Additively manufactured high strength and ductility CrCoNi medium entropy alloy with hierarchical microstructure

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T A B L E O F C O N T E N T S

1. Introduction

High entropy alloys (HEA), known as a branch of multi-principle element alloys (MPEA), have attracted much research interest due to the vast composition space and salient properties in multiple aspects, especially for the excellent strength-ductility combination in mechanical responses [1,2]. Among major families of HEAs in application, the ternary equimolar CrCoNi medium entropy alloy (MEA), known as a subset of the famous “Cantor alloy,” i.e., equimolar CrMnFeCoNi HEA [3], has aroused ever-growing attention. During deformation, this single phase face-centered cubic (FCC) MEA is reported to shift from dissociated partial dislocations and slipping in early loading stages to the subsequent unusual nano-twinning deformation mechanism, resulting in extraordinary strength-ductility combination, which is even superior to the base Cantor alloy [4–6]. As a primary deformation mechanism in CrCoNi MEA, nano-twinning weakly inhibits dislocation movement, contributes to stabilized work hardening rate, and prevents early necking. While bringing the “dynamic Hall-Petch effect” [7,8], the dense twinning behavior is inferred to be oriented from low stacking fault energy (SFE) in CrCoNi MEA, which may eventually achieve a negative

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ABSTRACT

The CrCoNi medium entropy alloy (MEA) is a technologically intriguing material showing superior cryogenic mechanical properties. In this work, we fabricated near full-dense hierarchical CrCoNi MEA via selective laser melting (SLM) and achieved superior yield strength of 860 MPa at 77K that surpasses that of conventionally fabricated counterparts, in addition to reasonable ductility. The strength and ductility increase as temperature drops, reaching a 1340 MPa ultimate tensile strength and a 47% elongation at 77K. EBSD, TEM, and in-situ synchrotron X-ray diffraction (SXRD) tensile tests disclose that the high strength stems from the hierarchical microstructure composed of high-density dislocations-formed cellular structures and low-angle grain boundaries (LAGB) within the complex heterogeneous columnar grains, and further validated by theoretical calculation. In-situ SXRD tensile tests and post-deformation TEM and EBSD reveal that nano-twinning response in the SLM-built CrCoNi MEA is suppressed by both high-density LAGB and near <100> growth texture. The results demonstrate that SLM is a viable technique for fabricating dense hierarchical CrCoNi MEA and suggest a design strategy to improve mechanical properties further.

1. Introduction

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value at 0K according to ab-initio calculations, leading to the exceptional damage tolerance at cryogenic temperature [9]. Besides the temperature, the nano-twinning behavior in CrCoNi MEA has been reported to be related to the orientation relationship between the overall grain orientations and tensile loading direction [6,10,11], suggesting a possible pathway to tailor the mechanical properties via texture manipulation. In the CrCoNi MEA produced by conventional methods such as cold rolling, annealing, and recrystallization, microstructures with specific grain size distributions, i.e., bimodal [12] or heterogeneous grain structures [13,14], are usually favored for their additional deformation accommodation by introducing Lomer-Cottrell locks and storing dislocations, stacking faults, as well as deformation twins, thus breaking the long disturbing dilemma “strength-ductility trade-off.” According to common manufacturing methods, the CrCoNi alloy tends to be cast in an inert-gas-protected furnace from pure metal ingots by arc melting, followed by thermal treatment such as homogenization, annealing, and subsequent cold rolling and cutting [4–6,15–21]. A spark plasma sintering (SPS) process is recently introduced for precisely tuning the lattice defects in the CrCoNi MEA with superior strength obtained [22]. These manufacturing methods previously employed had honorable contributions to the comprehensive understanding of CrCoNi MEA. However, in spite of the demand to further increase yield strength for structural use, complicated fabricating methods of conventional CrCoNi MEA have developed into a plateau area. Hence, new ideas should be introduced.

Additive manufacturing, also known as 3D printing, is widely acknowledged as a process to build a part up, usually layer-by-layer, with negligible material loss in contrast to those conventional “subtractive” manufacturing approaches such as turning, drilling, cutting, and so on [23]. Selective laser melting (SLM) is a laser-based additive manufacturing approach, in which the raw material powder is put on a substrate and fully melted by galvanometer-controlled laser scanning layer by layer [23,24]. The SLM process is an emerging practice suitable for the building of metal-base materials such as pure metals [24], Ti-based alloys [25,26], Fe-based alloys (steels) [27–30], Ni-based alloys [31], and high entropy alloys [32–36]. Among these works, the term “hierarchical microstructure” is frequently employed to describe the unique microstructure in SLM-built single-phase alloys and dual-phase “TC4” Ti–6Al–4V alloys. Coarser grains are separated by high angle grain boundaries (HAGBs) in which clusters of columnar-grains (dislocation cellular structure) are usually separated by dislocation walls formed during rapid solidification. They introduce exceptional dislocation and grain boundary (Hall-Petch) strengthening and promote yield strength. However, considerable deviation of the linear Hall-Petch relationship was also found [29,33,36] and is believed to be related to either dislocation pinning by grain boundaries or the Cottrell atmosphere induced by elemental segregation around low angle grain boundaries (LAGBs). These studies offered comprehensive discussion about SLM-built alloys and implied promising potential for their structural use. In this work, in order to optimize microstructure and mechanical properties, SLM process is adopted to manufacture CrCoNi MEA and the microstructure evolution during tensile loading is studied to elucidate the deformation mechanism and to expedite the development of MEAs.

