



Fostering strengths against hydrogen embrittlement: insights from nanotwin-ability and post-treatment effects in additively manufactured CoCrFeMnNi

Renhao Wu, Soung Yeoul Ahn, Yeon Taek Choi, Hyojin Park, Man Jae SaGong, Ganesh Sattineni, Hyeonseok Kwon, Sang Guk Jeong, Gitaek Lee, Ho Hyeong Lee, Haiming Zhang & Hyoung Seop Kim

To cite this article: Renhao Wu, Soung Yeoul Ahn, Yeon Taek Choi, Hyojin Park, Man Jae SaGong, Ganesh Sattineni, Hyeonseok Kwon, Sang Guk Jeong, Gitaek Lee, Ho Hyeong Lee, Haiming Zhang & Hyoung Seop Kim (2024) Fostering strengths against hydrogen embrittlement: insights from nanotwin-ability and post-treatment effects in additively manufactured CoCrFeMnNi, Materials Research Letters, 12:10, 689-699, DOI: [10.1080/21663831.2024.2371521](https://doi.org/10.1080/21663831.2024.2371521)

To link to this article: <https://doi.org/10.1080/21663831.2024.2371521>



© 2024 The Author(s). Published by Informa UK Limited, trading as Taylor & Francis Group.



[View supplementary material](#)



Published online: 09 Jul 2024.



[Submit your article to this journal](#)



Article views: 3096



[View related articles](#)



[View Crossmark data](#)



Citing articles: 15 [View citing articles](#)



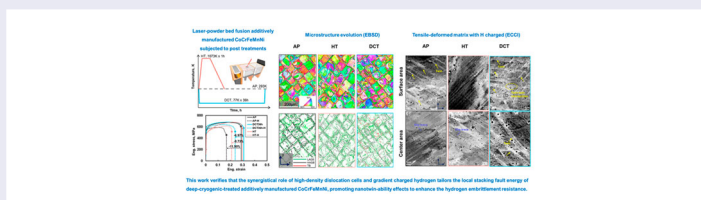
Fostering strengths against hydrogen embrittlement: insights from nanotwin-ability and post-treatment effects in additively manufactured CoCrFeMnNi

Renhao Wu^{a*}, Soung Yeoul Ahn^{b*}, Yeon Taek Choi^b, Hyojin Park^b, Man Jae SaGong^b, Ganesh Sattineni^b, Hyeonseok Kwon^b, Sang Guk Jeong^b, Gitaek Lee^c, Ho Hyeong Lee^a, Haiming Zhang^d and Hyoung Seop Kim^{ib a,b,c,e,f}

^aGraduate Institute of Ferrous & Eco Materials Technology, Pohang University of Science & Technology, Pohang, Korea; ^bDepartment of Materials Science & Engineering, Pohang University of Science & Technology, Pohang, Korea; ^cSchool of Convergence Science and Technology, Pohang University of Science & Technology, Pohang, Korea; ^dDepartment of Plasticity Technology, School of Materials Science & Engineering, Shanghai Jiao Tong University, Shanghai, People's Republic of China; ^eAdvanced Institute for Materials Research (WPI-AIMR), Tohoku University, Sendai, Japan; ^fInstitute for Convergence Research and Education in Advanced Technology, Yonsei University, Seoul, South Korea

ABSTRACT

This study delves into effects of deep cryogenic treatment (DCT) on enhancing the hydrogen embrittlement resistance of CoCrFeMnNi high-entropy alloy fabricated via laser powder-bed-fusion (L-PBF). Comparatively assessing as-print, conventional heat treatment, and DCT, we uncover how nanotwin formation within matrix serves as a critical mechanism to combat adverse effects of hydrogen embrittlement. This work reveals that DCT not only mitigates inherent residual stresses from L-PBF, thereby fostering dislocation redistribution and microstructural stabilization, but also synergizes with high-density dislocation cells. Our findings articulate a nuanced understanding of microstructural evolution in response to post-treatments and consequential enhancement of hydrogen embrittlement resistance.



ARTICLE HISTORY

Received 22 April 2024

KEYWORDS

Laser-powder bed fusion additive manufacturing; High-entropy alloy; Nanotwin-ability; Deep cryogenic treatment; Hydrogen embrittlement resistance

Highlights

- Laser-based additively manufactured CoCrFeMnNi undergoes post heat treatment and deep cryogenic treatment to tailor dislocations and residual stress.
- The inherent residual stress acts as the driving force for the redistribution of dislocations, leading to the development of a stable microstructure after deep cryogenic treatment.
- High-density dislocation cells and hydrogen collaborate to lower the local stacking fault energy, triggering gradient nanotwins.
- Nanotwin-ability effects by deep cryogenic treatment (77 K × 36 h) on the hydrogen embrittlement resistance of CoCrFeMnNi with interior defects are verified.

1. Introduction

The ongoing pursuit of advanced metals capable of reliable performance in hydrogen-related environments is

of paramount importance [1], particularly for structural materials that possess both high strength and enduring toughness. The CoCrFeMnNi high-entropy

CONTACT Renhao Wu ✉ wurenhao@postech.ac.kr; Haiming Zhang ✉ hm.zhang@sjtu.edu.cn; Hyoung Seop Kim ✉ hskim@postech.ac.kr

*The authors contributed equally to this work.

Supplemental data for this article can be accessed online at <https://doi.org/10.1080/21663831.2024.2371521>.

© 2024 The Author(s). Published by Informa UK Limited, trading as Taylor & Francis Group.

This is an Open Access article distributed under the terms of the Creative Commons Attribution-NonCommercial License (<http://creativecommons.org/licenses/by-nc/4.0/>), which permits unrestricted non-commercial use, distribution, and reproduction in any medium, provided the original work is properly cited. The terms on which this article has been published allow the posting of the Accepted Manuscript in a repository by the author(s) or with their consent.

alloy (HEA), characterized by its stable single-phase face-centered cubic (FCC) microstructure [2,3], exhibits superior mechanical properties such as high fracture toughness, effective strain hardening, and significant resistance to hydrogen embrittlement [4,5], rivaling the performance of extensively utilized austenitic stainless steels [6,7].

The advent of laser-based metal additive manufacturing (MAM) [8–10] offers a versatile solution for tailoring hierarchical microstructures that are structurally originated [11,12]. A key feature is the evolution of dislocation cells, which are engendered by residual stresses inherent in alloys processed through the laser-based MAM process [13,14]. Nonetheless, the propensity of dense dislocation cells and phase interfaces in the complex and hierarchical microstructures of AM metallic materials are the preferred sites for hydrogen accumulation, leading to an increase in vacancy formation, thereby diminishing the hydrogen resistance of laser-based MAM processed FCC materials [2,9,15]. The incidence of hydrogen embrittlement phenomena can potentially be diminished in AM metallic materials that exhibit higher uniformity and minimal defects [9], which includes the reduction of high-energy interfaces, such as precipitates, inclusions, and micro-cracks. Consequently, the activation of certain underlying mechanisms, such as nanotwins, might be imperative for enhancing hydrogen resistance, thus paving the way for the design of strong, ductile, and hydrogen-tolerant metallic materials.

