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1 **Probing deformation mechanisms of a FeCoCrNi high-entropy alloy at 293 and**
2 **77 K using *in situ* neutron diffraction**

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15 **Abstract**

16 The deformation responses at 77 and 293 K of a FeCoNiCr high-entropy alloy,
17 produced by a powder metallurgy route, are investigated using *in situ* neutron
18 diffraction and correlative transmission electron microscopy. The strength and ductility
19 of the alloy are significant improved at cryogenic temperatures. The true ultimate
20 tensile strength and total elongation increased from 980 MPa and 45% at 293 K to 1725
21 MPa and 55% at 77K, respectively. The evolutions of lattice strain, stacking fault
22 probability, and dislocation density were determined via quantifying the *in situ* neutron
23 diffraction measurements. The results demonstrate that the alloy has a much higher
24 tendency to form stacking faults and mechanical twins as the deformation temperature
25 drops, which is due to the decrease of stacking fault energy (estimated to be 32.5 mJ/m²
26 and 13 mJ/m² at 293 and 77 K, respectively). The increased volume fraction of nano-
27 twins and twin-twin intersections, formed during cryogenic temperature deformation,
28 has been confirmed by transmission electron microscopy analysis. The enhanced
29 strength and ductility at cryogenic temperatures can be attributed to the increased
30 density of dislocations and nano-twins. The findings provide a fundamental
31 understanding of underlying governing mechanistic mechanisms for the twinning
32 induced plasticity in high entropy alloys, paving the way for the development of new
33 alloys with superb resistance to cryogenic environments.

34 **Keywords:** high entropy alloy, deformation twinning, neutron diffraction, cryogenic
35 deformation, stacking fault energy

36

37 **1. Introduction**

38 High-entropy alloys (HEAs) were first introduced in 2004 [1, 2], which aimed to
39 maximise the configuration entropy to form a single phase microstructure via
40 combining four or more principle elements in equimolar or near equimolar ratios. The
41 high configuration entropy, sluggish diffusion, cocktail effect and large lattice
42 distortion lead to their promising properties such as high strength, excellent ductility,
43 and superior fracture toughness [3-8].

44 One type of HEA and its variants, based on five 3d transition elements (Fe, Co, Cr, Mn,
45 Ni), can form a single phase face-centered-cubic (fcc) structure, displaying an excellent
46 combination of high strength, ductility and fracture toughness at both room and
47 cryogenic temperatures. Their mechanical properties improve significantly with
48 decreasing deformation temperatures [3-7]. We termed this group of HEA as tHEA to
49 distinguish them from other high entropy alloys (such as multi-phase HEAs [8]). tHEAs
50 have attracted significant interests for cryogenic applications, such as liquid nitrogen
51 storage and transportation of liquid gas from offshore.

52 Many microstructural studies [3-7], on strained or failed tensile specimens, have been
53 carried out, confirming the occurrence of nano-twinning during low temperature
54 deformation of tHEAs. Hence twinning induced plasticity is attributed to the tHEAs'
55 superb mechanical performance. Twinning induced plasticity has been at the forefront
56 of research recently as it is one of the micro-mechanistic mechanisms that can overcome
57 the strength-ductility trade-off, which has been demonstrated by fcc metals and alloys
58 with low stacking fault energy (SFE) such as the tHEAs and TWIP steels [9-11].

59 The deformation mechanisms of fcc metals and alloys are strongly related to the
60 temperature- and composition- dependent stacking fault energy (SFE) [12]. With the
61 drop of SFE, the deformation mechanisms change from dislocation glide alone, to
62 dislocation glide and mechanical twinning, to dislocation glide and martensite
63 transformation [13-15]. This has been demonstrated in many fcc metals and alloys,
64 including austenite steels [16], TRIP and TWIP steels [3,4], and Cu-Al alloys [17]. The
65 SFE of the tHEAs has been measured or calculated to be 10-40 mJ/m² at room
66 temperature [18-20]. In this SFE range, deformation twinning is usually activated,
67 which has been confirmed in tHEAs by a few experimental studies [3-7]. Recently,
68 martensite phase transformation have been observed when tHEAs were deformed under
69 hydrostatic high-pressure conditions [21, 22] at both room and high temperatures,
70 demonstrating that the fcc tHEAs can be destabilized into hcp phase at high pressure
71 (e.g. over 14 GPa [21]).

72 It is known that the SFE will drop as the temperature decreases, hence at cryogenic
73 temperatures, the formation of shear bands, deformation twins and stacking faults can
74 be enhanced [6, 23]. Simulations using first-principles methods [24, 25] confirm the
75 temperature dependent behaviour of SFE and some predict that the SFE of tHEAs can
76 even be negative at cryogenic temperatures [19, 26-28]. To validate the simulated
77 results, the SFE of tHEAs at cryogenic temperatures need to be determined
78 experimentally. Although a few studies have measured room temperature SFE of
79 tHEAs using TEM based methods [18], it is not a straight-forward task to measure low

80 temperature SFE using TEM, as the samples deformed at cryogenic temperatures need
81 to be warmed up to room temperature for sample preparation, during which the
82 dislocation and fault structure may have changed. Thereby the development of new
83 methods to measure low temperature SFE is critically needed, which will provide
84 much-needed validation for the simulations[19, 26] and pave the way for designing new
85 tHEAs.

86 To study deformation mechanisms of tHEAs, quantitative *in situ* mapping of
87 microstructure evolution of tHEAs at room temperature has previously been carried out,
88 using TEM [26, 29, 30], SEM [31], synchrotron X-ray diffraction [32] and neutron
89 diffraction [33, 34]. The *in situ* TEM directly observed the motion of Shockley partials,
90 the formation of stacking faults and 3D network of nano-twins [29, 30]. *In situ* neutron
91 and X-ray diffraction, on the other hand, can quantify the grain-level behaviour during
92 deformation, which includes the measurement of stacking fault probability [33], single-
93 crystal elastic constants [34], phase transformation [32], and SFE [33]. Those *in situ*
94 works significantly improved our understanding of the microstructural and mechanistic
95 origin of tHEAs' superb mechanical properties. Carrying out *in situ* studies at cryogenic
96 temperatures can provide similar benefits, not only unravelling the underlying
97 mechanisms determining the dramatic increase of strength and ductility at cryogenic
98 temperatures of the alloys, but also determining critical material parameters such as
99 SFE.

100 In the current study, we conducted uniaxial tensile deformation on a FeCoCrNi high-
101 entropy alloy at 293 and 77 K. With the help of *in situ* neutron diffraction, we monitored
102 and quantified the microstructural responses during tensile deformation, including the
103 evolution of lattice strain, stack fault probability and dislocation density versus imposed
104 strain at both temperatures. The different responses between 293 and 77 K were
105 compared. We also calculated the stacking fault energy of the alloy at both 293 and 77
106 K. TEM observations were carried out on the deformed samples, providing correlative
107 analysis. The work provides in-depth micro-mechanistic understanding involving the
108 complex interaction of stacking faults, twins and dislocations for the studied tHEAs at
109 cryogenic temperatures, which could pave the way for designing advanced metallic
110 materials resistant to cryogenic environments.

111 **2. Experimental details**

112 The FeCoCrNi high entropy alloy was fabricated by powder metallurgical processes,
113 which are detailed in Refs. [33, 35], namely, hot extrusion of gas-atomized FeCoCrNi
114 powders. The alloy has a single fcc structure and the average grain size of the as-
115 extruded specimen was approximately 35 μm . The mechanical properties and
116 microstructure of the alloy at room temperature can be found in Ref. [35].

117 *In situ* time-of-flight neutron diffraction measurements during tensile deformation were
118 performed on the ENGIN-X neutron diffractometer, Rutherford Appleton Laboratory
119 (RAL), ISIS, UK [36, 37]. A stress rig with a load capability of 100 kN was used for
120 the experiments. An in-house built cold chamber, integrated with the stress rig, was
121 used which provides a controlled cryogenic temperature environment (10-293 K) [38].

122 A schematic of the setup is shown in Fig. 1a. A low temperature extensometer was used
123 to measure the displacement of the part of gauge length (10 mm). The rig was mounted
124 on the diffractometer horizontally. The loading axis was oriented horizontally, parallel
125 to the extruded direction and orientated 45° relatives to the incident beam. The two
126 detectors (axial and radial) allow collection of the diffraction patterns at fixed
127 horizontal scattering angles of $\pm 90^\circ$, with diffraction vectors parallel and perpendicular
128 to the loading direction, respectively.