2. Materials and methods

2.1. Powder and materials fabrication

Pre-alloyed equimolar CrCoNi MEA powder with a particle size distribution of 15–53 μm was used in this study. Particle size distribution maps, powder morphologies, and elemental distribution maps were obtained using Microtrac S3500 Laser Particle size Analyzer (LPA) and TESCAN LYRA3 GMU scanning electron microscope, respectively, and are demonstrated in Fig. 1, showing fine quality homogeneous alloy powder with good fluidity promised by sphericity. There is no elemental segregation within CrCoNi MEA powder, as shown in EDS mapping. The SLM system is HBD-200 provided by Shanghai Hanbang United 3D Tech Co., Ltd. Prior to SLM fabrication, CrCoNi MEA powder was sieved, dried at 80 °C in a vacuum chamber, and was transported to the SLM system immediately to avoid contamination and dampness. Cubic testing blocks and dog-bone-shape tensile specimens were subsequently built directly on stainless steel substrate employing a scanning strategy presented in Fig. 1(c). Notably, an additional rotation angle of 67° was applied between each two successive layers to eliminate anisotropy on the X-Y

Fig. 1. Characterization of pre-alloyed equimolar CrCoNi powder feedstock used in this study: (a) Particle morphology; (b) Particle size distribution; (c) Schematic of the “67°” scanning strategy; (d–f) EDS elemental scans exhibit no elemental segregation.
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Secondary electron microscopy (SEM) 

The X-Y-Z axes are sample coordinates involved in electron backscatter diffraction (EBSD) characterization, that is, the relative position of samples inside the vacuum chamber of EBSD system. After the SLM process, cubic testing blocks and tensile specimens were cut off from the substrate by electrical discharge machining (EDM), ground (with 80-, 180-, 240-, 400-, 800- and 1200-grit SiC abrasive paper), and polished (with up to 1 μm diamond spray polishing agent) for further characterizations. The post-deformation specimens were ground and polished as well.

2.2. Microstructure characterization

Etching was performed on ground-and-polished specimens with a solution containing 5 g of CuCl₂ in 100 ml of HCl and 100 ml of ethanol for 4 min. Metallography was obtained by optical microscope (Zeiss Axio Imager A2m) at multiple magnifications on the as-printed, as-etched cubic samples to reveal the microstructure at large scales as well as examine mesoscopic defects formed during the SLM process. A supplementary 3-D computerized tomography (3-D CT) using an X-ray microscope (XRM, Xradia 520 Versa) was performed to accurately measure the relative volumetric density as well as pore distribution at high spatial resolution (0.7021 μm/pixel, 3001 projections) for a 0.7 × 0.7 × 2.1 mm³ sample. The voltage and scanning angle is 120 kV and 360°, respectively. The XRM results were processed by Dragonfly software. Further explorations of pre-deformation microstructures were conducted on as-printed and as-etched samples using multiple characterization devices. X-ray diffractometry (XRD, Rigaku Ultima IV X-ray diffractometer, λ = 1.54056 Å) was adopted for phase identification. Secondary electron microscopy (SE–SEM, TESCAN LYRA3 GMU), energy dispersive spectrometer (EDS, TESCAN LYRA3 GMU), as well as EBSD (NOVA Nano-SEM 230) were used to examine surface morphology, elemental distribution, and crystal orientation, respectively. Before conducting EBSD, additional vibratory polishing using VibroMet® 2 device for 6 h was applied to improve surface quality, release residual stress introduced by grounding, and prevent oxidation interference. In terms of specimens observed by transmission electron microscopy (TEM), as-printed and post-deformation specimens were cut by EDM and mechanically ground into 100 μm-thick plates, punched into wafer-like pieces with 3 mm diameter, thinned by a twin-jet polishing facility using a 20% perchloric acid ethanol solution at 10–13 V, –30 °C and finally ion-milled using a Gatan PIPS II 695 precise ion polishing system. A JEOL JEM-2100F TEM and a spherical aberration-corrected TEM (ACTEM, JEOL JEM-ARM200F) were used in this work.

2.3. Mechanical testing

Ex-situ uniaxial tensile tests were performed on pre-polished, dog-bone shaped, specimens using Instron-5982 testing system with a strain rate of 0.02/min at 77 K (liquid nitrogen), 195 K (liquid carbon dioxide), and 293 K (room temperature, RT). The specimens were 80 mm in length, 18 mm in width and 2 mm in thickness. The gauge section was 25 mm in length and 4 mm in width. The specimens were immersed in liquid nitrogen in the environmental testing chamber for precise temperature control, and multiple specimens were tested at each temperature to ensure repeatability and validate mechanical stability.