Printing defects, including porosity and micro-cracks on the surface and within the metal's interior, amplify the local stress intensity factor and hydrogen accumulation [9]. These defects originate from the thermal residual stress induced by a rapid cooling rate and cyclic heating history [10,13]. Deep cryogenic treatment (DCT) emerges as a potent and green strategy for mitigating residual stress and tailoring microstructure [16,17]. Moreover, the DCT induced deformation twins in the MAM parts [18,19], offering a potential bulwark against hydrogen embrittlement [20]. However, ambiguities persist regarding the capacity for nanotwin formation within dislocation cells of laser-based MAM-processed materials subjected to DCT, and implications thereof on their behaviors in hydrogen-rich environments.

In the present work, a comparative experimental study was conducted on the hydrogen embrittlement of a model material, CoCrFeMnNi HEA, fabricated by the L-PBF process. Post-processing strategies, including heat treatment and DCT, were implemented to elucidate the underlying deformation mechanism of hydrogen-charged MAM samples. This work demonstrates that the nanotwinning capability, induced by the inherent residual stress, can be redistributed through DCT, thereby

augmenting strengths and mitigating weaknesses under hydrogen-rich conditions.

2. Materials and methods

This work employed a laser-powder bed fusion (L-PBF) process to fabricate the CoCrFeMnNi. The spherical CoCrFeMnNi powders were initially produced using gas atomization (d_{10} : 14.9 μm , d_{50} : 29.3 μm , d_{90} : 51.2 μm). The measured flow-ability using a Hall-flowmeter was 16.1 s for flowing 50 g of powders, and the apparent density was 4.45 g/cm³. Specific processing parameters were used, including a laser power of 200 W, scanning speed of 750 mm/s, hatch spacing of 90 μm , laser beam diameter of 90 μm , bidirectional scanning, layer thickness of 30 μm , and 180° rotation between layers. Cuboid samples measuring 12 × 10 × 10 mm³ on each side were fabricated and subsequently sliced into 0.5-mm-thick slices via electrical discharge machining. Three groups of L-PBF processed samples (labeled as as-printed, AP) underwent annealing in heat treatment (1073 K for 1 h and water cooling, labeled as HT) and DCT (77 K for 36 h, labeled as DCT), as depicted in Figure 1(a). The relative densities of AP, HT, and DCT samples, measured using the Archimedes method, are $99.16 \pm 0.53\%$, $99.00 \pm 0.30\%$, and $99.89 \pm 0.16\%$, respectively. As shown in Figure 1(b), the AP sample exhibits some interior defects (gas pores and solidification microcracks), regarded as an inherent deficiency in the L-PBF process. Moreover, the chemical composition distribution at high magnification revealed negligible element segregation or fluctuation, as illustrated in Figure 1(c). The HT and DCT samples also exhibit similar interior defects and uniform chemical composition distribution, as provided in the Supplementary file.

Electron channeling contrast imaging (ECCI) analysis was performed on the X-Z plane to evaluate how hydrogen affects tensile deformation. The morphology of the AP sample in the X-Y plane was characterized using a field-emission scanning electron microscope (Ultra 55, ZEISS) equipped with backscattered electrons (BSE) and electron backscattered diffraction (EBSD). Fractography was observed using a JEOL FE-SEM instrument. Chemical composition analysis was conducted using an energy dispersive spectrometer (EDS).

The samples were subjected to electrochemical hydrogen charging at a constant current density of 100 A/m² at 293 K using potentiostat/galvanostat equipment (6035A, Agilent) in a 1L NaCl + NH₄SCN (10:1, wt%) solution for 12 h. The hydrogen-charged counterparts of the AP, HT, and DCT specimens are designated as AP-H, HT-H, and DCT-H, respectively. Dog-bone-shaped samples,

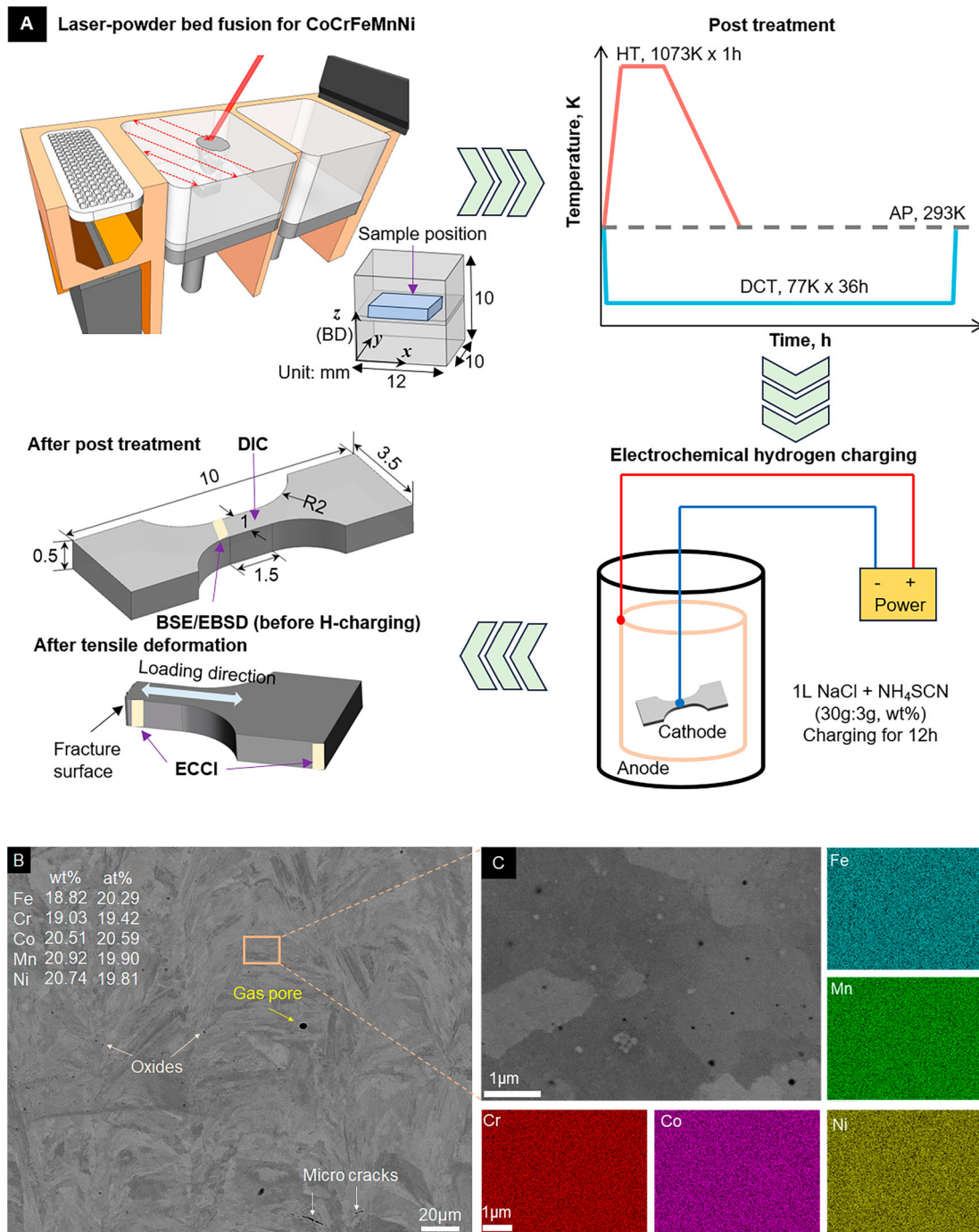


Figure 1. (a) Schematic illustration detailing the overall experimental procedure. The operation protocols for the L-PBF process are followed by subsequent post-treatment of the HT and DCT, and hydrogen charging. The tensile sample and microstructure observation areas are also shown; (b) The AP sample on the X-Y plane showing typical defects. The insert presents the ratio of elemental compositions; (c) Microstructure of the AP sample on the X-Y plane with element distributions.

with a gauge length of 1.5 mm, were prepared for tensile tests under a slow strain rate of $1 \times 10^{-4} \text{ s}^{-1}$. The tensile samples were finely polished up to a 1200 grit finish, yielding a final thickness of $\sim 350 \mu\text{m}$. Strain measurements were precisely conducted using the digital image correlation method (ARAMIS 5M, GOM Optical Tech.) [21].

