methods to create nanoporous layers on the NF strut surfaces [42]. Cai et al. electrodeposited Zn onto NF followed by a heat treatment to create a Zn-Ni alloy at the surface, which is then dealloyed to create a nanoporous surface layer [43]. However, only a limited number of studies have investigated modifications to the entire cross-section of metal foam struts; when such modifications are considered, the emphasis is typically placed on functional properties. For example, Wang et al. fabricated HN Ni by using a two-step gaseous oxidation-reduction method on a 1 μm thin walled NF and then coated HN Ni with MnO_2 electrode material, achieving superior supercapacitive performance [12]. Shao et al. further combined this approach with electrodeposition to produce HN NiCu alloys, which exhibited outstanding electrocatalytic performance [44]. Both cases led to a complete porous network formation of the struts cross section but the mechanical properties were not investigated.

In this work, we demonstrate a simple and scalable approach to fabricate 2-level hierarchical network (2L-HN) Ni and 3-level hierarchical network (3L-HN) Ni by combining VPA, VPD and chemical dealloying. Both 2L-HN and 3L-HN Ni exhibit a significantly increased specific surface area compared with NF. For the 3L-HN Ni, the ligament size at the

lowest hierarchical level is as small as 13 nm. Furthermore, the mechanical properties of 2L-HN Ni were characterised through compression tests. The measured elastic properties align well with our newly developed scaling laws for the Young's modulus of hierarchical network materials. These scaling laws were derived by integrating the Gibson-Ashby scaling law [45] for the random NF structure at the uppermost hierarchical level and the modified Roberts-Garboczi scaling law [46] for the dealloyed porous structure at the lower hierarchical levels.

2. Experimental methods

2.1. Sample preparation

Commercial NF sheets with 95% porosity (Recemat BV; 110 PPI, 5.8–5.9 mm in thickness, Ni-4753) were cut into roughly $5 \times 5 \times 5.8 \text{ mm}^3$ samples. Similarly, NF sheets with 90% and 80% porosity (Foammetal New Material Co., Ltd.; 120 PPI, 3 mm in thickness) were cut into samples of roughly $3 \times 3 \times 4.5 \text{ mm}^3$ and $3 \times 3 \times 3.5 \text{ mm}^3$, respectively.

Fig. 1 presents a schematic of the fabrication routes for 2L-HN and 3L-HN Ni. First, VPA was conducted on all NF samples by vacuum sealing two samples each and Zn granules (99.999%, ChemPur) together in a quartz tube at approximately 0.4 mbar, followed by heat treatment in a furnace at 500 °C for 48 h, forming $\gamma\text{-Zn}_{84}\text{Ni}_{16}$ foams.

To fabricate 2L-HN Ni, VPD was applied to the $\gamma\text{-Zn}_{84}\text{Ni}_{16}$ foams at 700 °C for 1 h under Ar/H_2 flow using an infrared furnace (IRF 10, Behr).

To fabricate 3L-HN Ni, VPD at 500 °C for 2 h was applied to the $\gamma\text{-Zn}_{84}\text{Ni}_{16}$ foams to form 2L-HN $\beta\text{-Zn}_{50}\text{Ni}_{50}$ alloys instead of 2L-HN Ni. Afterwards, 2L-HN $\gamma\text{-Zn}_{84}\text{Ni}_{16}$ alloy samples were prepared by applying VPA to 2L-HN $\beta\text{-Zn}_{50}\text{Ni}_{50}$ at 500 °C for 24 h. Finally, the obtained 2L-HN $\gamma\text{-Zn}_{84}\text{Ni}_{16}$ samples were chemically dealloyed in 1 M $(\text{NH}_4)_2\text{SO}_4$ (ultra pure, VWR Chemicals) aqueous solution at 50 °C for 5 days, forming 3L-HN Ni. Moreover, coarsening of as-prepared 3L-HN Ni was conducted by annealing at 300 °C for 1 h under Ar/H_2 flow.

2.2. Microstructural characterisation

The microstructure of the samples was analysed using stereo light microscopy (Leica M205 C), light microscopy (Leica DMR), scanning electron microscopy (SEM, Zeiss Supra VP55) and transmission electron microscopy (TEM, Thermo Fisher Scientific Talos F200X). TEM specimens were prepared by crushing a sample piece in a mortar and drop-casting a dilute suspension in pure *n*-hexane onto a TEM grid made of copper with 200 mesh.

The volume, strut and ligament sizes were manually measured using the measuring module in Leica Application Suite (Version 4.13.0) for the stereo light microscopy and light microscopy images, and with ImageJ (1.54p) [47] for the SEM images. Note that “strut” and “ligament” are

used to describe the solid beam of the foam structure and dealloyed porous structures, respectively. The diameter of the triangular struts is defined as the average length of the perpendicular segments measured from each vertex to the opposite side and is determined by measuring at least 5–15 struts per production step using the light microscopy images (Supporting Information Figure S1a–i). Ligament size or diameter is taken as the average of the neck diameters of at least 15 ligaments as shown in Figure S1j.

The chemical composition of each sample at each step was calculated using the weight measurements. The chemical composition of individual samples was also analysed using energy dispersive X-ray (EDX) analysis equipped on the SEM device (Zeiss Supra VP55). Phase identification was performed by wide-angle X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer with Mo K α radiation.

The solid fraction (φ) of each sample at each step was calculated using the measured weight and sample volume, along with the density of solid materials having the same chemical composition. The solid fraction of a deformed sample with a compressive strain (ϵ) was estimated in the same way but instead of using the original sample volume the volume dependent on the state of deformation was calculated at each strain. To incorporate the lateral expansion of the material the plastic Poisson's ratio ν was determined for each sample by measuring its dimensions before and after compression. The compressed samples volume was then $((1-\epsilon) \times z) \times (x + (\nu \times \epsilon \times x)) \times (y + (\nu \times \epsilon \times y))$ with z being the height, x the width and y the depth of the sample.

2.3. Mechanical testing and analysis

The NF, 2L-HN Ni and annealed 3L-HN Ni samples were subjected to cyclic loading–unloading compression tests. A universal mechanical testing machine (ZwickRoell Z005) with a laser speckle extensometer (LaserXtens) was used for strain measurement. The engineering strain rate was set to $0.01\% \text{ s}^{-1}$ and the preload to 0.2 N. The resulting stress-strain curves were analysed for determining Young's modulus and yield strength. Young's modulus was determined by a linear fit for each unloading curve as shown in the supporting information Figure S2.

2.4. Surface area analysis

To determine the surface area of the pristine, 2L-HN and 3L-HN Ni produced from the 90% porosity precursor, two different methods were used. The first one was the Brunauer-Emmett-Teller method (BET) on their nitrogen gas adsorption/desorption curves using the Autosorb iQ MP-XR by Quantachrome. The total mass of measured samples was 389 mg for the pristine Ni and 31–36 mg for 2L-HN and 3L-HN Ni materials. Usually for BET analysis, samples are heated while a vacuum is applied to get rid of all adsorbates on the surface (e.g., water). This was done at 100°C for the 2L-HN Ni while the 3L-HN Ni was tested without prior heating to avoid contamination of the device by vaporisation of residual Zn.