2.4. In-situ synchrotron X-ray diffraction tensile tests

To further inspect microstructural response with high spatial and temporal resolution, in-situ synchrotron X-ray diffraction (SXRD) interrupted tensile tests were performed at beamline BL14B1, Shanghai Synchrotron Radiation Facility (SSRF) at RT. High energy (18 KeV) X-ray beam with 3° grazing incidence had a wavelength of 0.6888 Å. A customized mechanical testing system was employed to cooperate with the sample platform at the synchrotron facility. During interrupted loading, we employed a time-controlled method: a circulation of 2 min of loading and 1 min of break for diffraction pattern acquiring. With this testing method and advanced characterization device, high-quality in-situ diffraction data with excellent spatial and temporal resolution could be obtained, helping understand the deformation mechanism in SLM-built CrCoNi MEA.

3. Results

3.1. Powder morphology and as-printed microstructure

XRD was performed on CrCoNi MEA powder, cubic blocks, and result in Fig. 2 indicated a single-phase FCC structure. Cubic blocks had a minor lattice constant of 3.561 Å, in comparison to those of MEA powder (3.564 Å) and fully recrystallized bulk CrCoNi MEA (3.567 Å [5]). Surprisingly, a strong growth texture of <100> could be identified from the distinctive (200) peak in cubic specimens, in contrast to that of raw powder. To clarify, (200) is equivalent to (100) orientation due to multiplicity and extinction in the XRD phase identification process of disordered solid solution FCC metals. Prior to further characterizations, an evaluation of SLM parameters must be carried out first. Volumetric energy density (VED) is a derivative quantity which has been proved vital in the fabrication of SLM parts [36,38]. The definition of VED is given as:

\[
VED = \frac{P}{vht}
\]  

P is laser power, v represents scanning speed (laser speed), h stands for hatching space, t would be layer thickness. However, the effects of individual decisive parameters involved in the SLM process such as laser power, scanning speed, hatching space, layer thickness, laser focus diameter, and scanning strategy were already comprehensively reported elsewhere [29–31,33,36,38,39]. A brief evaluation of SLM parameters (laser power, scanning speed, hatching space, and VED) was conducted in this work to maintain simplicity and conciseness without losing control of product quality. In the orthogonal tests, laser power, scanning speed, scanning speed, and hatching space would lie in the range of 140 W–180 W, 1000
mm/s-1500 mm/s, and 50 μm–90 μm, respectively. Laser focus diameter and layer thickness were fixed at 60 μm and 30 μm, respectively. As VED went greater, the relative density reached a local optimum at 109.1 J/mm³. By applying a semi-empirical criterion, the parameter combination yielded the highest sample relative density: 180 W of laser power, 1100 mm/s of scanning speed, 50 μm of hatching space, and a corresponding VED of 109.1 J/mm³ was chosen in the following primary manufacturing processes. To ensure maximized quality control, a 3-D CT image acquired by an X-ray microscope (XRM) revealed a high relative density of 99.7% in the optimized specimen, slightly superior to 98.2% reported in Ref. [33], 99.2% addressed by Ref. [29] and 99.2% declared by Ref. [36], close to ~99.6% in a novel 3D ink-extruded CrCoNiFe MEA [40], implying an outstanding product quality built by simple methodological approaches. Fig. 3 acquired by XRM could also demonstrate a spatial and statistical distribution of mesoscopic pores and cracks, providing essential information to further evaluate defects on properties.

To inspect microstructures, etching was performed on the X-Z plane of as-printed samples as very few defects were observed, indicating good quality of our SLM-built alloy. Additionally, SE–SEM images in Fig. 4(d–f), EBSD results in Fig. 5, as well as TEM results in Fig. 6, image acquired under scanning transmission electron microscopy (STEM) mode in Fig. 7 confirmed the hierarchical structure. In SE–SEM and EBSD results, columnar sub-grains could be observed nucleating on the melt pool bottom, stretching alongside BD. While sub-grains yielding a morphology of rough hexagonal prism, the mean diameter or mean cell height of them distributed from several micrometers to several tens of micrometers. The mean cell size would be employed in computing the dislocation strengthening effect later in the discussion section. In EBSD PFs and IPFs, similar near <100> growth texture aligned to BD could be observed as well, in coincidence with that carried out in XRD patterns as well as previous works. On the other hand, in EBSD PFs and IPFs, the relatively lower multiples of uniform density (MUD) explicates smoother granular orientation distribution, which yields better anisotropy on the X-Y plane. The “67”° scanning strategy employed in this work is believed to be a dominant factor in eliminating anisotropy on the X-Y plane [31,37]. Hence, the loading direction (LD) in mechanical testing does not need to be parallel to either the X or Y axis since there is little difference.