3. Results and discussion

Uniaxial tensile tests were conducted for the AP, HT, and DCT samples, along with their hydrogen-charged counterparts. The representative engineering stress-strain plots and the work hardening rate are depicted in Figure 2(a,b). Hydrogen charging is observed to adversely affect

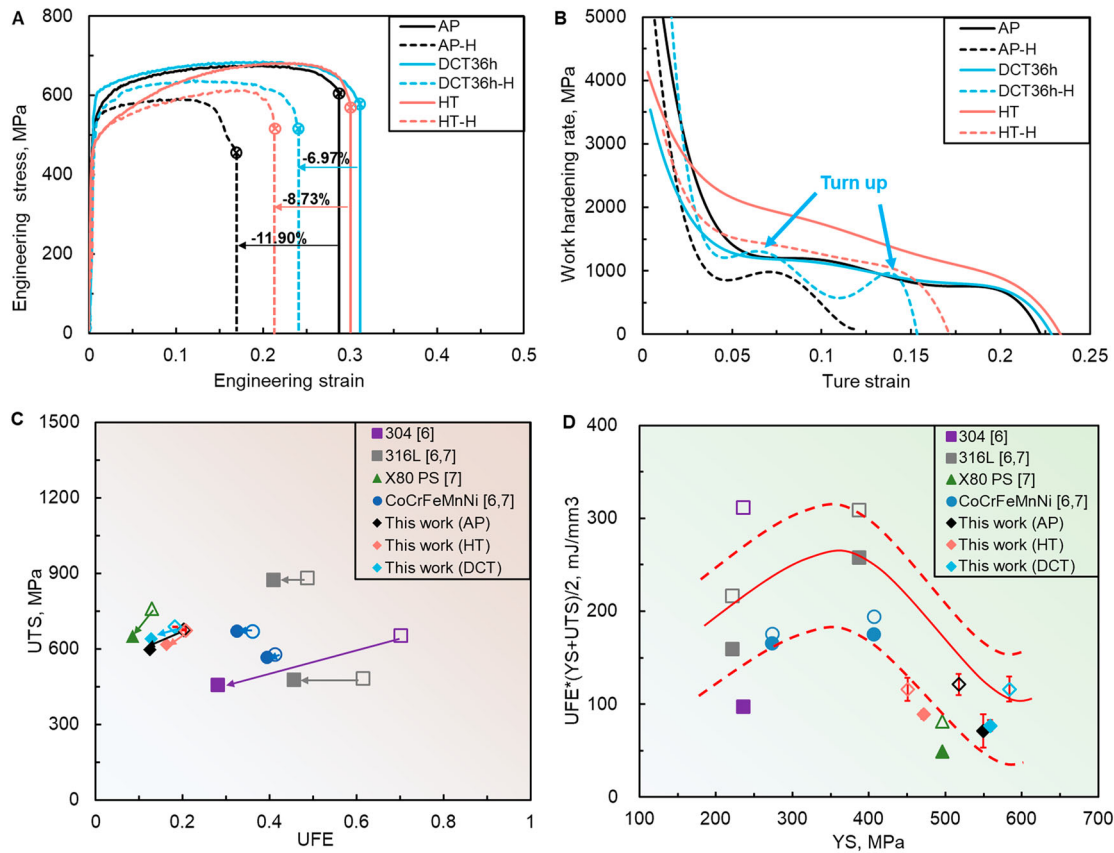


Figure 2. (a) Tensile stress-strain curves of the AP, HT, and DCT samples with/without hydrogen charging (marked by dashed/solid lines). The symbols '⊗' indicate the threshold of fracture points; (b) Work hardening rate of the samples; (c) Ashby diagrams plotting UFE versus UTS for the present work in comparison with reported results [6,7]. The symbols '◆/◇' filled/unfilled inside denote the matrix with/without hydrogen charging; (d) $UFE \cdot (YS + UTS)/2$ plotted versus YS for the FCC alloys in various conditions.

Table 1. Summary of mechanical properties of the AP, HT, and DCT samples in hydrogen-free/charged status after tensile tests.

Sample	YS, MPa	UTS, MPa	UFE, %	TE, %	$UFE \cdot (YS + UTS)/2$, mJ/mm ³
AP	518 ± 8	675 ± 2	20.32 ± 2.12	30.71 ± 2.51	121.15 ± 11.64
AP-H	550 ± 12	597 ± 6	12.41 ± 3.16	20.58 ± 5.02	71.11 ± 17.71
HT	451 ± 33	672 ± 16	20.67 ± 1.31	27.01 ± 4.41	116.13 ± 12.40
HT-H	472 ± 25	616 ± 0	16.35 ± 0.47	22.81 ± 0.20	88.93 ± 4.58
DCT	584 ± 16	687 ± 1	18.29 ± 0.89	31.82 ± 0.89	116.25 ± 13.31
DCT-H	559 ± 25	641 ± 3	12.82 ± 0.77	23.60 ± 0.88	76.90 ± 6.02

the ductility of these samples, with total elongation (TE) losses of 11.90%, 8.73%, and 6.97% for the AP, HT, and DCT samples, respectively, when compared to their hydrogen-free counterparts. A comprehensive summary of the mechanical properties is presented in Table 1 for the repeated tensile tests. The DCT samples exhibit a significant enhancement in achieving a higher synergy of ductility and strength, with a TE of 31.82% and a yield strength (YS) of 584 MPa, among all samples without hydrogen charging. In the context of hydrogen embrittlement susceptibility, both HT-H and DCT-H samples show viable resistance to hydrogen embrittlement compared to the AP-H counterpart regarding ductile elongation.

Moreover, as seen in Figure 2(b), global work hardening rates were also affected by hydrogen. The stacking fault energy (SFE) of the CoCrFeMnNi is a critical factor affecting the mechanical properties [22–24] because the deformation twinning induced at elevated dislocation density stages can significantly enhance the work hardening capability. Notably, the DCT-H sample features two distinct inflections, indicating the activation of sequential deformation mechanisms. The thermal desorption spectroscopy (TDS) experiments were carried out to evaluate the hydrogen content of these samples, which indicated no significant differences in the primary desorption behaviors. The details are presented in the Supplementary file.