The second method is the “Beta” method [48], which uses the reduction peak of β -NiOOH to evaluate the electrochemically active surface area (ECSA). The specific charge density was taken as $420 \mu\text{C cm}^{-2}$. It was carried out by cyclic voltammetry (CV) in 1 M NaOH aqueous solution using a Hg/HgO electrode (R0501, Beijing Jingke Instrument) as the reference electrode and a carbon cloth (Goodfellow) as the counter electrode. Each sample was cycled 5 times at a scan rate of 0.1 mV s^{-1} with potential steps of 2 mV. Moreover, ECSA measurements at a scan rate of 5 mV s^{-1} were also performed for pristine Ni and 2L-HN Ni samples.

3. Scaling laws for Young's modulus

To predict the mechanical properties of metal foams, like Young's modulus, there exist multiple scaling laws. They were each derived on the basis of a mathematical model that attempts to represent the structure of the actual foam. The Gibson-Ashby scaling laws [45] for open

cell foams use a well-connected beam structure as their base. This resulted in the following equation for the Young's modulus E as a function of the solid fraction:

$$E_1 = AE_0\varphi^a \quad (1)$$

$A = 1$ and $a = 2$ are constants for small solid fraction and bending-dominated networks ($\varphi < 0.3$) and E_0 is the Young's modulus of the bulk material. The modified Roberts-Garboczi scaling law, as derived by Soyarslan et al. [46] using a leveled-wave model, has been shown to agree very well with experimental data for dealloyed nanoporous metals:

$$E_1 = BE_0 \left(\frac{\varphi - \varphi_{\text{per}}}{1 - \varphi_{\text{per}}} \right)^b \quad (2)$$

$B = 2.03$ and $b = 2.56$ are constants [46]. $\varphi_{\text{per}} = 0.159$ represents the percolation threshold—the critical solid fraction at which the system shifts from a continuous, load-bearing network to disconnected clusters. The significant difference from the classical Gibson-Ashby model stems from solid fraction-dependent connectivity. In leveled-wave-like structures, such as nanoporous metals, not all of the mass contributes to load bearing. Dangling ligaments do not contribute to the load-bearing capacity. Therefore, the solid fraction taking part in load-bearing is lower than the apparent solid fraction [49,50]. With the changed term for the solid fraction in the scaling law (Eq. 2) this factor is incorporated [46].

The structure of the 2L-HN Ni fabricated in this study combines the Gibson-Ashby open cell foam model and leveled-wave model. This allows for lower solid fractions, as the upper level hierarchical structure is not limited by the percolation threshold of the leveled-wave model. For simplicity, equal solid fractions are assumed at each hierarchy level. The scaling laws based on the different models in Eqs. (1) and (2) by Gibson-Ashby/Soyarslan (GAS) are combined to predict the mechanical properties of the 2L-HN Ni structure by recursive homogenisation, giving rise to the “GAS-2L” scaling law for the Young's modulus:

$$E_2 = ABE_0\varphi^{a/2} \left(\frac{\varphi^{0.5} - \varphi_{\text{per}}}{1 - \varphi_{\text{per}}} \right)^b \quad (3)$$

For n levels (nL) HN Ni with the uppermost level always being a Gibson-Ashby open cell foam structure (Eq. 1) and any further levels consisting of a leveled-wave structure (Eq. 2) with equal solid fraction, the GAS-nL scaling law for the Young's modulus is derived as follows:

$$E_n = AB^{n-1}E_0\varphi^{a/n} \left(\frac{\varphi^{1/n} - \varphi_{\text{per}}}{1 - \varphi_{\text{per}}} \right)^{b(n-1)} \quad (4)$$

4. Results and discussion

4.1. Microstructural analysis

4.1.1. Pristine Ni foams

The pristine NF provides the basic structure for the uppermost hierarchical level of all subsequent hierarchical samples. Therefore, the microstructure of NF was first analysed. Three NFs with different porosities (95%, 90%, and 80%) were analysed using light and electron microscopy. A comparison of their sample sizes and geometries is shown in Fig. 2(a). The sample size was chosen differently to ensure roughly the same number of struts per base for better comparability of the mechanical tests. Additionally, the 80% porosity NF was kept in a rectangular shape but made slightly shorter to reduce the overall mass. This resulted in 95% porosity NF samples each weighing between 65–70 mg, 90% porosity NF samples each weighing between 30–35 mg and 80% porosity NF samples each weighing between 40–45 mg. Fig. 2(b) and (d) show that the 95% and 90% porosity NFs have a slight anisotropy.

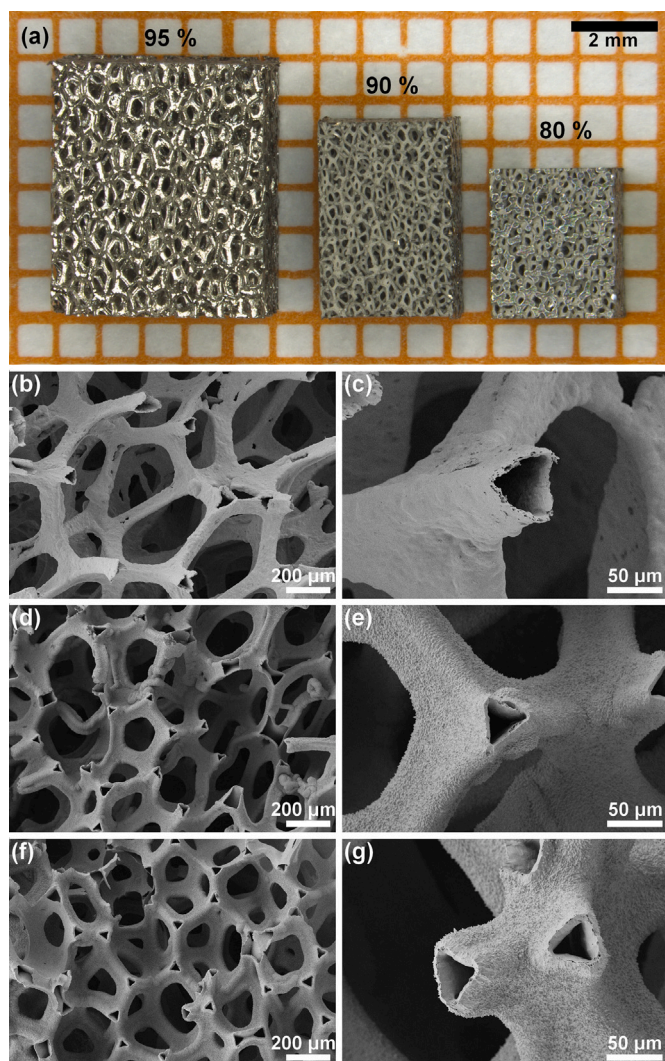


Fig. 2. Comparison of the three pristine NF materials with different porosities. (a) stereo light microscopy images of NFs with porosities of 95% (left), 90% (middle), and 80% (right), showing different sample sizes but a similar number of struts or pores in each sample. (b–g) SEM images of NFs with porosities of 95% in (b,c), 90% in (d,e) and 80% in (f,g). The slight elliptical shape of the pores in (b,c), 90% in (d,e) and 80% in (f,g) illustrates the anisotropic nature of the structure.