129 Dog bone-shaped uniaxial tensile specimens with a gauge length of 34.5 mm and
130 diameter of 8 mm were prepared from the as-extruded material. A $4 \times 4 \times 4 \text{ mm}^3$ neutron
131 measurement gauge volume was used. Diffraction patterns were acquired for 20 min
132 intervals between tensile loading steps, iterating until the sample failed. During the
133 cooling down process for the cryogenic temperature deformation test, a stress level of
134 5 MPa was maintained via stress-control. During loading up, a stress-control was used
135 before the yielding point, which was followed by strain-control. The diffraction spectra
136 was analysed by Open G software which provides the information of d-spacing, peak
137 intensity and full width at half maximum (FWHM).

138 In order to calculate the stacking fault energy and dislocation density from the measured
139 diffraction spectra, single peak fitting with a pseudo-voigt convolution was developed
140 in Matlab. The measured diffraction patterns, after being deconvoluted with the
141 instrument function, can be described by the convolution of a Gaussian and a Lorentz
142 function.

$$I(x) = I(0) \left[\mu \exp \left[-\pi \frac{(x - x_0)^2}{\beta_G^2} \right] + (1 - \mu) \frac{1}{\frac{\beta_C^2}{\pi^2} + (x - x_0)^2} \right] \quad (1)$$

143 where x_0 is the peak centre, and β_G and β_C are constant parameters of the Guassian and
 144 Lorentz respectively. μ and $(1-\mu)$ denote the fraction of Guassian and Lorentz used. The
 145 size strain and microstrain contribution are then related to the parameters of the
 146 Gaussian and Lorentz function by

$$D_{eff} = \frac{1}{\beta_C} \quad (2)$$

147 And

$$\langle \xi^2 \rangle_{hkl}^{1/2} = \left(\frac{2}{\pi} \right)^{1/2} \beta_G d_{hkl} / 2 \quad (3)$$

148 respectively. D_{eff} is the effective dimension of coherently diffraction blocks (e.g. grains)
 149 and ξ is the microstrain and its root-mean-square could be interpreted to be proportional
 150 to the square root of dislocation density ($\rho^{1/2}$) as follows:

$$\rho = \frac{k \langle \xi^2 \rangle}{F b^2} \quad (4)$$

151 where b represents the magnitude of Burgers vector. F and k are two constants, and F
 152 =1 and $k = 1.61 \text{ nm}$ were chosen according to [39] for fcc crystal with a Burgers vector
 153 along $\langle 110 \rangle$.

154 Transmission electron microscopy (TEM) study was conducted on a JEOL-2100 TEM
 155 operated at 200 kV to examine the microstructure of the specimens after the *in situ*
 156 neutron diffraction experiments. The TEM samples were extracted from regions close

157 to and away from the fracture surfaces which represent samples with different strain
158 levels. On the sample deformed at 77 K, TEM foils were extracted from the regions
159 with cross-section diameters equal to 6.8 mm and 6.24 mm which correspond to
160 reduction in the cross section area (ψ) during the tensile test of 27.8% and 39.2%,
161 respectively. For sample deformed at 293 K, TEM foils were extracted from the regions
162 with the cross-section diameters equal to 7.15 and 6.47 mm which correspond to the
163 reduction in cross section area (ψ) during the tensile test of 20.1% and 34.6%,
164 respectively. The foils extracted were ground down to $\sim 80 \mu\text{m}$, then disks of 3 mm
165 diameter were punched out and twin-jet electro-polished in a solution containing 100
166 mL HClO_4 and 900 mL CH_3COOH at approximately -10°C .

167 **3. Results and discussion**

168 **3.1 Mechanical properties**

169 Fig. 1b shows the true stress-true strain curves of the polycrystalline FeCoCrNi alloy
170 tensile deformed to fracture at 77 and 293 K. The yield strength (YS) and ultimate
171 tensile strength (UTS) increase from approximately 260MPa and 980MPa at 273 K to
172 480MPa and 1725 MPa at 77 K. The total elongation also increases from about 45% to
173 55% (corresponding to engineering strain of 55% and 72% respectively) as the test
174 temperature is decreased from 293 to 77 K. This enhancement of strength and ductility
175 of the tHEA alloys at cryogenic temperatures is also compared to a few selected
176 previous studies, as summarized in Tab. 1. It can be shown that the yield strength and
177 UTS often increased 1.5-2 times while the maximum elongation often increased 10-
178 15% when the deformation temperature was dropped from 293 to 77 K. **The mechanical**

179 properties of FeCoCrNiMo_{0.23} alloy at both temperatures are also provided in Table 1
180 for comparison. It shows that micro-alloying the tHEA with Mo enhances the
181 mechanical properties.

182 The strain hardening rate (SHR), which represents by the derivative of the true stress
183 with respect to the true strain, is shown in Fig. 1c as a function of true stress. The area
184 below the line $d\sigma/d\varepsilon = \sigma$ reveals the region in which necking is predicted to occur
185 according to Considre's criterion. The SHRs of the alloy at 77 and 293 K show a similar
186 trend, whereas two distinguished stages can be found in both curves – rapid drop of the
187 strain hardening rate at small stress level, then the decrease slows down at higher stress.
188 The transition points between the two stages are marked in Fig. 1b. The transition point
189 for room temperature tensile test is at 410 MPa (5.6 %) true stress (strain) level, whereas
190 at 77 K, it is 682 MPa (6.3 %) true stress (strain). The SHR at 77 K is higher than at
191 room temperature, which is consistent with other studies [5, 6, 23].

192 In summary, the FeCoCrNi alloy has significantly improved strength, ductility and
193 strain hardening capability at 77 K than at room temperature. The underlying
194 mechanisms will be discussed with the help of *in situ* neutron diffraction and correlative
195 electron microscopies in the following sections.

196 3.2 The evolution of lattice strain

197 As shown in Fig. 2, the tHEA is a fcc single phase structure at both 293 and 77 K before
198 deformation. The lattice parameters at 293 and 77 K are 0.3604 and 0.3563 nm,
199 respectively, calculated by the average of five diffraction peaks. Cooling the sample to
200 cryogenic temperature results in the drop of lattice parameter. During the course of

201 deformation at both 293 and 77 K, the tHEA stays as a fcc structure (no additional peaks
202 belongs to bcc and hcp structure appears), which means that martensite transformation
203 do not occur in this alloy.

204 The changes in lattice strains can be calculated using

$$205 \quad \varepsilon_{hkl} = \frac{d_{hkl} - d_{hkl}^0}{d_{hkl}^0} \quad (4)$$

206 where ε_{hkl} is the lattice strain in the $\{hkl\}$ grain family, d_{hkl} is the current sample
207 lattice spacing and d_{hkl}^0 is the stress-free lattice spacing. The stress-free lattice spacing
208 was taken from the measurement point at 5 MPa at the temperatures.

209 Elastic lattice strains along the axial and radial directions in grain families having
210 $\{111\}$, $\{200\}$, $\{220\}$, $\{311\}$ and $\{222\}$ crystallographic planes during tensile
211 deformation at 77 and 293K, are shown in Fig. 2a and 2b, respectively. The
212 uncertainties in the measured internal strains were approximately 30 microstrain [40].

213 Fig. 2a shows that the lattice strains increased with applied stress linearly from 0 to 450
214 MPa, and then nonlinearly when the applied stress was greater than 450MPa during
215 tensile loading at 77 K. This is due to the fact that the load transfers from softer grain
216 families (e.g. 220) to harder grain families (e.g. 200) [33]. The trend of lattice strain
217 evolution at 293 K is similar to that at 77 K, except the nonlinear transition happened
218 earlier than that at 77 K (above ~ 250 MPa). Overall, at 77 K, the lattice strain values of
219 all grain families in the axial direction are larger than at 293 K under similar
220 deformation level.

221 We determined grain orientation dependent diffraction elastic constants (E_{hkl}) and
222 Poisson's ratios (V_{hkl}) through fit linear responses to the purely elastic parts of each
223 curve in Fig. 2. E_{Rietveld} and V_{Rietveld} have also determined through perform the Rietveld
224 fitting of 8 peaks. All these values are listed in Tab. 2. The E_{hkl} values are very similar
225 for both temperatures. The E_{Rietveld} , V_{Rietveld} and V_{hkl} , are slightly lower at cryogenic
226 temperatures than room temperature. Daymond et al. [41] show that the value of E_{Rietveld}
227 is very similar to the macroscopic Young's modulus. The current temperature
228 dependent values of E_{Rietveld} are compared with the temperature dependent Young's
229 moduli of CoCrFeMnNi in Ref. [42] with excellent agreement.