Figure 2(c) presents a comparison between conventionally forged/rolled FCC alloys [6,7,25] and L-PBF CoCrFeMnNi HEA, aiming to explore the hydrogen impacts of material type and manufactured status. However, the dislocation cells exhibit vulnerability to hydrogen embrittlement [15,26], indicating that the level of hydrogen embrittlement resistance is below par with that of their forged/rolled counterparts. Hydrogen embrittlement manifests significantly in the AP sample that possesses inherent interior defects, leading to a pronounced reduction in ductility [6,27,28]. From the perspective of the capacity to resist damage from external energy [29], as illustrated in Figure 2(d), a peak-shaped distribution is observed between the YS and the plastic deformability. The MAM samples emerge as a trade-off between strength and toughness owing to their interior process-induced defects (e.g. gas pores and solidification microcracks) suffering from hydrogen embrittlement. While the DCT sample demonstrates potential in remedying or even enhancing mechanical performances in hydrogen-related applications.

Figure 3 facilitates multiscale characterization of the AP, HT, and DCT samples. Figure 3(a) presents the inverse pole figure and kernel average misorientation (KAM) maps of these samples in the X-Y plane. A notable accumulation of misorientation is observed within the melt pool center, as delineated by the KAM and misorientation angle boundaries. Specifically, in the DCT samples, the presence of twin boundaries (red line) is distinctly visible, as also confirmed by the local misorientation. The average grain sizes for AP, HT, and DCT samples are $54.45 \pm 15.62 \mu\text{m}$, $58.35 \pm 16.50 \mu\text{m}$, and $50.63 \pm 14.32 \mu\text{m}$, respectively. The respective fractions of a twin boundary are 0.2%, 0.2%, and 3.0%. While the post-treatment processes result in minor alterations in the grain size, they do not influence the distribution of grain size. Consequently, this work effectively excludes effects of variations in grain size and Mn segregation (refer to Figure 1(c)) on hydrogen resistance [30].

The ECC images in Figure 3 reveal both the evolution of columnar grain structures and internal dislocation cells, progressing from the surface to the center regions. Despite the inherent heterogeneity characteristic of the metallic parts [31], the HT sample demonstrates a diminished degree of cellular dislocation entanglement. This reduction is attributed to recovery and recrystallization [6,30], leading to the partial dissolution of dislocations. In both AP and DCT samples, dislocations appeared as high-energy-state cells and manifested as intricate networks, with the DCT sample exhibiting more elongated and thinner grains. The variations in the structural adaptation of the grain boundary and dislocation cells are driven by substantial misorientation and

crystalline defects [32], further driven by mechanisms of hydrogen trapping and diffusion [33,34] across micro and nano scales [35].

Figure 4 presents the ECC images of the deformed microstructure of L-PBF CoCrFeMnNi HEA samples subjected to hydrogen charging, particularly near the necking region, observed in the cross-sectional (X-Z plane) view. Due to the inherently limited hydrogen diffusivity in the FCC alloys facilitated by the electrochemical hydrogen charging [7,36,37], hydrogen penetration is predominantly superficial, leading to a bifurcation into two distinct zones: the hydrogen-affected (H-affected) zone near the surface and the less affected (less-H-affected) zone at the center. As provided in the Supplementary file, the deformed AP and DCT samples in a hydrogen-free state also show the dislocation cells and column grains near the fracture area. However, the twins cannot be observed for these counterparts.

As shown in Figure 4(a–c), the deformed microstructures in the H-affected zone of the AP, HT, and DCT samples present a high density of dislocations with the observed unidirectional slip traces. The critical tensile stress required to initiate deformation twinning typically ranges between 720 and 750 MPa, as reported by existing literature [23,38,39]. However, the SFE, a key factor influencing the onset of twinning, varies under diverse microstructural conditions [20,40,41]. Near the surface H-affected zone, where the hydrogen concentration is notably high, the local SFE is reduced [40], thereby inversely promoting a higher concentration and compatibility of hydrogen [20,41] as well as the formation of nanotwins [22,42–44] during low strain rate tensile deformation. Consequently, the occurrence of a turn-up trend in the tensile curve, as expected, is observed in Figure 2(b) at $\sim 7\%$ true strain. Intriguingly, two distinct peak shapes are observed in the DCT sample. The latter turn-up trend at $\sim 13\%$ true strain can be attributed to the interaction of nanotwins induced by residual stress and plastic deformation. Information regarding residual stress developed in the AP, HT, and DCT samples is detailed in the Supplementary file. Conversely, the limited diffusivity of hydrogen hinders its migration toward the center of the sample via cathodic hydrogen charging [45,46]. This effectively inhibited the twinning ability in the AP sample.

Upon undergoing heat treatment and hydrogen charge, the HT sample exhibits a bifurcated mechanical behavior characterized by a notable decrease in yield strength alongside a resistance to toughness loss compared with the AP sample. In FCC alloys with high Mn content, the interaction between hydrogen and Mn catalyzes hydrogen-related plastic slip, which induces brittle fracture on the surface of the MAM matrix [30].