4.1.2. One-level Zn-Ni foams

VPA leads to an overall volume increase of 94–125%. The relative volume change increases with decreasing porosity of NF precursors: approximately 94% for 95% NF, 114% for 90% porosity NF and 125% for 80% porosity NF (Figures S3a–b). This can be attributed to the different morphologies of the initial struts. Metallographic cross sections of the materials in the pristine and alloyed states were used to characterise the morphological changes of the initial struts. As exemplified by the 90% NF in Fig. 3, the strut grows outwards and inwards during alloying.

Depending on the initial wall thickness and strut diameter, VPA results in completely or partially closed struts (Fig. 3, Figures S1a–f and S4). With the closure of the hollow struts, further material expansion can only be directed outwards as happened for the 90% and 80% porosity NFs. This leads to an overall larger volume growth and a morphology change from a hollow triangular to a nearly solid circular strut, accompanied by increased crack formation (Figure S1e–f). The 95% porosity NF with very thin walls and a large diameter shows the least overall volume growth and crack density (Figure S1d), as the struts keep their

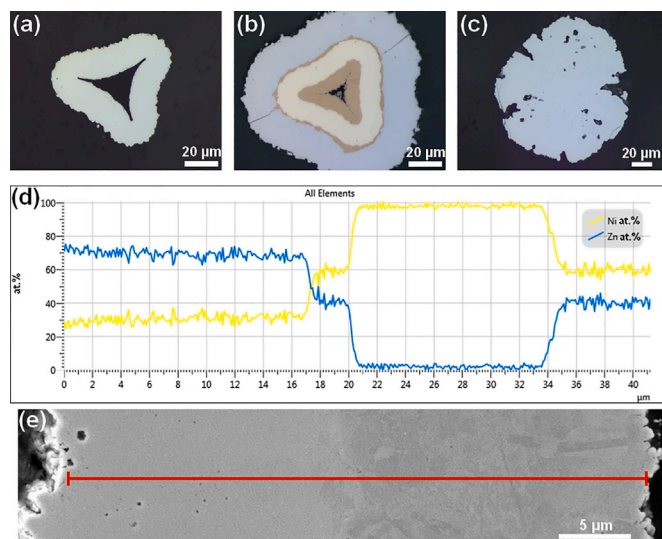


Fig. 3. Composition evolution during vapour phase alloying of a 90% porosity NF. Light microscopy images of strut cross sections at (a) the initial pristine state, (b) the partially alloyed state after VPA at 500 °C for 30 h and (c) the fully alloyed state after VPA at 500 °C for 48 h. (d) EDX line scan across the strut wall of sample (b), showing the variation in chemical composition from the outer edge to the centre of the strut. (e) SEM image corresponding to (d) showing the exact line scan position on the strut wall.

initial hollow, triangular cross-section. The values of strut sizes including strut diameter and wall thickness are determined according to Section 2.2 and summarised in Table 1.

Fig. 3(d) shows the EDX analysis of partially alloyed samples (500 °C, 24 h). The chemical composition distribution from the strut surface to the centre shows good agreement with the light microscopy observations in Fig. 3(b). The different colours in Fig. 3(b) correlate with three distinct phases: Ni (bright core), γ -NiZn (blue shell, ~75 at. % Zn); β -NiZn (brown layer, ~40 at. % Zn). In this work, the alloying time of 48 h is used to form γ -NiZn foams with ~84 at. % Zn (Fig. 3c and Figure S4). This long alloying time is used to prevent the formation of γ -NiZn foams with varying Zn content and different crystal structures [51]. Lower alloying temperatures reduce the alloying kinetics, requiring longer holding times to achieve complete alloying, but do not alter the characteristic alloying pathway. Although higher temperatures accelerate diffusion kinetics, temperatures significantly above the melting point of Zn, such as 600 °C, lead to contamination by excess molten Zn, reducing experimental reproducibility.

4.1.3. Two-level hierarchical porous nickel networks

VPD of the as-prepared γ -Zn₈₄Ni₁₆ foams leads to the 2-level hierarchical structures (Fig. 4), macroscopic volume shrinkage (Figure S3b–c) and substantial removal of Zn. The lower level ligament diameter is ~2.0 μ m. The upper strut diameters range from 75.9 μ m, to 105.9 μ m and 124.2 μ m, all consistently smaller than those of the corresponding γ -Zn₈₄Ni₁₆ foams (Table 1). This indicates that the VPD process results in the shrinkage of local struts in all samples, consistent with the macroscopic volume change (Figure S3b–c).

The volume expansion during VPA and shrinkage during VPD are not identical and therefore the final solid fraction of 2L-HN Ni is not exactly the same as that of the corresponding NF. The initial 80% and 90% porosity NFs end up with $\phi = 19 \pm 2\%$ and $\phi = 11 \pm 2\%$, respectively, in the corresponding 2L-HN Ni. The 95% porosity NF ends up with $\phi = 8 \pm 1\%$ in the corresponding 2L-HN Ni. The 95% NF shows an obvious decrease in overall volume (with an average decrease of 60%) after VPA-VPD, while the 80% and 90% NFs show minor changes in volume (with an average increase of approximately 5% and decrease of 10%,

Table 1

A comparative summary of the strut dimensions and wall thicknesses of the NFs at each stage of the fabrication process.

condition	95% NF		90% NF		80% NF	
	diameter [μm]	wall thickness [μm]	diameter [μm]	wall thickness [μm]	diameter [μm]	wall thickness [μm]
pristine	82.3 ± 9.4	13.3 ± 1.8	63.2 ± 5.0	17.8 ± 2.7	77.5 ± 9.1	21.9 ± 1.7
VPA	117.8 ± 12.1	32.8 ± 5.7	130.2 ± 10.9	–	205.8 ± 28.5	–
VPD	75.9 ± 6.7	21.2 ± 3.1	105.9 ± 10.9	–	124.2 ± 12.7	–

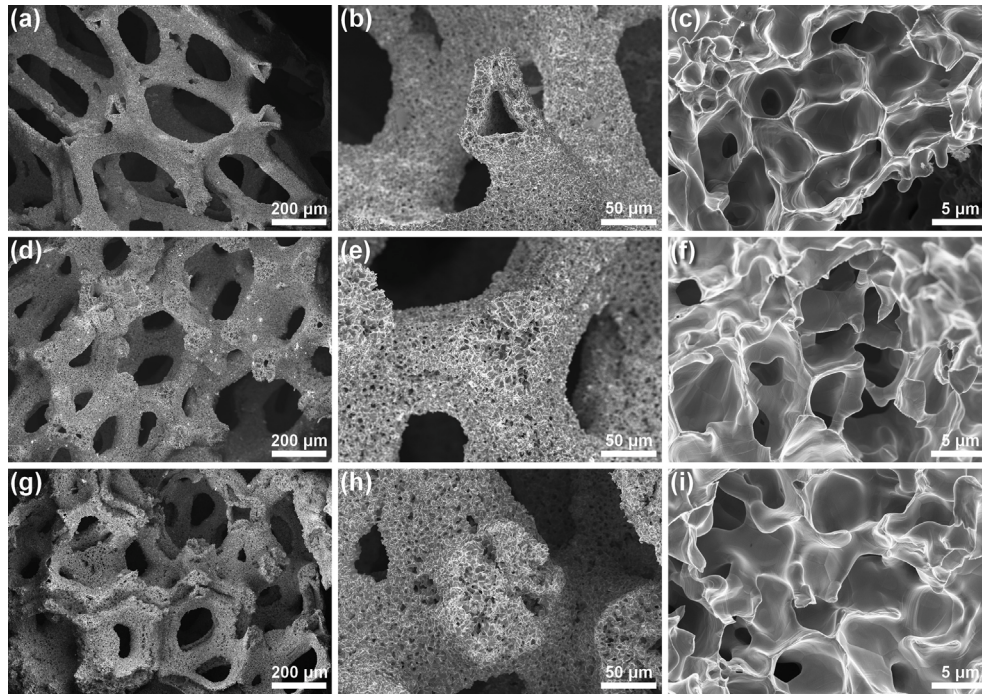


Fig. 4. SEM images of 2L-HN Ni. The precursors were NFs with porosities of (a–c) 95%, (d–f) 90% and (g–i) 80%. Magnification increases from left to right, revealing the distinct upper- and lower-level structures formed after VPD at 700 °C for 1 h.