The dislocation network separating columnar sub-grains was shown by etching, SE—SEM, TEM in Fig. 6 and STEM in Fig. 7. Due to the low misorientation between adjacent sub-grains, massive geometrically necessary dislocations (GND) should form to compromise the misorientation-induced stress energy [41]. EBSD kernel average misorientation (KAM) images could confirm the minor misorientation in Fig. 5(c) and (g). The dense GNDs had formed into thick dislocation walls and progressively into dislocation network [29]. Since dislocation walls would act as grain boundary of adjacent columnar sub-grains while the misorientations may be in low scale as demonstrated by EBSD, these dislocation walls could be referred to LAGBs as well in this work. Besides, the instantaneous temperature drop in the SLM process inhibited post-solidification grain growth, resulting in a large quantity of nanoscale columnar sub-grains and a high-density dislocation network, resulting in predominant dislocation strengthening [36]. Considering ductility, however, it is believed that high-density pre-existing dislocations might reduce total elongation by consuming available dislocation capacity as well as inhibiting dislocation movement. However, the pre-existing dislocation network as observed in SLM-built parts is believed to partly inhibit dislocation movement and contribute to steady work hardening, thus promotes elongation [29,30,36]. These opposed ideas still need to be confronted in the more in-depth exploration in the SLM process, but the yield strength is sure to be improved.

While EDS area scan in Fig. 4(g–i) performed on the X-Z cross-section indicated no evident macro elemental segregation, further EDS carried under STEM mode acquired by ACTEM in Fig. 7(b–d) suggested negligible nanoscale segregation in complement, unlike other SLM-built alloys previously reported [29,33,36], implying insignificant precipitation strengthening. Beyond the strengthening effect, solute atoms enriched at grain boundaries are believed to promote both dislocation and twinning nucleation. Detailed discussion around elemental segregation in SLM-built CrCoNi MEA would be carried out later in the discussion section.

3.2. Mechanical testing

Ex-situ uniaxial tensile tests were performed at 293 K, 195 K and 77 K. The engineering stress-strain curves (σ-ε) and strain hardening curves (dS/de-ε, S for true stress and e for true strain) are presented in Fig. 8. Given the excellent anisotropy, the loading directions were arbitrarily set on the X-Y plane but assumed to be parallel to the Y-axis for the ease of narration and notation. The SLM-built CrCoNi MEA exhibited increasing mechanical properties as temperature decreased, in agreement with conventionally built counterparts, as shown in Table 1. It is notable that in addition to convenient and straightforward building methods, competitive yield strength and UTS values were successfully achieved compared to conventional CrCoNi MEA [5,18–21] and are to

![Fig. 3. (a) X-ray microscope (3D computer tomography, 3D CT) result revealing dense (99.7%) with reasonable pore distribution, well above the average of SLM-built metals; (b) Pore volume distribution map indicating a large majority of small pores (<1000 μm³) rather than large pores.](image-url)
be quantitatively analyzed in the discussion section. Nonetheless, reasonable values of total elongation were acquired as well. As shown in strain hardening curves in Fig. 8(b), a near-horizontal steady hardening occupied most. From the end of elastic sections to the onset of failure, no explicit secondary hardening response was observed until failure, unlike those exhibited in highly oriented single-crystalline CrCoNi MEA [10]. These behaviors suggested a distinct deformation mechanism or a different strengthening response in SLM-built CrCoNi.

Nano-twinnings is considered an indispensability in later deformation stages of CrCoNi MEA, acting as a subsequence of dissolved partial dislocations and slipping. Once a critical stress or strain is achieved, twinning would nucleate and expand, contribute to continuous and steady work hardening, prevent early necking by introducing extra barriers in dislocation movement. However, the measurement of the onset of twinning is yet an uneasy task to perform. Mayers et al. [42] offered a constitutive description about predicting the onset of twinning in metals, but no experimental approach was given. In recent studies, G. Laplanche et al. [43] addressed several ways include: (1) making multiple TEM or EBSD samples at different levels of deformation; (2) observing, analyzing the strain hardening curves (dS/de-e) to search for characteristic hardening feature; (3) applying pre-strain at 77 K, reloading at RT and comparing to those deformed at RT at the entire stage. The authors concluded that the critical true stress (S_c) of twinning was estimated to be as low as 4%. Note that true stress (S) and true strain (e) values would be greater than corresponding engineering stress (σ) and strain (ε) values. Keli et al. [44] carried out a novel tensile specimen geometry coupling with the finite element method (FEM) to determine the onset of twinning in a swaged and recrystallized CrMnFeCoNi HEA. Researchers could easily finish the detection using this technique within a single trial. He Huang et al. [45] constructed and applied a Peierls-Nabarro (P–N) model to describe twinning nucleation and to predict the critical resolved shear stress (CRSS) of FCC CrCoNi-based MHEAs. The theoretical predictions agreed very well with the experimental values listed above. These approaches contributed to their respective researches, and reliable achievements were acquired. However, disadvantages such as time consuming, large unexplored blankness, inaccuracy and lack of validation should not be ignored.