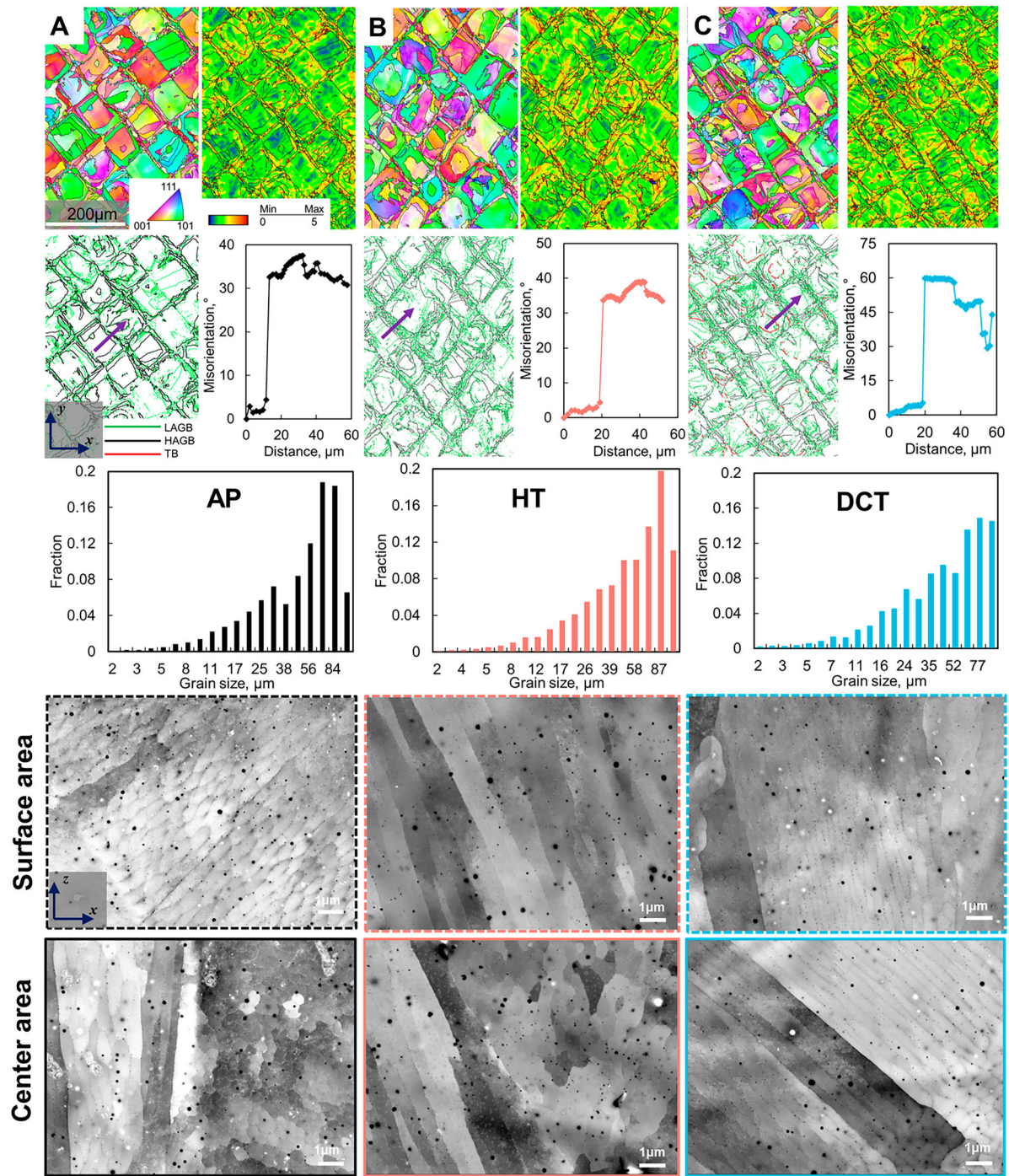


Figure 3. Grain morphology, boundary, and KAM in the X-Y plane by EBSD maps of H-free samples: (a) AP, (b) HT, and (c) DCT. The ECC images show more spidery columnar grains produced by DCT, not seen in AP and HT, in the X-Z plane. L/HAGB and TB stand for low/high angle grain boundary and twin boundary, respectively.

This HT process helps absorb partial high-density cellular dislocations in the laser-based MAM CoCrFeMnNi matrix to reduce residual stress [27] and enable a more uniform distribution of elements [33]. This simultaneously hinders the genesis of microcracks and curtails the rapid diffusion of hydrogen or hydrogen-vacancy interaction [25], a phenomenon largely facilitated by the Mn-hydrogen reaction [26]. The resilience of the DCT sample

stems from their high surface separation energy, marked coherency, and low hydrogen solubility, collectively triggering hydrogen-enhanced local plasticity [36,47]. The presence of nanotwins in the DCT sample enhances local strengthening by the aggregation of hydrogen through impeded diffusion [20,48], thereby elevating the energy threshold required for hydrogen desorption and inhibiting the initiation and propagation of hydrogen-induced

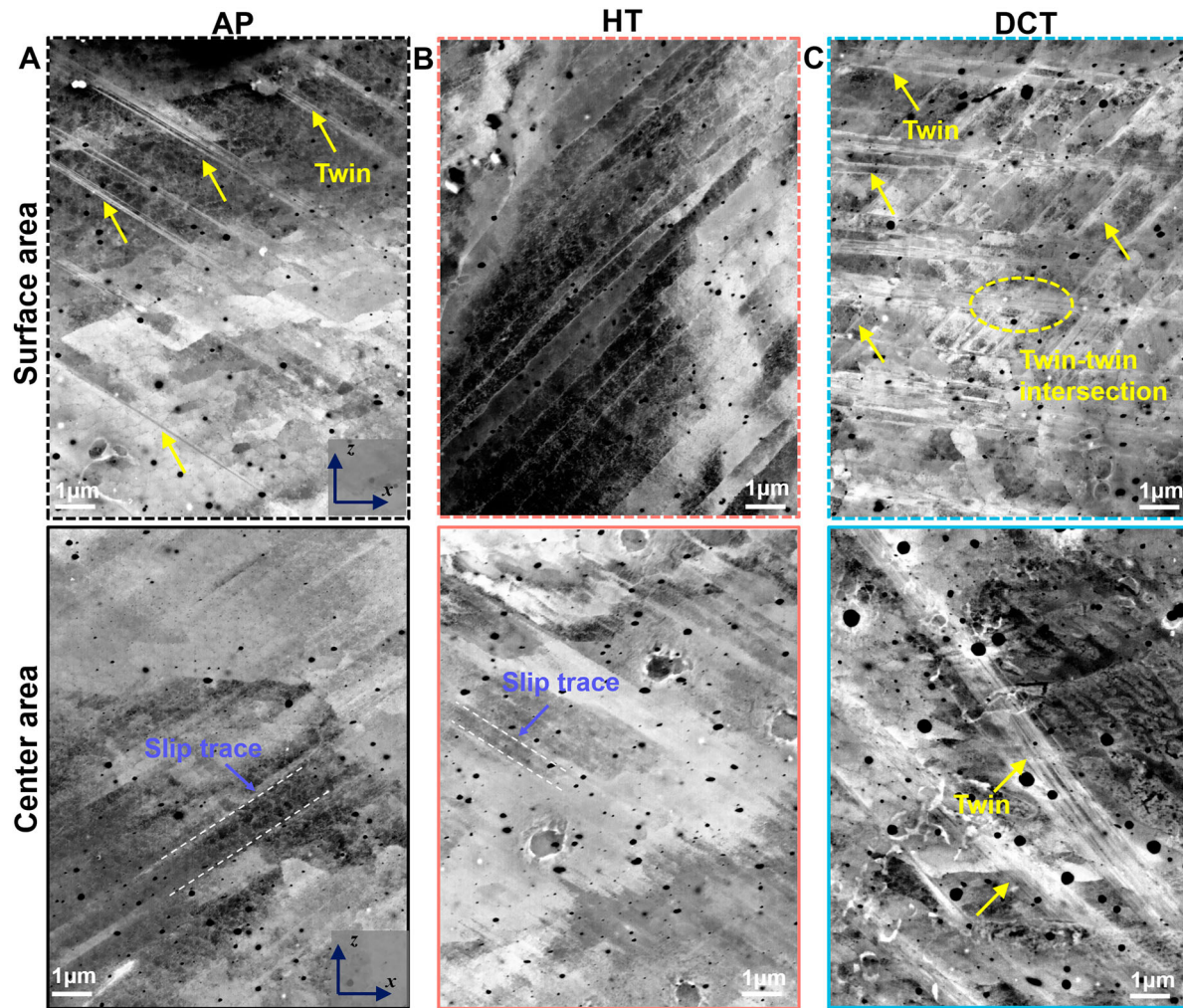


Figure 4. ECC images of surface and center areas of samples near the fracture area in the X-Z plane of deformed specimens: (a) AP-H, (b) HT-H, and (c) DCT-H. The yellow arrows indicate nano-sized deformation twins.

cracks and even fractures. Such enhancements are instrumental in alleviating the detrimental influence, thus providing substantial protection against the deleterious effects of hydrogen [49].