respectively) after VPA-VPD (Figure S3). This is also reflected by the variation of strut diameters (Table 1). Whereas the 80% and 90% porosity NFs end up with a larger upper level strut diameter and undergo a morphological transition from hollow to solid struts (Fig. 4e and h), the 95% porosity NF shows a smaller upper level strut diameter and hollow struts (Fig. 4b) after the VPA-VPD process.

4.1.4. Three-level hierarchical nanoporous nickel networks

The 90% porosity pristine NF was used as the precursor for the fabrication of 3L-HN Ni. To reach the desired third level the fabrication method for the 2L-HN Ni was slightly altered and further developed. After the same first step of VPA, the second step of VPD was done at a lower temperature of 500 °C for ~2 h. This led to 2L-HN $\text{Zn}_{50}\text{Ni}_{50}$ with its composition situated in the β -phase field of the classical Ni-Zn phase diagram (Fig. 5a). This 2L-HN β - $\text{Zn}_{50}\text{Ni}_{50}$ alloy was reallocated using the same technique as in step one, which led to 2L-HN $\text{Zn}_{84}\text{Ni}_{16}$ with its composition situated in the γ -phase field. Representative SEM images of 2L-HN β - and γ -phase samples are shown in Figure S5. Performing VPD on the obtained 2L-HN γ - $\text{Zn}_{84}\text{Ni}_{16}$ at 700 °C resulted in 2L-HN Ni again. This is due to the high temperature of VPD, which then led to significant coarsening and hindered the formation of smaller porosities (the third level) within the lower struts of the 2L-HN γ - $\text{Zn}_{84}\text{Ni}_{16}$ during VPD. As a result, chemical dealloying is utilised to create a third level.

By applying chemical dealloying to the 2L-HN γ - $\text{Zn}_{84}\text{Ni}_{16}$, a third hierarchical level at the nanoscale (with a ligament size of ~13 nm) is

achieved, as shown in Fig. 6(c). It should be emphasised that chemical dealloying at 50 °C in this work enables the formation of 3L-HN Ni with a nanoporous structure and, consequently, a large specific surface area. This feature is highly beneficial for enhancing surface-controlled functional performance as well as mechanical strength (“the smaller, the stronger”). However, the presence of cracks in the as-dealloyed 3L-HN Ni (Figure S6a) prevents systematic macroscopic mechanical testing.

Annealing the as-dealloyed 3L-HN Ni at 300 °C for 1 h results in an annealed 3L-HN Ni with an increased lower level ligament size of ~206 nm (Fig. 6f), while the strut or ligament sizes at the upper two hierarchical levels remain nearly unchanged (Fig. 6a, b d, and e). In addition, Fig. 6(e) shows that fewer cracks can be observed at the middle hierarchical level after annealing. This observation explains the improved mechanical integrity in annealed 3L-HN Ni samples, compared with as-dealloyed ones (see the improved mechanical properties in Figure S6b). This annealing-induced healing phenomenon agrees with the observation by Kashani et al., who also found that annealing at 800 °C can even heal all dealloying micro-cracks due to enhanced surface and bulk diffusion [53]. However, it needs to be noted that annealing hierarchical nanoporous metals at excessively high temperatures and/or for prolonged durations can lead to coarsening or even disappearance of the lower-level structure [54]. Further detailed investigations on structural optimisation are required to address the trade-off between crack-healing-induced improvements in mechanical properties

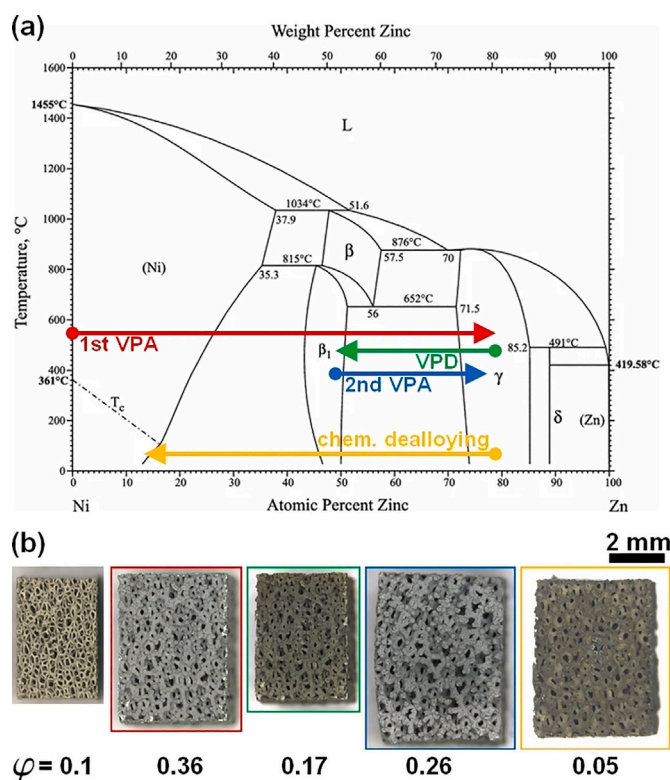


Fig. 5. Illustration of the chemical evolution and macroscopic dimensional changes during the synthesis processes of 3L-HN Ni starting from a 90% porosity NF. (a) the Ni–Zn phase diagram [52] was used to indicate the phase transformations occurring during each step: 1st VPA (red arrow), VPD (green arrow), 2nd VPA (blue arrow) and chemical dealloying (yellow arrow). Temperatures are not drawn to scale because all vapour-phase steps are performed at 500 °C. (b) shows the stereo light microscopy images of the sample after each synthesis step colour-coded to match the arrows in the phase diagram. From left to right: NF, γ -Zn₈₅Ni₁₅ (red), 2L-HN β -Zn₅₀Ni₅₀ (green), 2L-HN γ -Zn₈₄Ni₁₆ (blue) and 3L-HN α -Ni (yellow). The scale bar shown in the top right applies to all stereo light microscopy images. Additionally, the solid fractions of each state are displayed underneath. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

and ligament coarsening-induced reductions in specific surface area, which directly governs interface- and surface-controlled functional properties.