230 3.3 Stacking fault probability

231 Before we start analysing the stacking fault probability (SFP), we shall note the
232 relationship between twins and stacking faults. Upon deformation, passage of Shockley
233 partial dislocation with Burger vector $1/6\langle 112 \rangle$ on neighbouring two (111) planes
234 creates an intrinsic stacking fault, and continuous passage of the partial dislocations on
235 successive (111) planes creates multi-layer faults forming twin nucleuses; in the end
236 larger twins can be formed by passage of more partials on neighbouring (111) planes
237 [43]. For alloys with stacking fault between $18 < \text{SFE} < 45 \text{ mJ/m}^2$, twinning is more
238 favourable to occur with external straining. At SFE values $< 18 \text{ mJ/m}^2$, martensite
239 formation occurs when the molar Gibbs energy of martensitic is negative. This
240 martensitic transformation takes place either by fcc-hcp, or, for even lower SFE,
241 martensite formation by fcc-hcp-bcc becomes the favoured transformation mechanism
242 that affects the further deformation of the material [13]. The fcc to hcp transformation

243 can occur by shifting every two neighboring fcc (111) planes in the [11-2] direction by
244 a distance of $a/\sqrt{6}$ (where a is the lattice parameter), which is realised by the partial
245 dislocation movements in the (111) planes [14]. When SFE exceeds 45 mJ/m^2 ,
246 plasticity and strain hardening are controlled solely by the glide of dislocations [15].

247 Many studies [33, 44-46] have shown that stacking faults, if they occur in fcc crystals,
248 can change the Bragg scattering positions compared with a fault-free lattice. The peak
249 position shifts for successive orders of reflections such as {111} and {222} might be
250 different arising from the structure factor for stacking faults. This can be used to
251 estimate the stacking fault density in the sample.

252 We plot the lattice strain evolutions of {111} and {222} at axial and radial directions
253 for 77 and 293 K tensile tests in Fig. 4a and 4b, respectively. The separation of {111}
254 and {222} lattice strain in the axial direction after certain amount of strain is obvious
255 for both temperatures, which indicates the formation of stacking faults and possibly
256 twins in grains whose {hkl}|| plane-normals oriented “parallel” to the loading axis.
257 Interestingly, at room temperature, the {111} and {222} lattice strain curves in the
258 radial detector bank, almost overlap for the sample deformed. However, at 77K, the
259 two lattice strain show distinct difference. The radial detector registers a portion of the
260 grains whose {hkl}⊥ plane-normals are “perpendicular” to the loading axis. The
261 results suggest that those grains registered are unfavourable for twinning at room
262 temperature but form stacking faults and twins at 77 K. In addition, it shows that
263 twinning and stacking fault formation are strongly orientation-dependent (e.g. grains

264 with {hkl}|| plane-normal oriented “parallel” to the loading axis are easier to form
 265 stacking faults and twins). At cryogenic temperature, twin nucleation and growth can
 266 be triggered in grains whose orientation is unfavourable for twinning at room
 267 temperatures.

268 Both (hkl) dependent macro-strain (ϵ_{hkl}^{strain}) and stacking faults (ϵ_{hkl}^{sf}) can contribute to
 269 the change of lattice strain (ϵ_{hkl}^{exp}) measured by the peak shift in the experiment. The
 270 measured lattice strain (ϵ_{hkl}^{exp}), (hkl) dependent macro-strain (ϵ_{hkl}^{strain}) and stacking
 271 faults (ϵ_{hkl}^{sf}) follow a relationship:

$$\epsilon_{hkl}^{exp} = \epsilon_{hkl}^{strain} - \epsilon_{hkl}^{sf} = \epsilon_{hkl}^{strain} - \frac{\sqrt{3}}{4\pi} \frac{\sum_b \pm(h+k+l)}{(u+b)(h^2+k^2+l^2)} SFP \quad (7)$$

272 where u and b are the numbers of non-broadened and broadened component due to
 273 stacking faults; SFP represents stacking fault probability. With the help of Eq. (7), we
 274 are able to calculate the stacking fault probability, which directly indicates the density
 275 of stacking faults.

276 The evolution of the stacking fault probability during loading up at 77 and 293 K
 277 obtained from Eq. 7 are shown in Fig. 4a and 4b. At 77 K, the SFP increases from 0 to
 278 3×10^{-3} after true strain reaches approximately 4.8%. After this, the SFP increases
 279 almost linearly with the increase of true strain, especially after the true strain is larger
 280 than 10%. The SFP increases to 25.6×10^{-3} at the strain level of 47% (close to failure).
 281 At 293 K, the SFP fluctuates below 0 when the true strain is smaller than 10%. After

282 10% true strain, the SFP becomes positive and increases with true strain steadily up to
283 5.4×10^{-3} at the strain level of 48.6%, which is about five times smaller than that at 77
284 K. The evolutions of SFP with applied true strains for both temperatures can be fitted
285 with a linear function in the true strain range from 3% to 55% (Fig. 4a and 4b). The
286 slope at 77 K is 0.72, which is about three times larger than that at 293K (0.24).

287 The fact that at 77 K, compared to room temperature, the sample shows much higher
288 SFP at similar strain level and the SFP curve is much steeper, suggests that at low
289 temperatures, the FeCoCrNi alloy can form more stacking faults in the sample and the
290 nucleation and growth of twins might be much quicker than at room temperature.

291 We then plot the SFP as a function of true stress of the FeCoNiCr and FeCoNiCrMo_{0.23}
292 at both 77 and 293 K, as shown in Fig. 4c. For both alloys, the SFP values of the two
293 deformation temperatures almost overlap at the same stress level when the true stress
294 is over roughly 450 MPa. This implies that the density of stacking faults of tHEAs is
295 mainly a function of stress levels, regardless of deformation temperature.
296 FeCoNiCrMo_{0.23} alloy shows similar behaviour. At the same stress, the alloy with Mo
297 addition has a slightly higher SFP.

298 3.4 Stacking fault energy

299 The stacking fault energy (SFE) represents the easiness of dissociating a perfect
300 dislocation into two partial dislocations and the tendency for the formation of SFs. It
301 can be calculated by Reed and Schramm's equation [47]. Note that the SFE we

302 measured here by neutron diffraction is the so-called intrinsic stacking fault energy
303 (γ_{ISF}).

$$\gamma_{ISF} = \frac{6.6a_0}{\pi\sqrt{3}} \left(\frac{2c_{44}}{c_{11} - c_{12}} \right)^{-0.37} \frac{\langle \xi^2 \rangle_{111}}{SFP} \left(\frac{c_{44} + c_{11} - c_{12}}{3} \right) \quad (8)$$

304 where, γ_{ISF} is the intrinsic stacking fault energy, a_0 is the lattice parameter.
305 $\langle \xi^2 \rangle_{111}$ is the mean square microstrain, which is obtained by an integral breadth
306 method with a pseudo-voigt convolution [48]. The single crystal elastic constants
307 (SCEC) ($C_{11}=271.0$ GPa, $C_{12} = 175.0$ GPa, and $C_{44}=189.3$ GPa) are adopted from *ab*
308 *initio* atomistic simulation on an fcc FeCoNiCr alloy at 0 K [49]. The SCEC varies only
309 slightly between 77 K and room temperature according to the simulation work [25].
310 The stacking fault probability is measured at around engineering strain level of 48% for
311 both temperatures. The SFE of the FeCoCrNi high-entropy alloy is then estimated by
312 Eq. 8 to be 13 mJ/m² at 77 K and 32.5 mJ/m² at 293 K (Tab. 3). Expression (8),
313 however, is still approximate and we cannot determine reliable error values. There are
314 likely errors related to the calculation of the mean square micro-strain. Also, the
315 variation of SCEC between different temperatures and the measurement of SCEC by
316 atomistic simulation is not taken into account and may add additional uncertainty in the
317 estimated SFE due to many assumptions included in the model [49]. However,
318 measurements of SCEC is very limited and we would expect that accurately measuring
319 SCEC, both by experiments and simulation as a function of temperature, will provide
320 a more robust determination of SFE using eq. 8. We also estimated the SFE of a

321 FeCoNiCrMo_{0.23} to be 19 mJ/m² at room temperature [33] and 10 mJ/m² at 77 K (Table
322 3), which is lower than that of the FeCoNiCr alloy, suggesting that micro-alloying of
323 Mo can reduce the stacking fault energy of the tHEAs.

324 The estimated SFE at room temperature (32.5 mJ/m²) agrees with the experimental
325 measurement on FeCoCrNi tHEA by the combined use of XRD and DFT simulation
326 (e.g. 17.4, 34.3 and 31.7 mJ/m² depending on alloy composition used [50]) and TEM
327 (27±4 mJ/m² [19]). Currently no experimental measurement of tHEAs' SFE at
328 cryogenic temperature is reported. Only a few simulations were performed on
329 FeCoNiCr alloy. Zhao *et al.* performed ab initio calculation on a series of fcc tHEAs.
330 Their results show that the SFE of FeCoNiCr stays negative at 0 K. Depending on which
331 models they used, the predicted SFE values vary around -20 mJ/m² [19]). Zhang *et al.*
332 [26] reported that SFE at 0 K of fcc FeCoNiCr falls from -82 to -180 mJ/m². Beyramali
333 Kivvy and Asle Zaeem's simulation gives a SFE value of 31.6±0.9 mJ/m² [19] although
334 the temperature at which the simulation was carried out is not reported. Our estimation
335 of SFE at 77 K may provide a validation for SFE simulations if one can carry out the
336 *ab initio* calculations at different temperatures such as the one performed by Huang *et*
337 *al.* on a FeCrCoNiMn alloy [25]. Their work obtains an SFE of 8 mJ/m² at 77 K on
338 FeCrCoNiMn alloy, which is slightly lower than our measurement on the FeCrCoNi
339 alloy, indicating that variations in Mn contents can cause a change to SFE values.