Figure 5(a–c) displays the fractography of the hydrogen-charged samples. Figure 5(a1, b1, c1) indicate overall fractography, and Figure 5(a2–3, b2–3, c2–3), Figure 5(a4–5, b4–5, c4–5) show detailed fracture plane of the surface and center regions, respectively. Note that the MAM-processed CoCrFeMnNi, as shown in Figure 1(b), contains inherent defects such as gas pores and micro-cracks in the AP sample. These defects serve as focal points for hydrogen and can be sources for crack propagation. Due to interaction with hydrogen, superimposed surface cracks easily form at a slow strain rate [19], aligning with the limited hydrogen diffusion in the CoCrFeMnNi HEA [6,7,25]. The concentration of cleavage failure in the surface area is due to the impact of hydrogen intrusion (refer to Figure 5(a2, b2, and c2)), and

the decrease in the area of cleavage failure in the post-processed specimens is associated with the improved hydrogen embrittlement susceptibility, as indicated in Figure 2(a). Despite these tendencies, all the hydrogen-charged samples exhibit the presence of ductile dimples in the center of the fracture surface, as displayed in Figure 5(a4, b4, and c4). These dimple formations, along with cracks, are primarily observed in the center region. The reduction of initial defects following post-processing potentially contributes to the high elongation, as magnified in Figure 5(a5, b5, and c5), indicating a noticeable plastic deformation preceding the fracture.

Figure 5(d) schematically summarizes the mechanisms of MAM-processed CoCrFeMnNi in fostering strengths and circumventing weaknesses in ductility loss. High-density dislocations increase the rate of hydrogen diffusion, which induces the rapid growth of micro-cracks along grain boundaries under tensile stress. Nevertheless, HT causes grain recovery, resulting in the

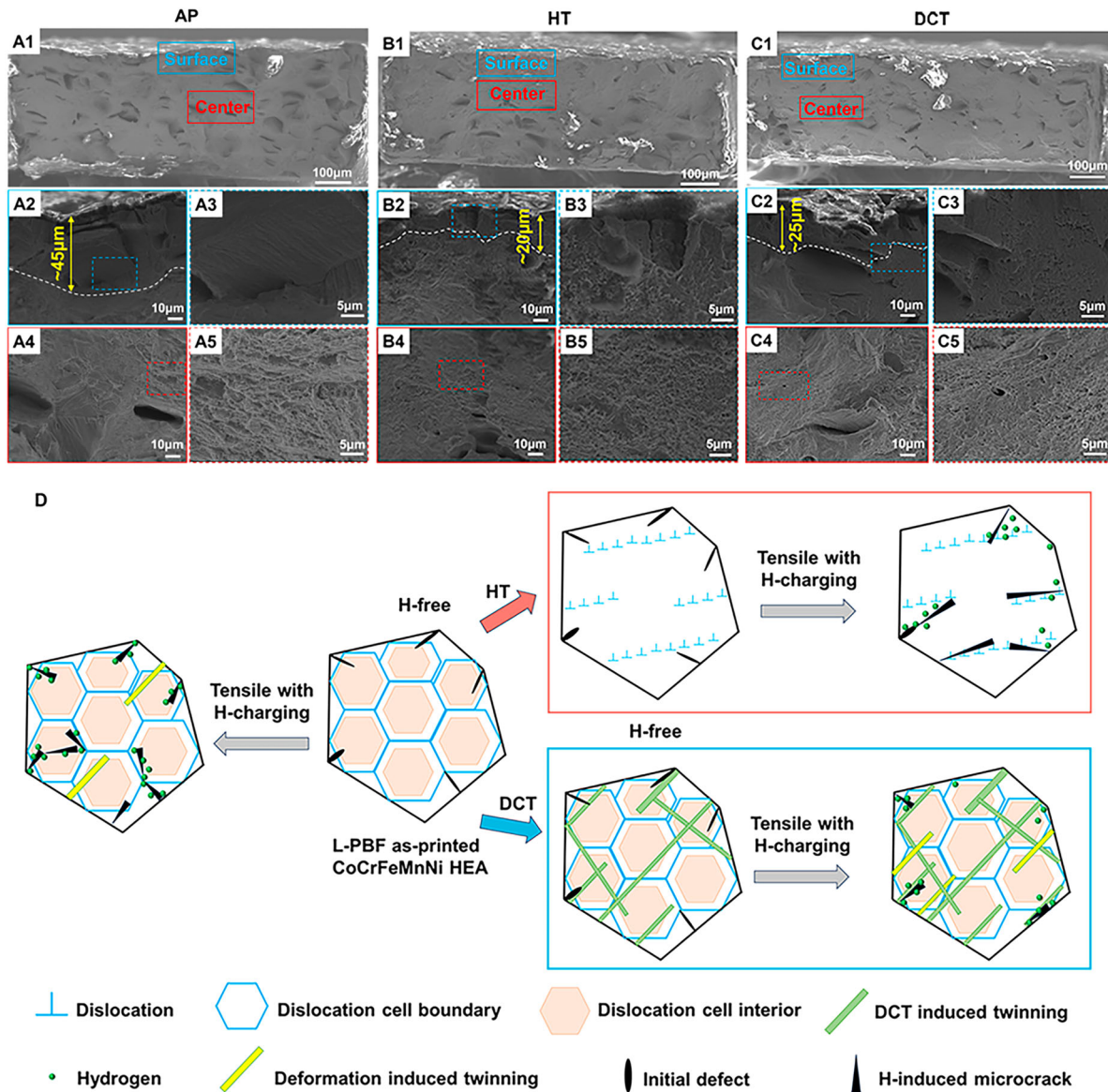


Figure 5. Fracture mechanisms of H-charged L-PBF CoCrFeMnNi HEA: (a) AP, (b) HT, and (c) DCT. Blue (surface area) indicates the H-affected zone, and red (center area) indicates the less-H-affected zone; (d) Schematic diagram of the microstructural evolution subjected to post-treatments and subsequent tensile deformation after hydrogen charging.

rearrangement, absorption of high-density dislocations, and significant reduction of strength. When the sample undergoes DCT, nanotwins are nucleated due to the remaining driving force of the high-energy dislocation cells and residual stress. Thus, DCT strategy ultimately results in high strength-ductility in a manner different from the AP and HT samples, even in the MAM-processed defect-rich matrix subjected to hydrogen.

4. Conclusions

This work utilizes the L-PBF CoCrFeMnNi HEA as a model material to experimentally demonstrate the nanotwin-ability of DCT samples, further proving their

effectiveness in hydrogen embrittlement resistance. Compared to AP and HT cases, this operation achieves simultaneously several objectives through underlying mechanisms:

- The inherent residual stress induced by the laser-based MAM process can be redistributed through the DCT strategy. This stress acts as the driving force for the redistribution of dislocation, leading to a stable microstructure;
- High-density dislocation cells and gradient-charged hydrogen collaborate to tailor the local SFE, thereby activating nanotwins during various tensile deformation;

- The presence of gradient nanotwins enhances hydrogen resistance by restricting hydrogen diffusion, potentially augmenting the hydrogen desorption energy, and suppressing the initiation and propagation of hydrogen-induced cracks in the printed matrix with inherent defects.