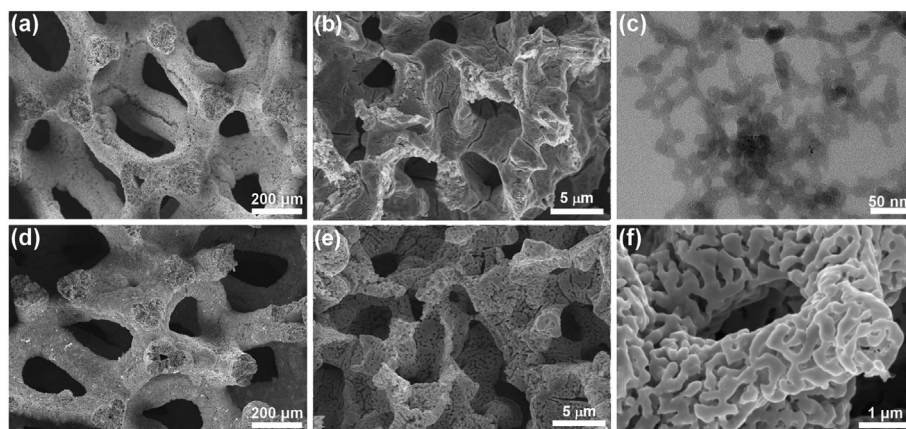


Fig. 6. Microstructure characterisation of 3L-HN Ni. (a–b) SEM images and (c) TEM images of as-dealloyed 3L-HN Ni. (d–f) SEM images of 3L-HN Ni annealed at 300 °C for 1 h. Images (a) and (d), (b) and (e), and (c) and (f) provide direct comparisons of the upper-, middle-, and lower-level hierarchical structures before and after annealing, respectively.

Table 2

Comparison of the surface area measurements via CV and BET for the pristine, 2L-HN, as-dealloyed 3L-HN and annealed 3L-HN Ni. For the CV measurements, scan rates of 0.1 mV and 5 mV s^{−1} were used for the pristine and 2L-HN Ni samples, whereas only a scan rate of 0.1 mV s^{−1} was employed for the as-dealloyed and annealed 3L-HN Ni samples due to the absence of distinguishable peaks at 5 mV s^{−1}.

surface area [m ² g ^{−1}]	pristine NF	2L-HN Ni	3L-HN Ni as-dealloyed	3L-HN Ni annealed
ECSA	0.04–0.05	0.37–2.65	22.37	11.95
BET	0.65	4.58	29.86	8.84

Fig. 5(b) shows the stereo light microscopy images of the sample after each synthesis step colour-coded to match the arrows in the phase diagram. The 1st VPA on NF with $\phi = 0.10$ leads to sample expansion and the formation of γ -Zn₈₅Ni₁₅ foam with $\phi = 0.36$. Subsequent VPD leads to shrinkage and the formation of 2L-HN β -Zn₅₀Ni₅₀ with $\phi = 0.17$. After 2nd VPA, 2L-HN γ -Zn₈₄Ni₁₆ is formed with $\phi = 0.26$. The final chemical dealloying results in 3L-HN Ni with $\phi = 0.05$ and a residual Zn content of 11 at.%. The formation of single-phase structures after each synthesis step was confirmed by XRD analysis (Figure S10). Remarkably, 3L-HN Ni realises a solid fraction, which is approximately half of that of the pristine NF. The pronounced decrease in ϕ is in good agreement with the nearly twofold expansion in overall volume following the entire fabrication process.

4.2. Surface area analysis

The results of the BET measurements vs. the ECSA estimations are listed in Table 2. It should be noted that the cleaning at elevated temperatures under vacuum was not performed for the 3L-HN Ni in order to avoid residual Zn (~10–15 at. %) vaporisation and its subsequent contamination of the device, as well as possible coarsening. Consequently, this may lead to an underestimation of the surface area because adsorbed foreign species (e.g., water) may remain within the porous network.

At the typical scan rates of 5 mV s^{−1} and 1 mV s^{−1} commonly used for ECSA measurements, the CV curves of 3L-HN Ni exhibit no distinguishable peaks. At a substantially lower scan rate of 0.1 mV s^{−1}, well-defined electrochemical peaks emerge as shown in Fig. 7. This behaviour is likely associated with the large bulk volume of the sample, which increases the diffusion length for electrolyte species to access and leave the internal electrode surface, as well as the ultrafine pore structure, which further restricts mass transport within the porous network. Consequently, higher scan rates may not provide sufficient time

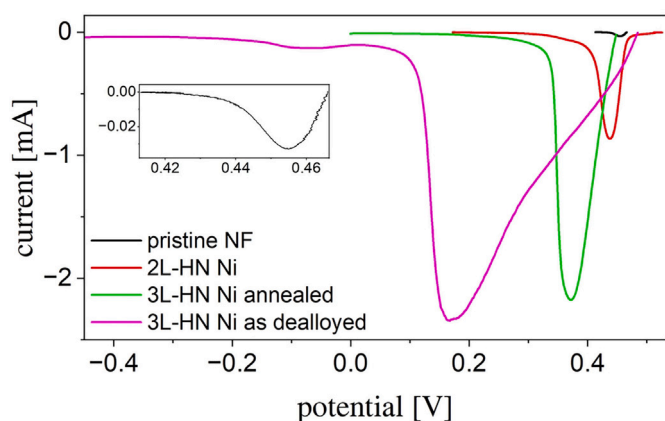


Fig. 7. Electrochemically active surface area determination. CV back scan curves of pristine (black), 2L-HN (red), as-dealloyed 3L-HN (magenta) and annealed 3L-HN Ni (green) in 1M NaOH at a scan rate of 0.1 mV s^{-1} . The potential windows were chosen individually for each sample type, with the lower limit set where the current approaches zero and the upper limit fixed at 0.65 V. The inset shows an enlarged view of the reduction peak of the pristine NF. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

for complete electrolyte penetration and electrochemical equilibration throughout the entire nanoporous structure. However, excessively low scan rates may also introduce complications, such as increased overlap between double-layer charging and faradaic currents, thereby distorting the electrochemical response. In addition, prolonged polarisation can promote the accumulation of adsorbed species on the electrode surface, potentially leading to an overestimation of the apparent electrochemically active surface area. This is particularly evident from the large difference in the ECSA of the 2L-HN Ni sample obtained at different scan rates: $\text{ECSA} = 0.37 \text{ m}^2 \text{ g}^{-1}$ at 5 mV s^{-1} and $\text{ECSA} = 2.65 \text{ m}^2 \text{ g}^{-1}$ at 0.1 mV s^{-1} .

Furthermore, careful selection of the potential window is required, because an excessively wide window may promote the formation of multiple surface monolayers on Ni, thereby causing an overestimation of the ECSA (Figure S7). Although both BET and ECSA methods have limitations in determining absolute values, they consistently reveal the same trend: the specific surface area increases substantially with increasing structural hierarchy and decreases upon coarsening. Further investigation is required to accurately determine the absolute values. Nevertheless, the specific surface area of the as-dealloyed 3L-HN Ni determined by the BET method ($30 \text{ m}^2 \text{ g}^{-1}$) is lower than the literature values of $49\text{--}61 \text{ m}^2 \text{ g}^{-1}$ reported for nanoporous Ni with a ligament size of $6\text{--}8 \text{ nm}$ [55], but this difference is consistent with the well-established inverse relationship between ligament size and specific surface area in nanoporous structures [26,56].