Fig. 4. Cellular sub-grain structures of as-printed CrCoNi MEA: (a–c) As-etched optical micrographs (OM); SEM on the front view (X-Z plane, d, e) and top view (X-Y plane, f); (g–i) EDS elemental maps indicating no macroscopic segregation. The statistics about mean cell size is performed on (e) and (f).
3.3. In-situ SXRD tensile tests

The advanced characterization technique of synchrotron radiation has been employed in various researches for phase identification, dislocation analysis, lattice study, and in-situ phase transformation analysis in twinning-induced plasticity (TWIP), phase transformation induced plasticity (TRIP) steels as well as HEAs [46–49]. Here we performed in-situ SXRD interrupted tensile tests at RT to precisely determine the onset of twinning with a schematic shown in Fig. 9(a). The advantages are, highly customizable testing methodology, fully quantitative data, and free of unloading creep, damage from sample preparation. The stress-strain curves and selected diffraction patterns acquired at corresponding interruptions and circular-integrated diffraction curves evolution are demonstrated in Fig. 9(b–d). Beside the typical peak heighten effect on (111) peak originated from (111) <11\Sigma2> twinning of FCC matrix alloy, diffraction peaks of the HCP phase were identified as well. In the later deformation stage of a low SFE FCC alloy, multiple stacking faults pile up in two distinctive ways, forming into nano-twinning or HCP phase at short-range level (several atom layers). Besides, it was reported that despite occupying a small volume unlike conventional TRIP steels, which rely on large-scale phase transformation, the HCP thin lamellae prefer to exhibit associated nucleation on twin-matrix...
interface (see Fig. 11(f)), which implies simultaneous development of FCC-HCP transformation and twinning [6]. Hence, we presume that the twinning and HCP phase should share proximate critical conditions, either stress or strain. As evinced in Fig. 9(b-d), the critical engineering stress ($\sigma_{crit}$) of twinning onset lies in a stress range of 793–804 MPa. The results are transformed into critical resolved shear stress (CRSS) and strain values with a Taylor factor of 3.01, and listed in Table 2 with results brought by peer authors in comparison. Hence, the onset of twinning in SLM-built CrCoNi MEA is precisely located and later than those CrCoNi counterparts. The influence of this behavior on macroscopic properties will be analyzed in the discussion section.

Of particular interest, note that except for FCC and HCP diffraction rings, complicated patterns such as high-order Laue rings and secondary diffraction rings (unindexed peaks) were acquired as well. In the grazing-incidence mode of SXRD, the thin free surface zone is the majority participating in the diffraction process. Given the sharp perception and exceptional energy density of SXRD device, simultaneous to deformation stages advancing, rapid change in lattice type as well as lattice parameter would cause severe distortion in reciprocal space, allowing the acquirement of complicated diffraction patterns such as double diffraction and streaking effect [50]. These patterns could offer valuable information about the SLM-built CrCoNi MEA and are to be investigated in future works.

3.4. Post-deformation characterization

Microstructures of post-deformation, near-fracture samples at RT and 77 K were characterized, employing EBSD, TEM, and STEM for a better understanding of deformation mechanism in SLM-built CrCoNi MEA. As indicated in EBSD PFs and IPFs in Fig. 10(d, h), classic $<100>\rightarrow<111>$ double-fiber deformation texture could be observed, and greater MUD values relative to those acquired before deformation suggested a greater texture intensity. This deformation texture behavior corresponds to those reported in SLM-built TWIP steels [51,52] and CrMnFeCoNi HEA [53] and is believed to originate from grain rotation induced by tensile force. However, due to the steady and slim prism-like morphology of sub-grains, grain rotation is naturally anticipated to be exhausting, sending little effort to elongation reduction as well. Direct EBSD observations revealed more details in deforming the SLM-built CrCoNi MEA. Lower hit rate in cryogenic-deformed counterparts do exist among the indexing on twinning regions, indicating smaller mean twin thickness. To do the calculation, mean twin spacings and mean twin widths in post-deformation samples at RT and cryogenic temperature were measured employing a similar method addressed in Refs. [43,54] within a few representative grains. TEM was conducted on post-deformation specimens of both RT (Fig. 11(a-c)) and 77 K (Fig. 11(d-f)) as well, revealing more deformation behaviors at an atomic level. Despite considerably severe deformation, no evident change in sub-grain shape or size was observed at both temperatures. Of particular interest, HCP lamellae formed by multiple pile-up stacking faults were captured by HRTEM in Fig. 11(f) in accord with distinctive peaks observed in in-situ SXRD patterns mentioned above. Additionally, EDS under STEM mode in Fig. 12 confirmed accordingly negligible precipitation at heavily twined area, suggesting little precipitation strengthening.

In terms of twinning-hierarchical structure interactions, in Fig. 10(b-c, f-g), twinning would be mostly blocked by HAGBs while mostly penetrate through LAGBs regardless of temperature. In Fig. 11, similar to those observed in EBSD results, red arrows and blue arrows show blocked and penetrating twinning, respectively, indicating that twin expansion was presumably hindered by LAGBs, or dislocation walls, and entirely blocked by HAGBs. Given the dense dislocation network, we presume that the suppressed twin expansion brought by hierarchical structure would be responsible for the observed repressed twinning response, and consequently, lower elongation. The origin of such action is to be discussed in the discussion section. However, apart from the obstructive effect, the massive dislocation network is reported to cooperate with twinning networks, contributing to steady work hardening by storing dislocation density and thus enhancing elongation [29]. Dislocation storage and pile-up could be noticed in TEM results as well in the SLM-built CrCoNi MEA.