This effective strategy promotes the mechanical properties of laser-based MAM materials, fostering strengths and circumventing weaknesses in hydrogen-rich conditions through the retention of dislocation features and gradient nanotwins.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

The authors are also greatly appreciated for the financial support by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIP) [grant numbers NRF-2021R1A2C3006662 and NRF-2022R1A5A1030054]. Dr. Renhao Wu is also supported by Brain Pool Program through the National Research Foundation of Korea [grant number NRF-RS202300263999].

CRediT authorship contribution statement

Renhao Wu: Conceptualization, Data curation, Project administration, Investigation, Methodology, Validation, Writing - original draft. **Soung Yeoul Ahn:** Project administration, Investigation, Methodology, Validation, Writing - review & editing. **Yeon Taek Choi:** Investigation, Validation. **Hyojin Park:** Investigation, Experiment, Visualization. **Man Jae SaGong:** Methodology, Investigation. **Ganesh Sattineni:** Investigation, Methodology. **Hyeonseok Kwon:** Methodology, Validation, Investigation. **Sang Guk Jeong:** Investigation, Experiment; **Gitaek Lee:** Investigation, Experiment; **Ho Hyeong Lee:** Investigation, Experiment; **Haiming Zhang:** Conceptualization, Methodology, Writing - review & editing. **Hyoung Seop Kim:** Supervision, Funding acquisition, Project administration, Resources, Writing - review & editing.

ORCID

Hyoung Seop Kim  <http://orcid.org/0000-0002-3155-583X>

References

- [1] Shang Y, Lei Z, Alvares E, et al. Ultra-lightweight compositionally complex alloys with large ambient-temperature hydrogen storage capacity. *Mater Today*. 2023;67:113–126. doi:10.1016/j.mattod.2023.06.012
- [2] Shahmir H, Mehranpour MS, Arsalan Shams SA, et al. Twenty years of the CoCrFeNiMn high-entropy alloy: achieving exceptional mechanical properties through microstructure engineering. *J Mater Res Technol*. 2023; 23:3362–3423. doi:10.1016/j.jmrt.2023.01.181
- [3] Sheikh S, Vela B, Attari V, et al. Exploring chemistry and additive manufacturing design spaces: a perspective on computationally-guided design of printable alloys. *Mater Res Lett*. 2024;12(4):235–263. doi:10.1080/21663831.2024.2316204
- [4] Yue W, Fan H, Ru W, et al. In-situ study of room temperature tensile deformation of a CrMnFeCoNi high-entropy alloy. *J Alloy Compd*. 2023;940:168904. doi:10.1016/j.jallcom.2023.168904
- [5] Bertsch KM, Nygren KE, Wang S, et al. Hydrogen-enhanced compatibility constraint for intergranular failure in FCC FeNiCoCrMn high-entropy alloy. *Corros Sci*. 2021;184:109407. doi:10.1016/j.corsci.2021.109407
- [6] Zhao Y, Lee D-H, Seok M-Y, et al. Resistance of CoCrFeMnNi high-entropy alloy to gaseous hydrogen embrittlement. *Scr Mater*. 2017;135:54–58. doi:10.1016/j.scriptamat.2017.03.029
- [7] Pu Z, Chen Y, Dai LH. Strong resistance to hydrogen embrittlement of high-entropy alloy. *Mater Sci Eng A*. 2018;736:156–166. doi:10.1016/j.msea.2018.08.101
- [8] Gao S, Li Z, Van Petegem S, et al. Additive manufacturing of alloys with programmable microstructure and properties. *Nat Commun*. 2023;14:6752. doi:10.1038/s41467-023-42326-y
- [9] Behvar A, Haghshenas M, Djukic MB. Hydrogen embrittlement and hydrogen-induced crack initiation in additively manufactured metals: A critical review on mechanical and cyclic loading. *Int J Hydro Energy*. 2024;58: 1214–1239. doi:10.1016/j.ijhydene.2024.01.232
- [10] Chen H, He Y, Dash SS, et al. Additive manufacturing of metals and alloys to achieve heterogeneous microstructures for exceptional mechanical properties. *Mater Res Lett*. 2024;12(3):149–171. doi:10.1080/21663831.2024.2305261
- [11] Xuan Y, Chang J, Ou Y, et al. Heterogeneous structure architected by additive manufacturing: facile route towards strong and ductile steel. *Mater Res Lett*. 2024; 12(3):199–207. doi:10.1080/21663831.2024.2314145
- [12] Deirmina F, Amirabdollahian S, Harris L, et al. Laser-directed energy deposition of dissimilar maraging steels with a defect-free interface: Design for improved surface hardness and fracture toughness. *Metals Mater Int*. 2023;29:2940–2954. doi:10.1007/s12540-023-01424-8
- [13] Tekumalla S, Seita M, Zaefferer S. Delineating dislocation structures and residual stresses in additively manufactured alloys. *Acta Mater*. 2023;262:119413.
- [14] Jiang W, Zhu Y, Zhao Y. Mechanical properties and deformation mechanisms of heterostructured high-entropy and medium-entropy alloys: A review. *Front Mater*. 2022;8:1–17.
- [15] He J, Liu Q, He M, et al. The hydrogen embrittlement of pure Ni fabricated by additive manufacturing. *Int J Hydro Energy*. 2023;48:16910–16922. doi:10.1016/j.ijhydene.2023.01.167
- [16] Huang X, Ding S, Yue W. Cryogenic treatment on Ti6Al4V alloy fabricated by electron beam melting: microstructure and mechanical properties. *J Mater Res Technol*. 2022;20:3323–3332. doi:10.1016/j.jmrt.2022.08.012