340 The SFE is a critical parameter in the deformation properties of fcc metals and alloys.
341 The SFE influences phenomena such as the capacity of a dislocation to cross slip, the

342 formation of partial dislocation and twin boundaries [51]. Low SFE can lead to the
343 domination of a highly planar slip on a well-defined (111) plane, suppressing
344 dislocation cross-slip, hence augmenting the yield strength [51]. Additionally, Norihiko
345 *et al.* [52] suggest that the increase of yield stress at cryogenic temperature of tHEAs is
346 due to the thermal component of solid-solution hardening. The increase of yield stress
347 at cryogenic temperature is due to both the thermal component of solid-solution
348 hardening and the suppression of dislocation cross-slip. The very low SFE of the tHEA
349 used in this study strongly supports the conclusion from section 3.3 that the alloy is
350 prone to form twins when strained. Additionally, the drop of SFE at cryogenic
351 temperatures suggests that more deformation twins are able to nucleate and grow when
352 deformed at lower temperatures.

353 **3.5 Critical stress for twinning (σ_{tw})**

354 Experimental determination of σ_{tw} is challenging. It has been obtained via identifying
355 the transition point in the work hardening curve [53], or through careful TEM
356 observation on interrupted strained specimens [23, 35]. The critical stress for twinning
357 was measured by a few studies using TEM previously, which demonstrates that the
358 critical stress for twinning was independent of temperature and estimated to be $\sim 720 \pm 30$
359 for FeCrNiCoMn alloy [35] and 790 ± 100 MPa for CrCoNi alloy [23]. The criteria used
360 in those studies for determining the critical twinning stress level is that nano-twins start
361 to be identified by TEM.

362 As we noted before, the stacking fault probability we measured is directly related to the
363 density of stacking faults. Hence the SFP curve might allow us to estimate critical points
364 of stacking fault and twinning formation. The SFP stays negative at very low strains,
365 and when it reaches over 0, it increases continuously as we increase deformation. The
366 first critical point we identify is when the stacking fault probability becomes positive
367 (just above 0). We use the linearly fitted equations (Fig. 4) to determine the stress level
368 at SFP=0, which are 450 ± 30 MPa/9.6% strain at 77K and 500 ± 15 MPa/0.717% strain
369 at 293 K. This point might mark the nucleation stage of stacking fault within the sample
370 as when stacking faults start to form, the peak positions of the (111) and (222) planes
371 begin to shift apart, reflecting the contribution from the stacking fault. However, due to
372 the large scattering of the SFP at lower strain levels, those values should be used with
373 cautions.

374 The second critical point we consider is when SFP = 0.003 (the purple line in Fig. 4a
375 and 4b), at which sufficient and sizable stacking faults should have formed, lead to the
376 nucleation of twin faults. The corresponding true stress values are 730 ± 30 MPa/21.2%
377 strain at 293 K and 635 ± 30 MPa/4.885% strain at 77 K (Table 3). The measurement is
378 consistent with previous studies using TEM [23, 35], suggesting that the SFP curve
379 could be a reliable way to measure the critical stress for twinning.

380 With regards to the twinning stress prediction, two approaches have been developed.
381 The classic approach, based on theories such as Venables' pole mechanism [54] and
382 the Manajan-Chin stacking fault process [55], predicts that the critical resolved shear

383 stress for twinning (τ_{twin}) is proportional to intrinsic stacking fault energy (γ_{isf}) [53]
384 ($\tau_{twin} \times b_p \sim \gamma_{isf}$). Based on this, various equations have been formulated, and we
385 choose a few as shown in Table 4, together with the twinning stress values predicted
386 based on the equations. The predicted twinning stress values seem to be temperature
387 dependent. A significant discrepancy among different equations can also be observed.
388 The huge variations of twinning stress among different models demonstrate that a
389 systematic validation of the models with experiments is critically needed. Narita and
390 Takamura's and Venable's models predict relatively low σ_{tw} . It is even lower than the
391 yield strength at 77 K. Byun's model, on the other hand, gives relatively high values.
392 According to Byun's model, a twinning stress of 1353 MPa is needed to prompt
393 deformation twin at room temperature, which is above the UTS of the alloy. If this is
394 the case, deformation twinning is very unlikely to form during room temperature
395 deformation, unless some grains experience significant stress concentration. This is in
396 contradiction with our TEM observation (TEM confirms the formation of nano-twins
397 within the tensile strained sample, section 3.8). It has been suggested that Byun's model
398 overestimates the twinning stress in TWIP steels [53], which seems to be the case
399 according to our result. The twinning stresses predicted by Steinmetz *et al.* model (661
400 MPa at 77K, 799 MPa at 293 K) seems to agree reasonably well with the twinning stress
401 values we determined from the SFP curves (635 MPa at 77K, 730 MPa at 293 K).
402 Steinmetz *et al.* model, based on Mahajan-Chin three-layer twinning mechanism, has
403 also been shown to accurately predict the twinning stress in TWIP steels [53].

404 It has been suggested that intrinsic SFE alone is not sufficient to predict deformation
405 twinning mechanisms [53]. The generalized planar fault energy concept, recently
406 developed, has proposed that the stacking fault formation and twinning process are
407 controlled by the energy barriers, rather than just the intrinsic stacking fault energy. The
408 energy barriers include the intrinsic stacking fault energy, the unstable stacking fault
409 energy, the extrinsic stacking fault energy and the unstable twin fault energy [53]. The
410 twinning stress is then directly correlated to the unstable twinning fault energy, together
411 with the intrinsic stacking fault energy. However, to determine the unstable twinning
412 fault energy by experiments is not possible, and it usually requires using first principle
413 calculation. Hence, to accurately determine the critical twinning stress, *ab initio*
414 calculation needs to be performed, which should be validated against the experimental
415 values via the combined use of interrupted TEM investigation [23, 35] and *in situ*
416 diffraction methods as demonstrated here.

417 **3.6 Evolution of dislocation density**

418 The higher strain hardening rate at 77 K could result from the high dislocation density
419 in fcc matrix as well as the interaction between dislocations and nano-twins. Here, the
420 dislocation density during tensile deformation at 77 and 293 K are measured using Eq.
421 3, which are shown in Fig. 5a as a function of true strain. It indicates that the dislocation
422 density increases as the strains/stress increases. At the cryogenic temperature, a much
423 higher density of dislocations is accumulated after plastic deformation. A linear

424 equation ($\rho = \rho_0 + K\varepsilon$) can be used to describe the dislocation density and true strain
425 relationship:

$$\rho = 1.4 \times 10^{15} + 7.6 \times 10^{13}\varepsilon \quad (10)$$

$$\text{and } \rho = 1.5 \times 10^{15} + 3.5 \times 10^{13}\varepsilon \quad (11)$$

426 at 77 and 293 K, respectively.

427 The increases in the tensile stress, $\Delta\sigma$, due to forest dislocation interactions can be
428 described by:

$$\Delta\sigma = \alpha M G b \rho^{1/2} \quad (12)$$

429 where α is a constant, M is the Taylor factor (3.06), G is the shear modulus (85 GPa
430 at 77 K; 80 GPa at 293K [42, 56]), b is the magnitude of the Burgers vector
431 (0.252 nm at 77 K and 0.253 nm at 293 K) and ρ is the dislocation density. Fig. 5b
432 shows the normalized increment of stresses $(\sigma - \sigma_y)/MG$ (where σ is the current stress)
433 at both 77 and 293 K, which can be fitted with a linear function. Only data beyond the
434 yielding is included. The slope of the linear function at 77 K is 0.53 which agrees with
435 that found in CrMnFeCoNi [6]. The slope of the linear function at 293 K is 0.95, which
436 almost doubles the value at 77 K. However, we note that the physical meaning of α is
437 not very clear hence it is hard to interpret, and Eq. 12 ignores the contribution from the
438 other sources including dislocation-mechanical twin boundary interaction.