4. Discussion

4.1. Mechanism for superior yield strength

Yield stress is widely confirmed as one of the most iconic properties of structural materials and has been thoroughly studied in various ma-
Fig. 8. Results of ex-situ mechanical tests: (a) Engineering stress-strain curves and (b) Strain hardening curves at various temperatures.

Table 1
Comparison of mechanical properties of the CrCoNi MEA fabricated by conventional methods and SLM, which exhibits superior yield strength and UTS manufactured in a rather convenient way. However, the origin of the only reasonable total elongation needs further investigation.

<table>
<thead>
<tr>
<th>Processing history</th>
<th>Testing temperature (K)</th>
<th>Yield strength (MPa)</th>
<th>UTS (MPa)</th>
<th>Elongation (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SLM</td>
<td>293</td>
<td>651.0 ± 19.2</td>
<td>907.7 ± 21.8</td>
<td>35.8 ± 2.2</td>
<td>This work</td>
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<tr>
<td></td>
<td>195</td>
<td>730.0 ± 29.9</td>
<td>1051.6 ± 51.1</td>
<td>44.1 ± 2.4</td>
<td>[4]</td>
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<tr>
<td></td>
<td>77</td>
<td>860.1 ± 43.7</td>
<td>1305.9 ± 83.7</td>
<td>46.9 ± 4.9</td>
<td>[29]</td>
</tr>
<tr>
<td>Cold forging, cross rolling, recrystallization</td>
<td>293</td>
<td>440 ± 13</td>
<td>884 ± 11</td>
<td>73 ± 1</td>
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<td></td>
<td>198</td>
<td>554 ± 24</td>
<td>1053 ± 13</td>
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<td>77</td>
<td>657 ± 22</td>
<td>1311 ± 27</td>
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<td>Swaged, recrystallized</td>
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<td>360 ± 10</td>
<td>–870</td>
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<td></td>
<td>77</td>
<td>560 ± 20</td>
<td>–1230</td>
<td>–45</td>
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<td>Cold rolled, annealed, recrystallized</td>
<td>RT</td>
<td>430</td>
<td>900</td>
<td>–60</td>
<td>[19]</td>
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<tr>
<td>Cold-rolled, cross-rolling, annealing</td>
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<td>–300</td>
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where κ is Hall-Petch slope; d is mean grain size; α is a material and temperature-dependent constant usually taken as 0.3–0.5; M is Taylor factor (3.01, based on EBSD result on top view, Fig.5(c)); G is shear modulus, b is the modulus of Burgers vector of perfect dislocation (a/√2 = 0.25 Å), and p is dislocation density. Since intrinsic friction stress σ_{fr}, Hall-Petch slope k, and shear modulus G is roughly material-dependent, we could arbitrarily fetch data from previous works without losing accuracy. Those are: σ_{fr} = 218 MPa [58]; k = 265 MPa μm⁻¹/² [58] and G = 87 GPa [21]. As for mean grain size d in the hierarchical structure, the grain boundary strengthening is about dislocation movement blocked by lattice misfit and intragranular misorientation rather than dislocation entanglement at dislocation walls, which ought to be evaluated as dislocation hardening later. Therefore, we should take coarser grains surrounded by HAGBs for calculating d, with a statistical value of 4.12 μm obtained from EBSD data. As for the solid solution hardening effect Δσ_{ss}, a method specifically modified for...
multi-component concentrated alloys reported by Toda-Caraballo and colleagues [59,60] was employed, with a final result of 109 MPa obtained. This method calculates the solid solution hardening effect by estimating lattice distortion by constructing a matrix to evaluate respective elemental atom sizes’ contributions. Detailed procedures should be referred to original articles.

In the hierarchical structure of SLM-built CrCoNi MEA, the pre-existing high-density dislocations formed in the additive manufacture process would contribute to substantial dislocation hardening. According to strengthening analysis carried by Z.G. Zhu et al. [36] around SLM-built CrMnFeCoNi high entropy alloy and U.F. Kocks [57], the dislocation density term is directly related to mean cell size \( \lambda \) (0.38 \( \mu \)m, based on SEM and TEM results):

\[
\rho \sqrt[\alpha]{c} = \frac{c}{\lambda} \quad (5)
\]

where \( c \) is a constant with \( \alpha \approx 1 \) [36,57]. Consequently, we have all terms in Eq. (4) determined with a final prediction of RT yield strength of 631 MPa acquired, which corresponds with experimental values precisely. Contributions to yield strength of Hall-Petch and dislocation strengthening constituted 131 MPa and 174 MPa, respectively. Hence, the dense dislocation network in the hierarchical structure is to be commended for its utmost dedication. Furthermore, with twinning delaying the onset of necking, high ultimate tensile strength could be obtained under a steady flow of work hardening as previously discussed, resulting in overall competitive mechanical properties achieved by simple building methodology.