- [17] Yao E, Zhang H, Ma K, et al. Effect of deep cryogenic treatment on microstructures and performances of aluminum alloys: a review. *J Mater Res Technol.* 2023;26:3661–3675. doi:10.1016/j.jmrt.2023.08.140
- [18] Li H, Zhao W, Chen T, et al. Beneficial effects of deep cryogenic treatment on mechanical properties of additively manufactured high entropy alloy: cyclic vs single cryogenic cooling. *J Mater Sci Technol.* 2022;115:40–51. doi:10.1016/j.jmst.2021.11.022
- [19] Li HG, Huang YJ, Zhao WJ, et al. Overcoming the strength-ductility trade-off in an additively manufactured CoCrFeMnNi high entropy alloy via deep cryogenic treatment. *Addi Manuf.* 2022;50:102546. doi:10.1016/j.addma.2021.102546
- [20] Luo H, Lu W, Fang X, et al. Beating hydrogen with its own weapon: Nano-twin gradients enhance embrittlement resistance of a high-entropy alloy. *Mater Today.* 2018;21:1003–1009. doi:10.1016/j.mattod.2018.07.015
- [21] Gu GH, Ahn SY, Kim Y, et al. Determining reliable wide-strain-range equivalent stress-strain curves using 3D digital image correlation. *J Mater Res Technol.* 2022;19:2822–2830. doi:10.1016/j.jmrt.2022.06.054
- [22] Luo H, Li Z, Raabe D. Hydrogen enhances strength and ductility of an equiatomic high-entropy alloy. *Sci Rep.* 2017;7:9892. doi:10.1038/s41598-017-10774-4
- [23] Laplanche G, Kostka A, Horst OM, et al. Microstructure evolution and critical stress for twinning in the CrMnFeCoNi high-entropy alloy. *Acta Mater.* 2016;118:152–163. doi:10.1016/j.actamat.2016.07.038
- [24] Lee T-H, Shin E, Oh C-S, et al. Correlation between stacking fault energy and deformation microstructure in high-interstitial-alloyed austenitic steels. *Acta Mater.* 2010;58:3173–3186. doi:10.1016/j.actamat.2010.01.056
- [25] Chen XH, Zhuang XQ, Mo JW, et al. Enhanced resistance to hydrogen embrittlement in a CrCoNi-based medium-entropy alloy via grain-boundary decoration of boron. *Mater Res Lett.* 2022;10(4):278–286. doi:10.1080/21663831.2022.2033865
- [26] Lin Y-T, An X, Zhu Z, et al. Effect of cell wall on hydrogen response in CoCrFeMnNi high-entropy alloy additively manufactured by selective laser melting. *J Alloy Compd.* 2022;925:166735. doi:10.1016/j.jallcom.2022.166735
- [27] Tong Z, Ren X, Jiao J, et al. Laser additive manufacturing of FeCrCoMnNi high-entropy alloy: Effect of heat treatment on microstructure, residual stress and mechanical property. *J Alloy Compd.* 2019;785:1144–1159. doi:10.1016/j.jallcom.2019.01.213
- [28] Örnek C, Şeşen BM, Ürgen MK. Understanding hydrogen-induced strain localization in super duplex stainless steel using digital image correlation technique. *Metals Mater Int.* 2022;28:475–486. doi:10.1007/s12540-021-01123-2
- [29] Wang Y, Huang C, Ma X, et al. The optimum grain size for strength-ductility combination in metals. *Int J Plast.* 2023;164:103574. doi:10.1016/j.iplas.2023.103574
- [30] Koyama M, Wang H, Verma VK, et al. Effects of Mn content and grain size on hydrogen embrittlement susceptibility of face-centered cubic high-entropy alloys. *Metallur Mater Transact A.* 2020;51:5612–5616. doi:10.1007/s11661-020-05966-z
- [31] Karthik GM, Kim HS. Heterogeneous aspects of additive manufactured metallic Parts: A review. *Metals Mater Int.* 2021;27:1–39. doi:10.1007/s12540-020-00931-2
- [32] Zhang C, Zhi H, Antonov S, et al. Hydrogen-enhanced densified twinning (HEDT) in a twinning-induced plasticity (TWIP) steel. *Scr Mater.* 2021;190:108–112. doi:10.1016/j.scriptamat.2020.08.047
- [33] Ding Y, Yu H, Lin M, et al. Hydrogen trapping and diffusion in polycrystalline nickel: The spectrum of grain boundary segregation. *J Mater Sci Technol.* 2024;173:225–236. doi:10.1016/j.jmst.2023.07.027
- [34] Lee DG, Kim JH, Kim SH, et al. Hydrogen trapping characteristics and mechanical degradation in a duplex stainless steel. *Metals Mater Int.* 2023;29:126–134. doi:10.1007/s12540-022-01212-w
- [35] Sun LG, Wu G, Wang Q, et al. Nanostructural metallic materials: Structures and mechanical properties. *Mater Today.* 2020;38:114–135. doi:10.1016/j.mattod.2020.04.005
- [36] Zhao Y, Park J-M, Lee D-H, et al. Influences of hydrogen charging method on the hydrogen distribution and nanomechanical properties of face-centered cubic high-entropy alloy: A comparative study. *Scr Mater.* 2019;168:76–80. doi:10.1016/j.scriptamat.2019.04.025
- [37] Lu X, Ma Y, Peng D, et al. In situ nanomechanical characterization of hydrogen effects on nickel-based alloy 725 under different metallurgical conditions. *J Mater Sci Technol.* 2023;135:156–169. doi:10.1016/j.jmst.2022.07.006
- [38] Thurston KVS, Hohenwarter A, Laplanche G, et al. On the onset of deformation twinning in the CrFeMnCoNi high-entropy alloy using a novel tensile specimen geometry. *Intermetallics.* 2019;110:106469. doi:10.1016/j.intermet.2019.04.012
- [39] Zhu ZG, Nguyen QB, Ng FL, et al. Hierarchical microstructure and strengthening mechanisms of a CoCrFeNiMn high entropy alloy additively manufactured by selective laser melting. *Scr Mater.* 2018;154:20–24. doi:10.1016/j.scriptamat.2018.05.015
- [40] Kim H-J, Cho M-K, Kim G, et al. Influence of hydrogen absorption on stacking fault of energy of a face-centered cubic high entropy alloy. *Metals Mater Int.* 2022;28:2637–2645. doi:10.1007/s12540-021-01163-8
- [41] Gibbs PJ, Hough PD, Thürmer K, et al. Stacking fault energy based alloy screening for hydrogen compatibility. *JOM.* 2020;72:1982–1992. doi:10.1007/s11837-020-04106-7
- [42] Koyama M, Akiyama E, Tsuzaki K, et al. Hydrogen-assisted failure in a twinning-induced plasticity steel studied under in situ hydrogen charging by electron channeling contrast imaging. *Acta Mater.* 2013;61:4607–4618. doi:10.1016/j.actamat.2013.04.030
- [43] Lee J, Park H, Kim M, et al. Role of hydrogen and temperature in hydrogen embrittlement of equimolar CoCrFeMnNi high-entropy alloy. *Metals Mater Int.* 2021;27:166–174. doi:10.1007/s12540-020-00752-3
- [44] Yao J, Tan Q, Venezuela J, et al. Recent research progress in hydrogen embrittlement of additively manufactured metals—A review. *Current Opinion Solid State Mater Sci.* 2023;27:101106. doi:10.1016/j.cossms.2023.101106
- [45] Galindo-Nava EI, Basha BIY, Rivera-Díaz-del-Castillo PEJ. Hydrogen transport in metals: Integration of permeation, thermal desorption and degassing. *J Mater Sci Technol.* 2017;33:1433–1447. doi:10.1016/j.jmst.2017.09.011

- [46] Huang CX, Hu WP, Wang QY, et al. An ideal ultrafine-grained structure for high strength and high ductility. *Mater Res Lett.* 2015;3(2):88–94. doi:[10.1080/21663831.2014.968680](https://doi.org/10.1080/21663831.2014.968680)
- [47] Birnbaum HK, Sofronis P. Hydrogen-enhanced localized plasticity—a mechanism for hydrogen-related fracture. *Mater Sci Eng A.* 1994;176:191–202. doi:[10.1016/0921-5093\(94\)90975-X](https://doi.org/10.1016/0921-5093(94)90975-X)
- [48] Cheng H, Luo H, Pan Z, et al. Effects of laser powder bed fusion process parameters on microstructure and hydrogen embrittlement of high-entropy alloy. *J Mater Sci Technol.* 2023;155:211–226. doi:[10.1016/j.jmst.2022.12.074](https://doi.org/10.1016/j.jmst.2022.12.074)
- [49] Lai Z-H, Lin Y-T, Sun Y-H, et al. Hydrogen-induced ductilization in a novel austenitic lightweight TWIP steel. *Scr Mater.* 2022;213:114629. doi:[10.1016/j.scriptamat.2022.114629](https://doi.org/10.1016/j.scriptamat.2022.114629)