439 Gini *et al.* [57] proposed an equation that incorporates Eq. 12 and the plasticity model
440 of Nes and Marthinsen [58]:

$$\Delta\sigma = \alpha M G b \rho^{1/2} + \frac{M \beta G b}{\Lambda} \quad (13)$$

441 where Λ is the dislocation mean free path, and β is a constant. The formation of
442 mechanical twins reduces the dislocation mean free path. Thereby, according to Eq.13,
443 it is the dynamic increase of boundaries, due to the formation of mechanical twinning,
444 together with the continuously increase of dislocation density that leads to the enhanced
445 strain hardening behaviour of the tHEA during plastic deformation.

446 **3.7 Peak intensity**

447 Fig. 6 also shows the normalized peak intensity evolution of several lattice reflections
448 parallel and perpendicular to the load axis versus true stress. A few points can be drawn
449 regarding the changes of peak intensity and the differences at 77 and 293K:

450 (i) The peak intensity of the axial (220) decreased significantly when the applied
451 load was larger than the macroscopic yielding, as shown in Fig. 6. The (220)
452 peak at axial direction almost vanished when the applied stress was above 1500
453 MPa at 77 k and 800 MPa at 293 K. The fact that the (220) peak disappears
454 when the sample is strained close to failure in both samples is very interesting
455 and has been observed before in a FeCoNiCrMo_{0.23} alloy as well. In contrast,
456 the peak intensity of 220 at radial direction increased by a factor of 1.1 to 2
457 during the whole deformation.

458 (ii) The peak intensity of (200) at both axial and radial directions increased
459 significantly at 77 K, but hardly changed at 293K.

460 (iii) For (111) and (222) grains families, the peak intensity increased in axial
461 direction by a factor of 3 at 77 K but decreased in radial direction. The final
462 peak intensity of (222) and (111) changed by a factor of ~5.5 at 293 K.

463 Significant difference in peak intensity evolution at 77 and 293 K was observed,
464 signifying the different behaviour in terms of the re-orientation of grains during the
465 tensile deformation, which could be due to slip/rotation of grains [59] and/or formation
466 of mechanical twins [60]. However, it is not easy to distinguish the contribution from
467 grain rotation and mechanical twins.

468 **3.8 Microstructure characterisation**

469 The microstructures of the deformed specimens after the *in situ* neutron studies were
470 analysed by transmission electron microscopy (TEM) in order to gain a better
471 understanding of the controlling deformation mechanisms. TEM bright field (BF)
472 images and selected area diffraction patterns (SADP) of the samples deformed at 77
473 and 293 K are shown in Figs. 7 and 8, respectively, showing that nano-sized lamellas
474 have formed to accommodate strain when the sample was deformed at both
475 temperatures. The lamellas are twin structure as confirmed by the diffraction patterns
476 in Fig. 7d and 8d. TEM samples for Fig. 7a and 7b are taken from the failed *in situ*
477 samples at different reductions in cross-section area (ψ). The twin-twin intersections
478 can also be readily observed in Fig. 7a and 7b, which can form a complex 3-dimensional
479 network inhibiting dislocation propagation. Fig. 7a and 7b also show that at 77 K more

480 twins are formed at higher strain level. Comparing Fig. 7 with Fig.8, we conclude that
481 less twins and twin-twin intersections are formed at room temperature, consistent with
482 our measurement from *in situ* neutron diffraction. We do not observe martensite phase
483 at both temperature through TEM, again, consistent with our observation by neutron
484 diffraction (Fig. 2). A further drop of deformation temperature might lead to the
485 formation of martensite as SFE will become ever lower.

486 The dramatic increase of nano-twins and twin-twin intersections at lower temperatures
487 plays a key role for the higher strain hardening ability the alloy achieved at 77 K than
488 293 K as shown in Fig. 1b. The combination of enhanced dislocation hardening (higher
489 dislocation density during cryogenic deformation) and mechanical twinning (higher
490 twin volume fraction during cryogenic deformation) provide a larger work hardening
491 rate during tensile deformation at 77 K than at 293 K.

492 **4. Conclusions**

493 In our work, we fabricated a FeCoNiCr high entropy alloy with a single phase fcc
494 structure using a powder metallurgy route. We used *in situ* neutron diffraction to map
495 the evolution of deformation microstructure at both 77 and 293 K, correlatively
496 characterized by TEM. Several conclusions can be drawn based on the experimental
497 results:

- 498 1. The alloy has a good combination of high ultimate tensile strength (UTS ~1725
499 MPa) and ductility (elongation~55%) at 77 K, which is much higher than the
500 room temperature properties (UTS ~ 980 MPa, and elongation ~45%). Higher

501 strain hardening rate is also obtained at cryogenic temperature than at room
502 temperature.

503 2. Via *in situ* neutron diffraction measurement, we are able to determine the
504 stacking fault probability (SFP) as a function of stress level at both 77 and 293
505 K. The SFP increases much quicker and reaches a much higher value at similar
506 strain levels at cryogenic temperature than room temperature.

507 3. Using diffraction line profile analysis, stacking fault energy is estimated to be
508 $\sim 13 \text{ mJ/m}^2$ at 77 K and $\sim 32.5 \text{ mJ/m}^2$ at 293 K. As the SFE drops at cryogenic
509 temperature, more twin faults form as the alloy is deformed at cryogenic
510 temperatures. Nano-twins at both 77 and 293 K of the alloy have been observed
511 by TEM, and at 77 K, many more twins and twin-twin intersections are formed
512 than at room temperature.

513 4. We used the stacking fault probability curve to determine the critical stress for
514 twinning. The critical stress for twinning is set to stress levels when the SFP is
515 0.003. The corresponding true stress values are $730 \pm 30 \text{ MPa}$ at 293 K and
516 $635 \pm 30 \text{ MPa}$ at 77 K, which agree with previous measurements on
517 CrCoNi and CrMnFeCoNi alloys as well as Steinmetz *et al.* model.

518 5. Dislocation density is calculated for both temperatures from neutron diffraction
519 spectra. Higher dislocation density is found during low temperature plastic
520 deformation than at room temperature.

521 6. The combination of dislocation hardening and mechanical twinning provides
522 large work hardening rate and high strength during tensile deformation for the
523 high entropy alloy. The superior mechanical properties at the cryogenic
524 temperature is attributed to the enhanced dynamic Hall-Petch hardening and
525 dislocation hardening as at lower temperatures, increased amount of nano-twins
526 and dislocation are formed.

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535 **Tables**

536 Table 1. Comparison of yield strength (YS), ultimate tensile strength (UTS), and total
 537 elongation obtained at 77K and 293K from the present study to selected prior studies.
 538

Materials	Temp. (K)	YS (MPa)	UTS (MPa)	Elongation (%)
FeCoCrNi	77	480	1725	55
	293	260	980	45
FeCoCrNiMo _{0.23}	77	602	1863	51
	293	360	1238	48
CrCoNi [23]	77	560	1625	44
	293	360	750	30
CrMnFeCoNi [6]	77	460	1060	60
	293	265	600	45

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Table 2. Uniaxial materials properties of FeCoCrNi HEA at 77 and 293 K

Temp.	a	E ₁₁₁	E ₂₀₀	E ₂₂₀	E ₃₁₁	E _{Rietveld}	V ₁₁₁	V ₂₀₀	V ₂₂₀	V ₃₁₁	V _{Rietveld}
(K)	(nm)	(GPa)	(GPa)	(GPa)	(GPa)	(GPa)					
77	0.3563	146.3	97.0	191.6	214.0	229	0.138	0.232	0.168	0.234	0.20
293	0.3604	136.6	98.0	175.0	237.2	190	0.198	0.349	0.348	0.321	0.27

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Table 3. Stacking fault energy of FeCoCrNi tHEA at 77 and 293 K

	FeCoCrNi	FeCoCrNi	FeCoCrNiMo _{0.23}	FeCoCrNiMo _{0.23}
Temperature	77 K	293 K	77 K	293 K
SFE (mJ/m ²)	13	32.5	10	19
Twinning Stress	635 ± 30	730 ± 30	-	-

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Table 4. Critical stress for twinning of FeCoCrNi tHEA at 77 and 293 K

Sources	Equations	Temp.	τ_{tw} (MPa)	σ_{tw} (MPa)
Narita and Takamura [55]	$\tau_{tw} = \frac{\gamma_{isf}}{2b_p}$	77 K	45	135
		293 K	110	337
Venable [54, 61]	$\tau_{tw} = \frac{b\gamma_{isf}}{b_p(nb - b_p)}$	77 K	37-63	113-193
		293 K	91-155	278-474
Byun [62]	$\tau_{tw} = \frac{2\gamma_{isf}}{b_p}$	77 K	178	545
		293 K	442	1353
Steinmetz <i>et al.</i> [63]	$\tau_{tw} = \frac{\gamma_{isf}}{3b_p} + \frac{3Gb_p}{L_0}$	77K	216	661
		293 K	261	799

553

* n is the stress-concentration factor ($n=1$ represents no stress concentration while $n \geq 3$ means static tension, here $n = 2-3$) [20];

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* L_0 is the width of a twin embryo (approximately 200 nm);

556

* $\sigma_{tw} = M\tau_{tw}$, where M is the Taylor factor.