### 4.2. Interaction between hierarchical structure and nano-twinning

Reasonable total elongation values were achieved in our work at room and cryogenic temperatures. However, when compared to conventional CrCoNi MEA counterparts, the potential to further promoting elongation is promising. Here we discussed the origin of reasonable elongation to understand the deformation mechanism in SLM-built CrCoNi MEA further and guide future investigation. As previously discussed, twinning is considered an essential accommodation mechanism in the later deformation stages of CrCoNi MEA by introducing the “dynamic Hall-Petch” effect [4,30]. By contributing to a steady work hardening rate, early necking is restrained, and elongation is promoted. Hence, the determination of the onset of twinning is vital to explain reasonable ductility. As evinced by in-situ SXRD results, the SLM-built CrCoNi exhibited postponed onset of twinning. Besides, as demonstrated in EBSD and TEM results, LAGBs seem to impede twin expansion. To understand the suppressed twinning response, we discussed two primary interactions between nano-twinning and the microstructures.

The first mechanism would be suppressed twinning expansion by high-density LAGBs in the hierarchical structure. Unique interactions between nano-twinning and grain boundaries work as a strong synergism in maintaining the continuous steady work hardening rate. The work hardening curves presented in Fig. 8(b) exhibited satisfactory stability, which was scarcely observed in those conventionally built counterparts. However, studying twinning interaction with HAGBs, as these columnar subgrain structures are usually considered harmful in casting processes [18]. Despite lacking relevant studies, it is crucial to understand how...
twinning penetrates LAGBs or dislocation walls in the comprehension of SLM-built CrCoNi MEA. Leifeng Liu et al. [30] reported twinning nucleation behavior on dislocation walls by an in-situ TEM observation in SLM-built 316L stainless steel. They declared that the twinning penetration mechanism should be originated by secondary nucleation from piling-up partial dislocations on the other side of the dislocation wall. Obviously, additional barriers would consequently slow down twinning spreading in contrast to those in dislocation-free grains.

Fig. 10. Post-deformation SE–SEM, EBSD IPF X’, PF and IPF images at (a–d) room temperature and (e–h) 77K at near-fracture area. Strong $<111>$–$<100>$ double fiber texture can be observed from PFs and IPFs in (d) and (h). Red arrows show twinning blocked by HAGBs, whereas blue arrows indicate that twinning partly penetrates through the LAGBs. EBSD step sizes are (b) 0.2 µm, (c) 0.075 µm, (f) 0.25 µm and (g) 0.05 µm. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)
delaying the onset of twin nucleation. Evidence supporting this thesis could be observed in post-deformation EBSD mappings in Fig. 10(b-c, f-g) and TEM results in Fig. 11(b-e), as twinning seemed to partly penetrate (indicated by blue arrows) through still LAGBs (dislocation walls) while most of which was blocked (red arrows) by HAGBs. Additionally, smaller mean cell size in SLM-built CrCoNi MEA may contribute since the critical stress of twinning penetration should be intensely dependent on intragranular misorientation and grain size [11,61], pushing the suppression to the twinning expansion.

4.3. Effects of growth texture on nano-twinning response

Another major factor is the suppressed twinning nucleation by near $<100>$ growth texture. Relativity between individual crystalline orientation and macroscopic uniaxial tension direction is reported strongly dominating twinning behavior. As reported by C.E. Slone et al. [6] and Benay Uzer et al. [10] via a combination of experiments and modeling, (1) grains with the initial orientation of $<100>$ parallel to LD would have a stronger propensity to deform by slipping instead of twinning even at large strains, while $<111>$-parallel-to-LD grains would have maximum inclination to twin. Grains with intermediate orientations ($<110>$, $<123>$, etc.) would respond intermediately as well; (2) grains with initial orientations other than $<100>$ would rotate till their respective $<111>$ crystalline direction aligned to LD, while $<100>$-oriented grains would remain still. These findings are similar to those reported in TWIP steels [11,61] and are commonly explained by Schmid’s law:

$$m\sigma_{crit} = \tau_{crit} = \sigma \cos \phi \cos \lambda$$

where $\sigma_{crit}$ is critical stress for the onset of twinning, m the Schmid factor, $\tau_{crit}$ the critical resolved shear stress for twinning, $\sigma$ without subscript for macroscopic uniaxial tensile stress, $\phi$ is the angle between the twinning interface normal ($<111>$ in the case of FCC CrCoNi) and LD, and $\lambda$ is the angle between the twinning shear direction ($<1\overline{1}2>$) and LD. When it comes to multi-crystals, Schmid factor $m$ should be replaced by Taylor factor $M$. In the SLM-built CrCoNi, a large amount of near $<100>$ oriented (aligned to BD, perpendicular to LD in this work) sub-grains occupied a majority, forming into fiber $<100>$ growth texture. On the other hand, as indicated by EBSD PFs and IPFs, those perpendicular-to-$<100>$ orientations (such as $<010>$, $<011>$, but not $<111>$) may primarily lie on X–Y plane with relatively uniform distribution (see uniform-colored outer edge in PF, Fig. 5(h)). Hence, the $<100>$ growth texture would impact relativity between granular orientations and LD, leaving the macroscopic part less sensitive to strain, resulting in the onset of twinning delayed and reflected by in-situ synchrotron diffraction results. Besides, the coherent “rotation effect” could...
be observed from a comparison between as-printed and post-deformation EBSD PFs, IPFs in Fig. 10(d, h) as well: PFs and IPFs tend to be “cleaner” after deformation, that is to say, grains with disorganized orientations epitaxially grown around <100> primary orientation had rotated and gathered, resulting in enhanced <111> peaks in post-deformation PFs and IPFs. This could be recognized by narrower granular orientation distributions in PFs and IPFs and could also be called the classic <100>—<111> double fiber texture. Additionally, from SEM and as-printed EBSS images, the columnar sub-grains are of several hundreds of nanometers on the X–Y plane with several micrometers along the Z direction, making the “slim” columnar sub-grains particularly hard to rotate in contrast to those equiaxial grains in conventionally built counterparts. This phenomenon may be responsible for the delayed twinning as well. To summarize, we could infer that both granular orientation and morphology would hinder the onset of twinning in SLM-built CrCoNi MEA.

To quantitatively evaluate twinning volume fraction, a method similar to those addressed by G. Laplanche et al. [43,54] was conducted on EBSS, HRTEM images with mean twin spacings (ι), mean twin widths (t) at room and cryogenic temperatures measured to be 3.46 μm, 13.1 nm, and 1.90 μm, 21.7 nm, respectively. Twin volume fractions (f) are to be calculated using Fullman’s equation [62]:

\[
N \lambda^{-1} = \frac{1}{2} \frac{f}{1-f}
\]

(7)

where N is twin count per unit length. Hence twin fractions would be 0.75% at RT, lower than 2.2% at cryogenic temperature. Therefore, we could infer that primary obstacles suppressing twinning onset are roughly temperature-independent and overweighed by increasing twinning nucleation [4,5] at lower temperatures, resulting in relatively higher elongation to failure and thus superior mechanical properties.

5. Conclusions

Equilomar CrCoNi MEA is prepared by selective laser melting. The microstructure and deformation mechanisms are characterized and analyzed systematically by OM, XRD, XRM, SEM, EBSS, TEM, ex-situ tension, and in-situ SXRD interrupted tensile tests. The following conclusions can be drawn.

(1) Good quality CrCoNi MEA specimens with simple FCC structure and high relative density of 99.7% are fabricated, confirming SLM’s viability to produce CrCoNi MEAs.

(2) The hierarchical structure consisting of coarse grains, columnar sub-grains (dislocation cellular structure), HAGBs, and LAGBs (dislocation walls) is observed. The columnar sub-grains exhibit growth texture of <100>/>BD. The dislocation walls lead to substantial dislocation hardening, while the HAGBs are responsible for grain boundary hardening. There is good consistency between theoretical and experimental assessments.

(3) The strength and ductility improve as temperature decreases due to enhanced dislocation and nano-twining behaviors. The yield strength at room temperature is 651 MPa and 860 MPa at 77 K. The ultimate tensile strength and elongation reach 1340 MPa and 47% at 77 K. The steady and continuous strain hardening response observed from tensile tests stems from the synergism of dislocation and twinning network. Hence, excellent mechanical properties are promised.

(4) A precise onset of twinning is revealed by in-situ SXRD tensile tests, and the suppressed twinning response originates from two major factors: high-density LAGB and <100> growth texture in the hierarchical structure. While these obstacles may be temperature independent, the twinning volume fraction at fracture increases as temperature drops, and so it is sensitive to temperature. These mechanisms imply possible pathways to enhance the mechanical properties further.

CRediT authorship contribution statement

Bolu Han: Laser processing parameter evaluations, ex-situ mechanical tests and microstructure characterizations, in-situ SXRD experiments and data processing, Writing – original draft. Chengcheng Zhang: Laser processing parameter evaluations, ex-situ mechanical tests and microstructure characterizations, in-situ SXRD experiments. Kai Feng: Performed in-situ SXRD experiments, drafted and revised the manuscript, Supervision, Project administration, Funding acquisition. Zhiyuan Li: Performed in-situ SXRD experiments, supervised the manuscript and provided valuable advises, provided funding support. Xiancheng Zhang: Contributed to revising the manuscript. Yao Shen: Performed in-situ SXRD experiments, supervised the manuscript and provided valuable advises. Xiaodong Wang: Contributed advanced ACTEM for nanoscale characterizations. Hiroyuki Kokawa: Performed in-situ SXRD experiments. Rui Feng: Inspected the manuscript and provided valuable advises. Zhiyuan Wang: Contributed explicit schematics. Paul K. Chu: Contributed to English quality control.

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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