4.3. Mechanical properties

4.3.1. Compressive stress-strain curves

The compressive engineering stress-strain curves of different pristine NFs and the corresponding 2L-HN Ni are presented in Fig. 8. Cyclic loading-unloading compression tests were performed on differently oriented samples. The 90% and 95% pristine NFs show an elliptical pore shape which persists even after the VPA/VPD process. Fig. 8(a) shows a visual comparison of anisotropy in 90% porosity NF samples, where the elliptical pores are oriented either parallel or perpendicular to the specimen's longitudinal axis. Anisotropic structures can lead to different mechanical behaviours depending on the loading direction. Therefore, two sample types were produced each oriented as shown in Fig. 8(a) for the 90% porosity and 95% porosity NFs.

Fig. 8(b) shows the results from 80% porosity NF and the corresponding 2L-HN Ni (hereafter 2L-HN Ni 80%). The isotropic pristine 80% NF shows a typical deformation behaviour of metal foams: linear elasticity, plastic collapse and a densification stage [45]. The plateau region corresponds to progressive cell wall buckling and collapse at nearly constant stress, enabling large strains without a significant increase in load. In contrast, the 2L-HN Ni 80% shows a continuously increasing stress with compressive strain without a plateau region. These distinct deformation behaviours can also be observed in the corresponding compression videos (Video 1 in the Supporting Materials). The increasing stress with compressive strain in 2L-HN Ni 80% may be caused by the higher solid fraction at the upper hierarchical level which hinders plastic collapse and enables densification to occur earlier at lower strains [45]. The same total solid fraction in the 80% NF and 2L-HN Ni 80% implies that the upper hierarchical structure of 2L-HN Ni 80% has a much higher ϕ than the 80% NF, since the total solid fraction is a combination of the upper and lower levels. Another possible reason might be densification and an increase in connectivity occurring at the lower hierarchical level during compression.

Fig. 8(c)–(f) show that the 90% porosity NF and 95% porosity NF exhibit different mechanical behaviour in the longitudinal ($\parallel$) and perpendicular ($\perp$) directions due to an anisotropic structure. Fig. 8(c) and (e) show that the pristine longitudinal 90% and 95% NFs exhibit the typical deformation behaviour in low density metal foams except for a drop of stress before the plateau regions. This is attributed to the high-slenderness-ratio struts aligned along the compression direction (left of Fig. 8a), which promote bending and buckling of the struts, in agreement with the compression videos (Videos 2 and 3 in the Supporting Materials). This bending mechanism becomes less likely to occur when the slenderness ratio decreases [57], as shown in Fig. 8(d) and (f). The pristine perpendicular 90% and 95% NFs exhibit a quasi plateau without a stress drop.

For 90%, similar stress–strain curve characteristics are observed in the corresponding 2L-HN Ni samples (Fig. 8c and d). For 95%, a pronounced non-linear elastic behaviour and an additional stress drop in the plateau region are observed in the 2L-HN Ni structures, as shown in Fig. 8(e) and (f). The video recordings of compressed longitudinal 2L-HN Ni 95% samples show that the initial non-linear elastic behaviour at the beginning is strongly associated with their irregular geometry. Furthermore, the stress drop observed in the plateau region is attributed to the lateral elongation of struts oriented perpendicular to the compression direction, which deform to the point of fracture.

At very small compressive strains, all 2L-HN Ni samples exhibit a lower cyclic stress-strain response than pristine NF, a result attributed to the reduced initial connectivity introduced during the dealloying process. Since both structures possess micrometre-scale strut/ligament dimensions, their mechanical response is primarily governed by the connectivity rather than by ligament-size strengthening effects. With increasing compressive strain, however, the flow stress of 2L-HN can remain lower (90% $\parallel$), comparable (90% $\perp$) or higher (80%, 95% $\parallel$, and 95% $\perp$) than that of the pristine NF samples. This behaviour can be attributed to the combined effects of (1) the lower initial connectivity of the leveled-wave structure compared with the conventional Gibson-Ashby-type architecture at an equivalent solid fraction, and (2) the different rate of increase in network connectivity during the densification stage.

It should also be noted that the deviation or variation in the solid fraction of the 2L-HN Ni samples caused by volume changes during dealloying can also contribute to the differences in flow stress. This effect is particularly evident for the 2L-HN Ni fabricated from the 95% porosity NF. In this case, the solid fraction increases from 5% in the initial NF to 8% in the corresponding 2L-HN Ni, thereby further enhancing the mechanical performance in addition to the structural effects discussed above, as shown in Fig. 8(e) and (f).