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564 **List of figures**

565 Fig. 1. (a) Schematic of the in situ neutron diffraction set-up; (b) True stress-strain
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588 the blue circled region in Fig. 8c which has contribution from both the matrix and the
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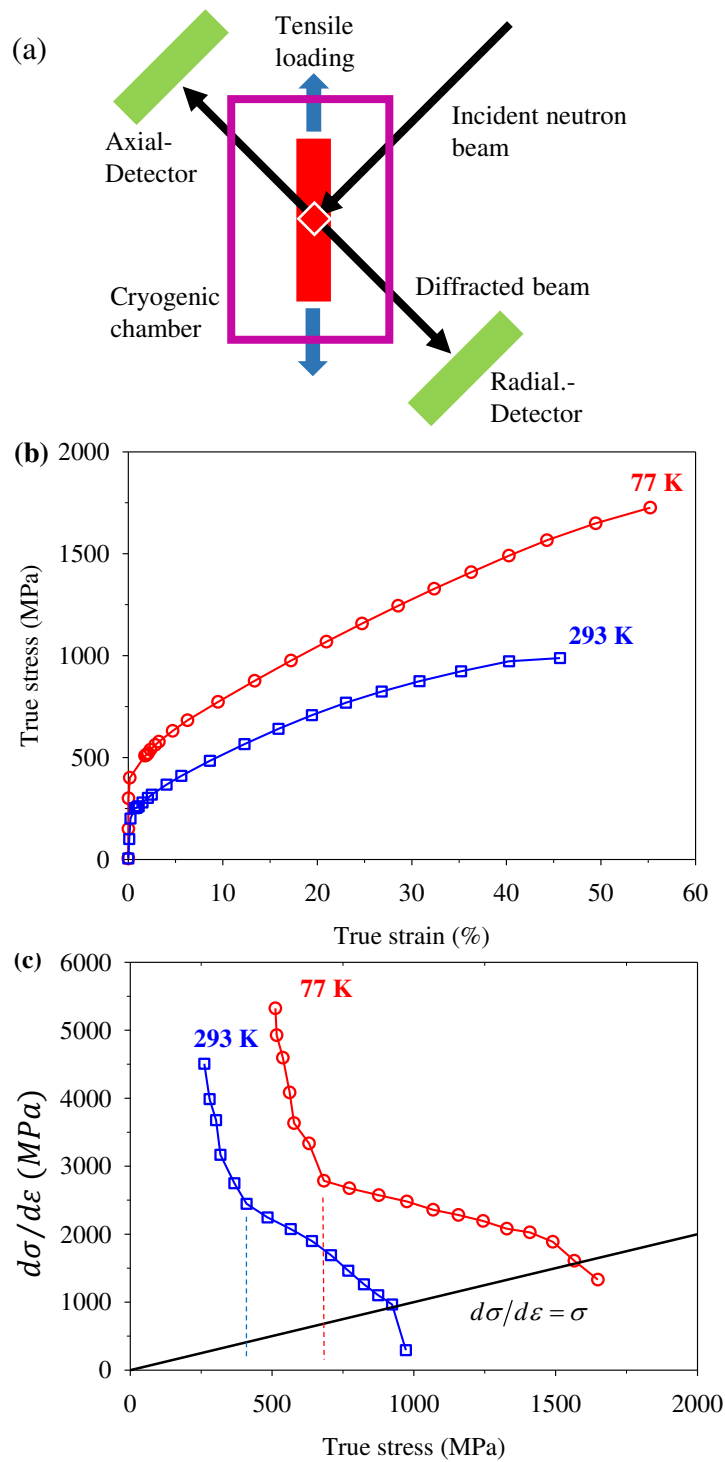


Fig. 1. (a) Schematic of the *in situ* neutron diffraction setup; (b) True stress-strain curves of uniaxial tensile tests at 77 K and 293 K and (c) the corresponding work hardening rate versus true stress.

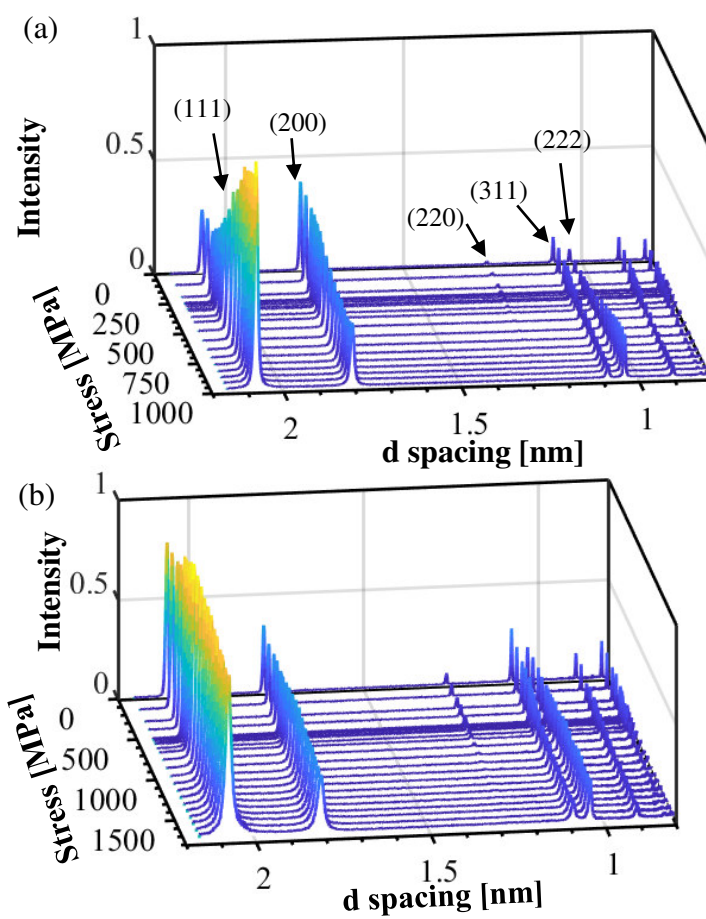


Fig. 2. Diffraction patterns collected at the axial detector as a function of stress at (a) 293 K; and (b) 77 K.

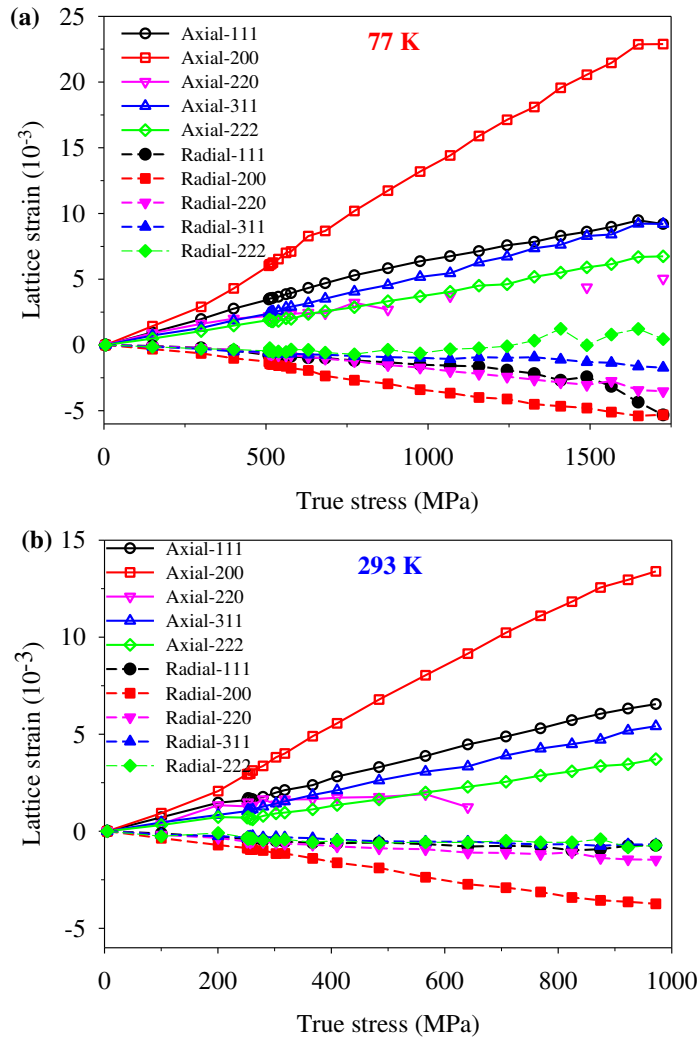


Fig. 3. The evolution of elastic lattice strains along the axial and radial directions in grain families having $\{111\}$, $\{200\}$, $\{220\}$, $\{311\}$ and $\{222\}$ crystallographic planes during tensile loading at (a) 77 K and (b) 293 K;

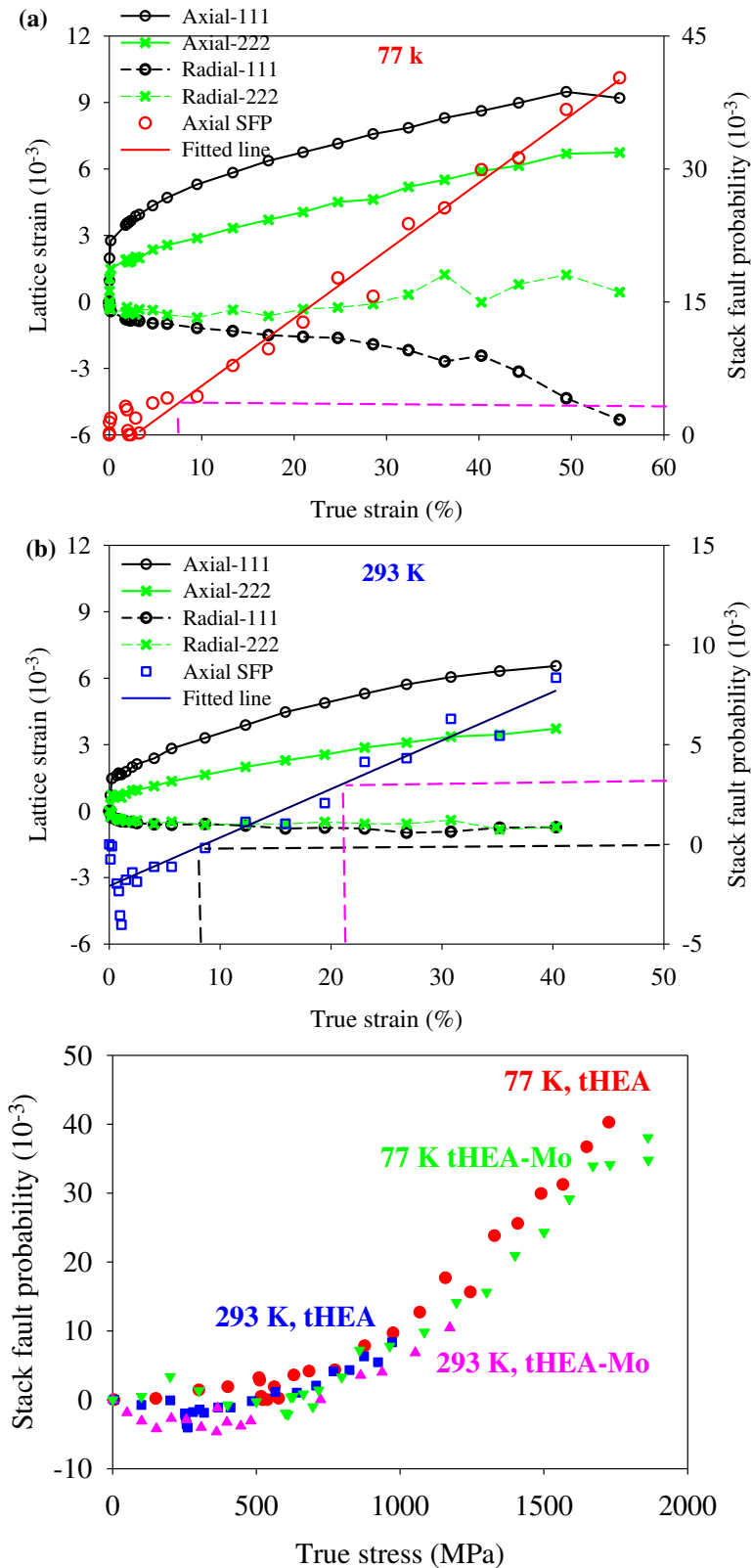


Fig. 4. The (111) first order and (222) second order reflections together with the stacking fault probability as a function of true strain at (a) 77 K and (b) 293 K; (c) stacking fault probability as a function of true stress (tHEA: FeCoCrNi; tHEA-Mo: FeCoCrNiMo_{0.23}).

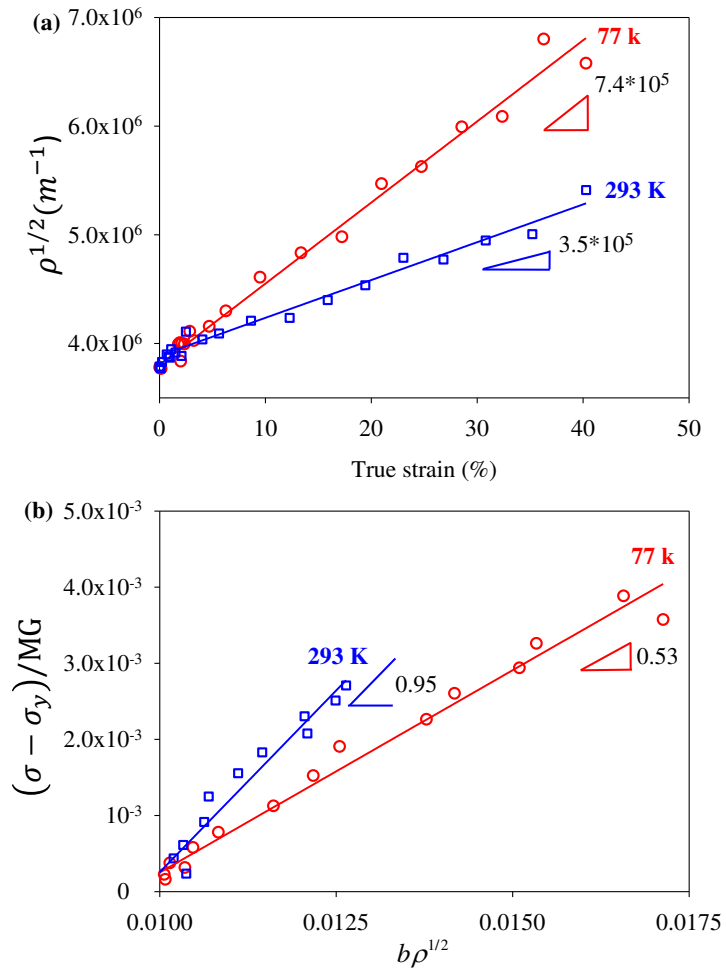


Fig. 5. The evolution of dislocation density versus (a) true strain, and (b) normalised work hardening $(\sigma - \sigma_y)/MG$ versus $b\rho^{1/2}$.

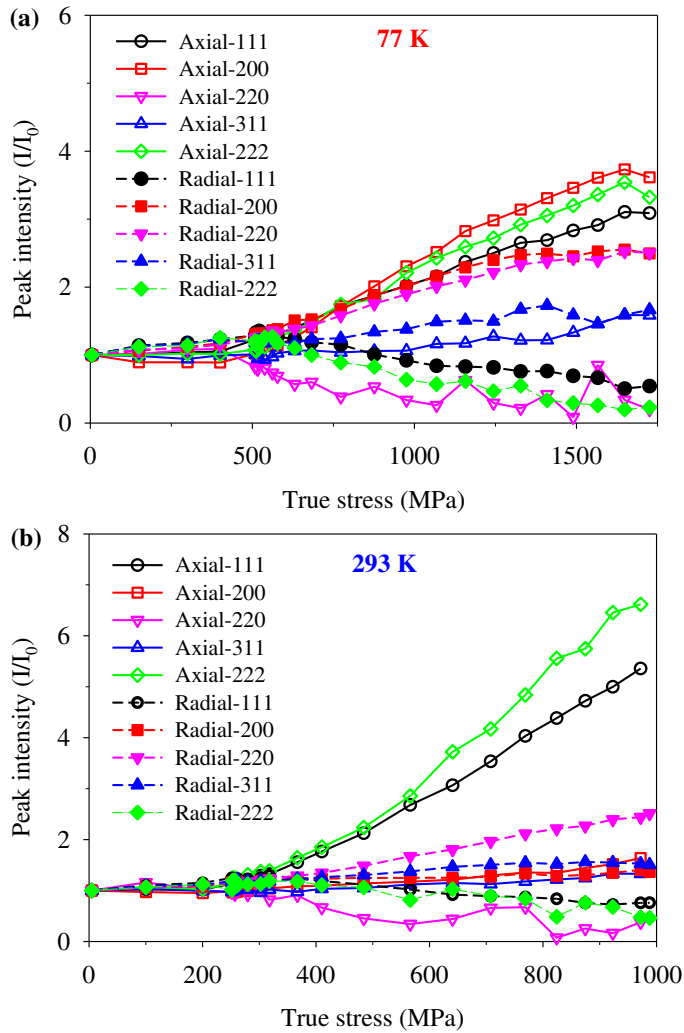


Fig. 6. The evolution of normalized peak intensity along the axial and radial directions in grain families having $\{111\}$, $\{200\}$, $\{220\}$, $\{311\}$ and $\{222\}$ crystallographic planes during tensile loading at (a) 77 K, and (b) 293 K.