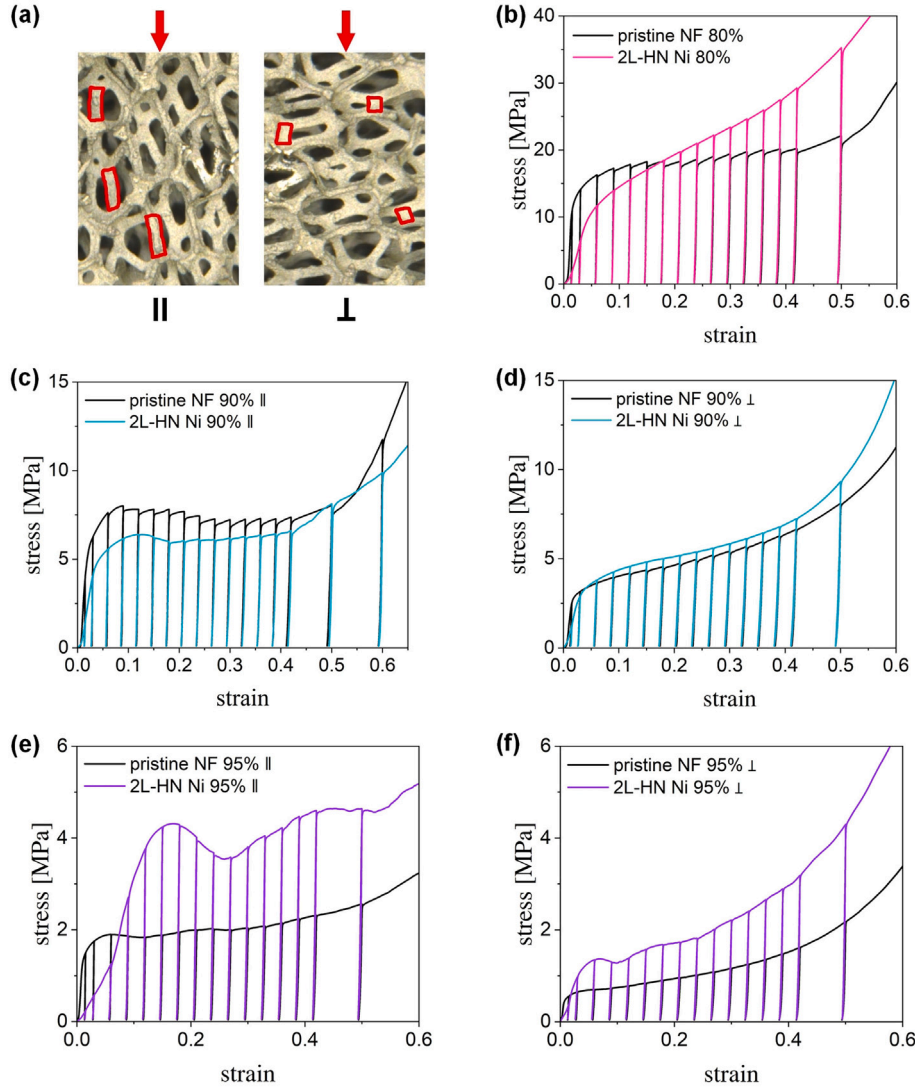


Fig. 8. Cyclic loading-unloading compression tests of pristine NF and 2L-HN Ni. (a) a visualisation of the pore orientations longitudinal $\parallel$ and perpendicular $\perp$ to the loading direction (red arrows). Some struts $\parallel$ to the loading direction are outlined in red. Stress-strain curves for (b) the 80% porosity pristine NF and its 2L-HN Ni, (c,d) the 90% porosity NF and its 2L-HN Ni, and (e,f) the 95% porosity NF and its 2L-HN Ni. $\parallel$ denotes pore elongation oriented longitudinally to the compression direction; $\perp$ denotes the pore elongation oriented perpendicular to the compression direction. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4.3.2. Scaling behaviour of Young's modulus

Young's modulus (E) was determined from a linear fit of the unloading portions of the stress-strain curves. Open-cell metal foams are known to exhibit an increase in Young's modulus up to the point of local yielding [45]. After yielding, E decreases and only rises significantly again during densification. This behaviour was observed for all NFs tested in this study. The highest E , measured just before the drop, was taken as the representative Young's modulus for each NF, typically occurring at strains of 0.03–0.09. This E is then normalised by the Young's modulus of bulk Ni ($E_0 = 200$ GPa).

Fig. 9 shows E/E_0 as a function of ϕ for all NFs and corresponding 2L-HN Ni samples investigated in this work. It shows that with decreasing ϕ , both 2L-HN Ni and pristine NF exhibit a reduction in E . At identical ϕ , the 2L-HN Ni consistently exhibits a lower E than the pristine NF. The reduced E/E_0 of 2L-HN Ni is expected and can be attributed to the lower effective connectivity of its combined leveled-wave (lower level) and Gibson-Ashby (upper level) structures compared to the fully Gibson-Ashby structure of NF. This reduction in stiffness achieved by introducing a leveled-wave or dealloyed structure can be advantageous

for metallic bioimplant applications, as it may help mitigate the stress-shielding effect by better matching the elastic modulus of surrounding bone tissue. In addition, the hierarchical structure offers an increased specific surface area, which may be beneficial for enhancing interfacial interactions and biological response in implant applications.

To quantitatively compare the experimental results with scaling law predictions, the scaling law (Eq. 3) for the Young's modulus of 2L-HN Ni with all constants applied becomes:

$$E_{\text{GAS-2L}} = 2.03 E_0 \phi^{0.5} \left(\frac{\phi^{0.5} - 0.159}{1 - 0.159} \right)^{2.56} \quad (5)$$

Following the previously proposed scaling law for n levels (Eq. 4) the scaling law for the Young's modulus of 3L-HN Ni with all constants applied becomes:

$$E_{\text{GAS-3L}} = 4.121 E_0 \phi^{2/3} \left(\frac{\phi^{1/3} - 0.159}{1 - 0.159} \right)^{5.12} \quad (6)$$

The prediction curves from Eqs. (1), (5) and (6) are shown alongside the experimental E/E_0 values of all NFs and 2L-HN Ni in Fig. 9.

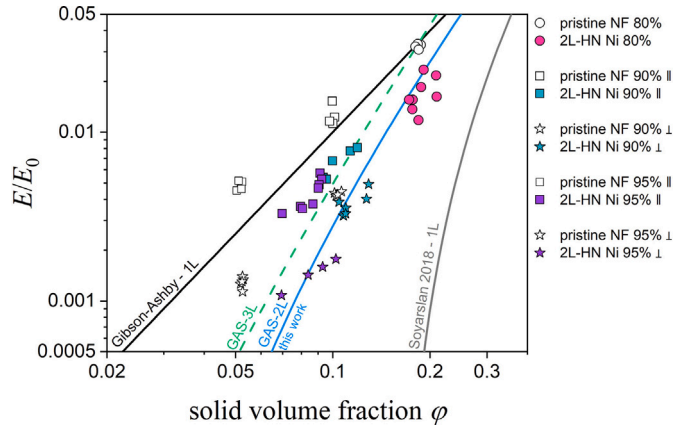


Fig. 9. Comparison of the experimental results to the scaling law prediction. Normalised Young's modulus versus solid fraction. Open symbols: experimental data for NFs; filled symbols: experimental data for 2L-HN Ni; black and grey lines: Gibson-Ashby equation [45] and Soysarslan equation [46] for non-hierarchical network structure, Eqs. (1) and (2); blue and green lines: GAS-scaling laws for two and three level hierarchical network structures in this work, Eqs. (5) and (6). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Additionally, a prediction curve based on Eq. (2), applicable to leveled-wave structures or as-dealloyed nanoporous metals is also included. It can be seen that the 90% and 95% porosity NFs show higher E/E_0 than predicted for the longitudinal samples and lower values than predicted for the perpendicular samples, reflecting the expected deviations due to structural anisotropy. Interestingly, this initial anisotropy persists after the VPA-VPD process and is still evident in the mechanical response of the 2L-HN Ni. Overall, the proposed scaling laws (Eqs. 3 and 5), which account for the combined leveled-wave and Gibson-Ashby structure, show good agreement with the experimental data (Fig. 9).

The 3L-HN Ni broke during the compression tests because of severe crack formation during chemical dealloying and could not be analysed. However, annealing can improve the mechanical integrity by crack healing as already discussed in Section 4.1.4. Annealing at too high temperatures can lead to an excessively coarsening effect combining the 2nd and 3rd levels into one structure. The highest temperature tested for annealing (500 °C) led to a sample that was able to be compressed a little bit further within its elastic regime before breaking while still showing well defined three levels of structure (Figures S8–S9). Even though the annealed sample broke prior to reaching its yield strength (Figure S6b), the last unloading curve already shows a Young's modulus that is on par with the 2L-HN Ni (Figure S8). Its real Young's modulus is probably even higher since the unloading curve corresponding to the yield strength has not been reached and the values for the Young's modulus rise with higher strain before they drop after yielding starts. This shows good agreement with the proposed scaling law for n levels (Eqs. 4 and 6).

4.3.3. Comparison with literature data

The mechanical properties of 2L-HN Ni in this work are compared with data from other dealloyed porous metals in the literature (Fig. 10). Two-level hierarchical nested-network nanoporous gold (2L-HNN) materials fabricated using two-step electrochemical dealloying by Shi et al. [22] are selected for comparison due to their two-level hierarchical structure and their level-wave structure at the lower hierarchical level. Compared to 2L-HNN Au, 2L-HN Ni achieves significantly lower solid fractions and a much higher mass-specific Young's modulus, as illustrated in Fig. 10. The same conclusion also holds when compared with as-dealloyed unimodal nanoporous gold, which follows the scaling relationship described by the Soysarslan equation (grey line in Fig. 10).