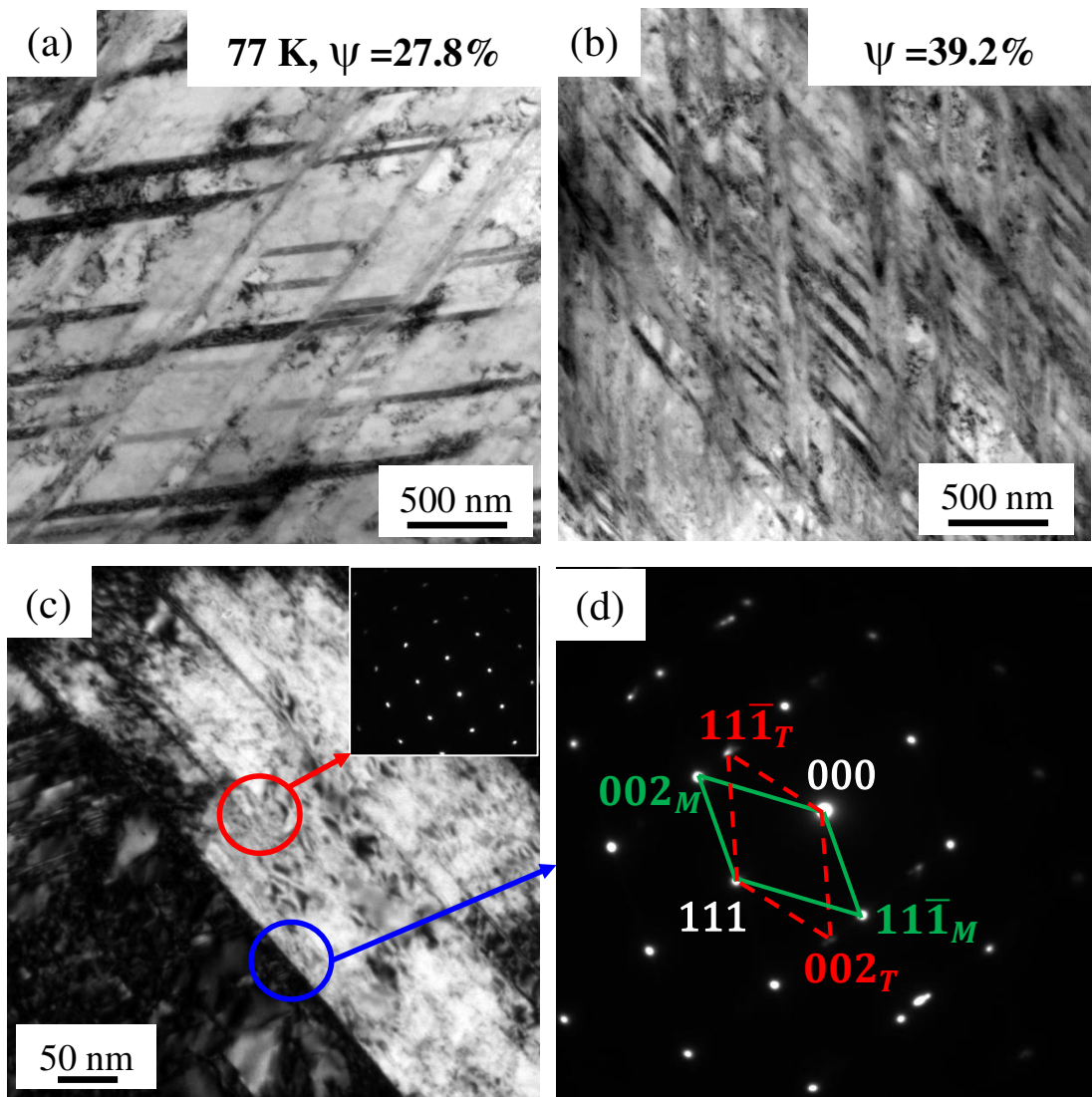


Fig. 7. TEM bright field micrographs of samples with (a) 27.8 % and (b) 39.2% strain at 77 K, which show nano-twins. (c) Higher magnification BF images with an inserted SAD pattern obtained from the matrix and (f) the composite SAD pattern obtained from the blue circled region in Fig. 7c which has contribution from both the matrix and the nano-twin.

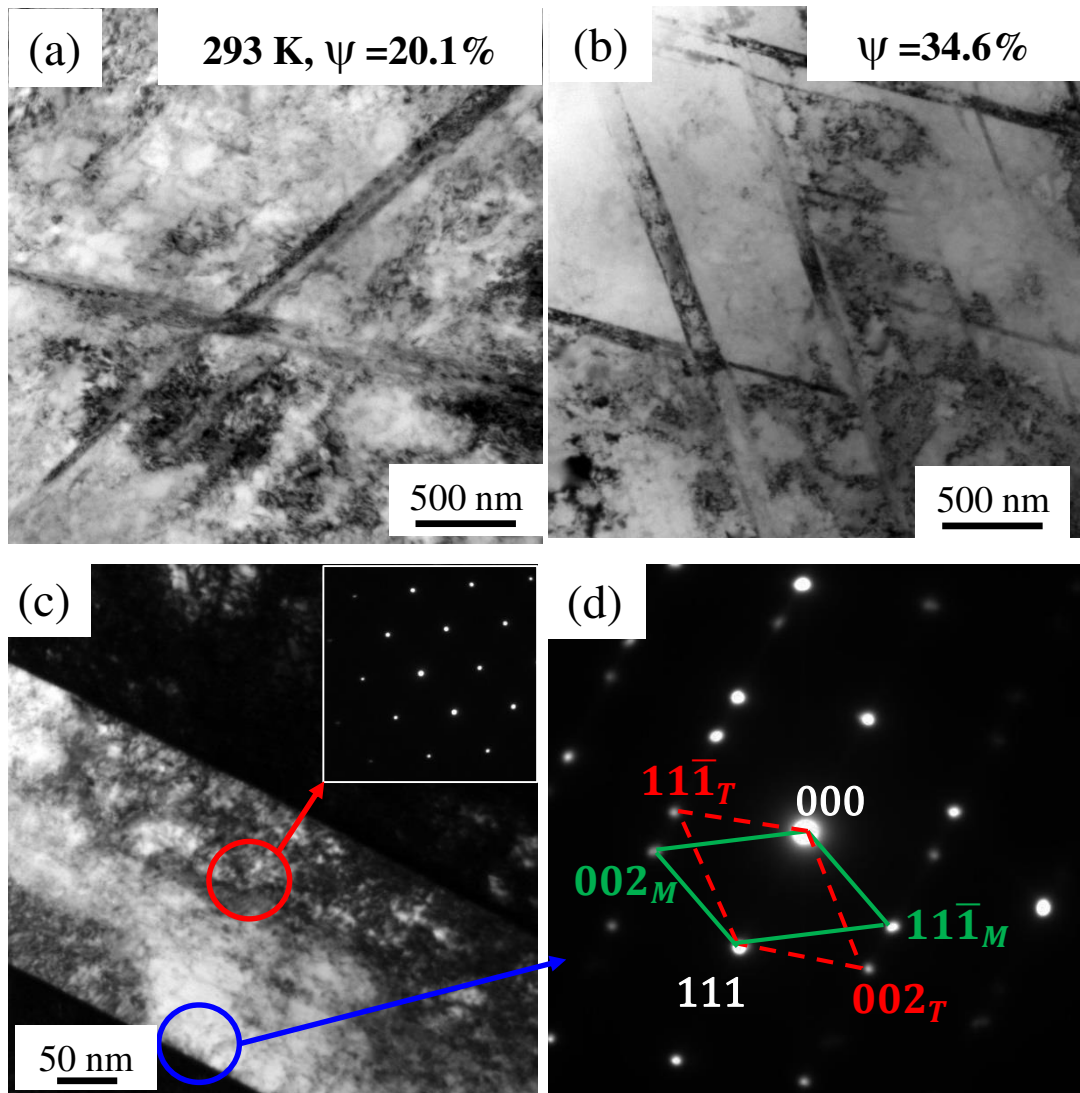


Fig. 8. TEM bright field micrographs of samples with (a) 20.1% and (b) 34.6% strain at 293k, which show nano-twins. (c) Higher magnification BF images with an inserted SAD pattern obtained from the matrix and (f) the composite SAD pattern obtained from the blue circled region in Fig. 8c which has contribution from both the matrix and the nano-twin.