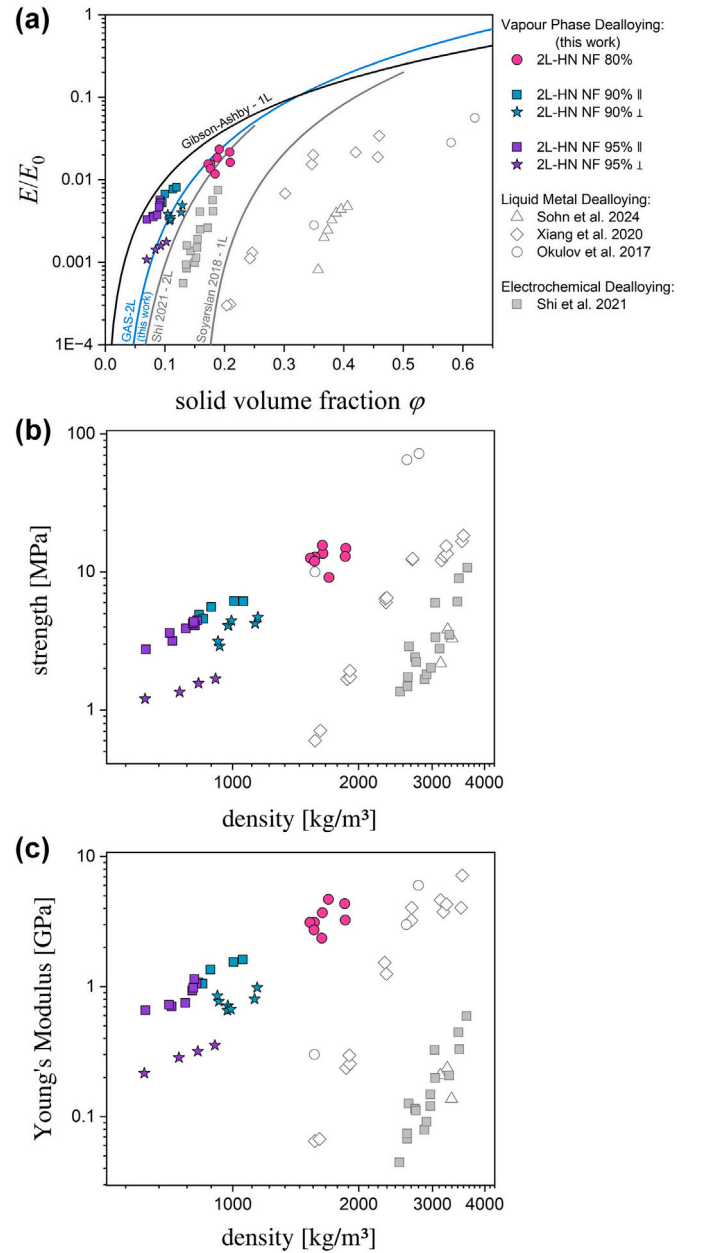


Fig. 10. Comparison of mechanical properties for 2L-HN Ni in this work with other dealloyed porous metals. (a) normalised Young's modulus versus solid volume fraction, (b) yield strength versus density, (c) effective Young's modulus versus density. Filled coloured symbols: 2L-HN Ni of this work (ligament size $L = \sim 2 \mu\text{m}$); open grey symbols: liquid metal dealloyed porous Nb ($L = 840 \text{ nm}$) [58], Ti ($L = 870\text{--}1270 \text{ nm}$) [59], FeCr ($L = 3 \mu\text{m}$) [60]; filled grey symbols: electrochemically dealloyed hierarchical nanoporous Au (2L-HNN Au, $L = 15 \text{ nm}$ at the lower hierarchical level). Black line: Gibson-Ashby equation [45]; grey lines: Soysarslan equation [46] and Shi equation [22] for one-level (1 L) and two-level (2 L) nested-network leveled-wave structures, respectively; blue line: GAS-scaling equation for 2 L hierarchical network structure in this work, Eq. (5). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Macroscopic compressive results of non-hierarchical porous metals (such as Ti [59], Fe-Cr alloys [60] and Nb [58]) fabricated by liquid metal dealloying are also included for comparison in particular their ligament sizes (800 nm - 3 μm) are comparable to the lower level ligament size of 2L-HN Ni ($\sim 2 \mu\text{m}$). 2L-HN Ni can reach much lower solid fractions and, at an equivalent solid fraction of 0.2, exhibits a normalised Young's

modulus that is approximately one order of magnitude higher than comparable liquid metal dealloyed structures (Fig. 10). This comparison further demonstrates that 2L-HN Ni, which integrates leveled-wave and Gibson–Ashby architectures, exhibits higher connectivity and stiffness than both single-level and two-level leveled-wave structures alone. Notably, this hierarchical design bridges the performance gap in the density–modulus space between naturally self-organised dealloyed porous metals and conventionally engineered Gibson–Ashby cellular architectures.

For structural functional applications, such as bio-implant metallic materials, structural power devices and actuation, mechanical performance high-surface area and weight play important roles. Analogous to the determination of the representative E , the effective yield strength σ of 2L-HN Ni in this work is taken as the flow stress at the strain corresponding to the highest Young's modulus E in the small strain regime (below 0.1), since the subsequent decrease in E results from the local yielding. The σ and E of 2L-HN Ni are then plotted against density and compared with literature data in Fig. 10(b) and (c). This shows that 2L-HN Ni materials can reach a much lower density regime and exhibit higher mass-specific properties for both yield strength and Young's modulus compared with other dealloyed porous materials.

5. Conclusions

In summary, a scalable fabrication route for macroscopic two- and three-level hierarchical porous Ni networks has been demonstrated using vapour phase alloying/dealloying in combination with chemical dealloying. The resulting architectures exhibit ligament sizes down to 13 nm and nearly three orders of magnitude increase in specific surface area compared to the precursor foam.

The Young's modulus–solid fraction relationship of 2L-HN Ni is well described by our newly developed scaling law derived from established single-level scaling relations within a recursive homogenisation approach. 2L-HN Ni retains mechanical properties close to those of the precursor while providing a substantially enhanced surface area. This highlights the potential of 2L-HN Ni as an advanced scaffold material for structural, electrochemical, and multifunctional applications. In particular, its combination of electrical conductivity, large surface area and mechanical robustness may enable improved performance compared to conventional NFs.

Overall, the presented alloying–dealloying strategy offers a versatile pathway for the design of mechanically robust, high-surface-area, hierarchical metallic networks. The VPA–VPD approach is not inherently limited to the Ni foam. In principle, it can be extended to other porous metals that are compatible with vapour-phase alloying and dealloying, such as Cu foams. The proposed scaling law provides a quantitative basis for predicting the mechanical response of multilevel hierarchical materials. Further optimisation of processing parameters and hierarchical design is expected to expand the accessible structure–property space and broaden the functional application range of hierarchical metallic foams.

CRedit authorship contribution statement

Ulrike Dette: Writing – original draft, Methodology, Investigation, Conceptualization. **Gunnar Schaan:** Writing – review & editing, Investigation. **Shan Shi:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

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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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.matdes.2026.117082.

Data availability

Data will be made available on request.

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