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The effect of carbon on the microstructures, mechanical properties, and deformation mechanisms of thermo-mechanically treated $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ high entropy alloys

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Abstract

The effects of cold rolling followed by annealing on the mechanical properties and dislocation substructure evolution of undoped and 1.1 at. % carbon-doped $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ high entropy alloys (HEAs) have been investigated. X-ray diffraction, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atom probe tomography (APT) were employed to characterize the microstructures. The as-cast HEAs were coarse-grained and single phase f.c.c., whereas the thermo-mechanical treatment caused recrystallization (to fine grain sizes) and precipitation (a B2 phase for the undoped HEA; and a B2 phase, and M_{23}C_6 and M_7C_3 carbides for the C-doped HEA). Carbon, which was found to have segregated to the grain boundaries using APT, retarded recrystallization. The reduction in grain size resulted in a sharp increase in strength, while the precipitation, which produced only a small increase in strength, probably accounted for the small decrease in ductility for both undoped and C-doped HEAs. For both undoped and C-doped HEAs, the smaller grain-sized material initially exhibited higher strain hardening than the coarse-grained material but showed a

much lower strain hardening at large tensile strains. Wavy slip in the undoped HEAs and planar slip in C-doped HEAs were found at the early stages of deformation irrespective of grain size. At higher strains, dislocation cell structures formed in the 19 μm grain-sized undoped HEA, while microbands formed in the 23 μm grain-sized C-doped HEA. In contrast, localized dislocation clusters were found in both HEAs at the finest grain sizes (5 μm). The inhibition of grain subdivision by the grain boundaries and precipitates lead to the transformation from regular dislocation configurations consisting of dislocation-cells and microbands to irregular dislocation configurations consisting of localized dislocation clusters, which further account for the decrease in ductility. Investigation of the formation mechanism and strain hardening of dislocation cells and microbands could benefit future structural material design.

Key words: High entropy alloy; Microstructures; Mechanical properties; Dislocation structures; Strain hardening.

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1. Introduction

High-entropy alloys (HEAs), which are designed based on maximizing the configurational entropy, have attracted tremendous attention due to their promise as structural materials [1–4]. In order to develop successful engineering alloys, various strengthening mechanisms, such as grain boundary and precipitation strengthening, have been introduced to improve the strength of f.c.c.-structured HEAs. For example, a significant increase in yield strength (from ~170 MPa to ~360 MPa) was observed in a f.c.c. CoCrFeMnNi HEA when the grain size was decreased from 155 μm to 4.4 μm [5], and Fu *et al.* [6] have produced the highest yield strength (1795 MPa) for a HEA, thus far, in nanocrystalline f.c.c. $\text{Co}_{25}\text{Ni}_{25}\text{Fe}_{25}\text{Al}_{7.5}\text{Cu}_{17.5}$ with a grain size of 95 nm.

The precipitation of intermetallic particles is also a promising way to strengthen HEAs [7]. For example, a fine dispersion of coherent L_{12} $\text{Ni}_3(\text{Ti}, \text{Al})$ -type nano-precipitates was introduced in a f.c.c. $(\text{FeCoNiCr})_{94}\text{Ti}_2\text{Al}_4$ HEA by thermo-mechanical treatment, producing a high yield strength (645 MPa) and good ductility (39 % elongation) [8]. Liu *et al.* [9] introduced brittle σ and μ intermetallic phases into a f.c.c. (CoCrFeNi) HEA through the addition of Mo, and achieved a high yield strength of 816 MPa.

Recently, using a different strengthening approach, Wang *et al.* [10,11] dissolved up to 1.1 at. % carbon in a f.c.c. FeNiMnAlCr HEA, which not only increased both the yield strength and ultimate tensile strength remarkably, but also produced a sharp increase in tensile elongation, i.e. 1.1 at. % carbon increased the yield strength from 159 MPa to 355 MPa while the tensile elongation increased from 41 % to 50 %. The simultaneous increases of both strength and ductility were ascribed to the formation of

microbands induced by the carbon, which was shown to reside interstitially. Microband-induced plasticity (MBIP), sometimes referred to as slip band refinement-induced plasticity (SRIP), is similar to the transformation-induced plasticity (TRIP) and twinning-induced plasticity (TWIP) effects that have been proposed as a novel strain hardening mechanisms in f.c.c. alloys [12–18]. Welsch *et al.* [17] quantitatively analyzed the dislocation substructure evolution in a high-Mn lightweight steel Fe-30.4Mn-8Al-1.2C (wt. %), by using electron channeling contrast imaging (ECCI) and transmission electron microscopy (TEM) to clarify the strain hardening mechanism. The superior strain hardening observed in that material resulted from the refinement of the dynamic slip band (microband) spacing, which is developed by the passing stress that acts between coplanar slip bands. However, no systematic study has been performed to address the influence of grain size and precipitation on microbands.

The proposed formation mechanism of microbands in f.c.c. alloys has been classified into two types: the double cross-slip model and the dislocation boundary splitting mechanism [19]. Based on the double cross-slip model, microbands are formed due to the onset of unstable glides on slip planes created by intense dislocation cross-slip [20]. The dislocation boundary splitting mechanism suggests that the formation of microbands depends on the grain subdivision [11,12,21]. The grain subdivides into misoriented volumes of material to accommodate the plastic strain, and the delimitation of dislocation substructure boundaries leads to the formation of plate-like microbands. In addition to the above mechanisms, Welsch *et al.* [17] recently proposed that microbands are mature slip bands, in which the fully developed slip bands are filled with dislocations.

Currently, most f.c.c. HEAs with good mechanical properties have a high total content of Co and Ni (around 40 to 50 at. %), e.g., CoCrFeMnNi [5], (FeCoNiCr)₉₄Ti₂Al₄ [8], CoCrFeNiMo_x [9], and Al_{0.3}CoCrFeNi [22]. The substantial use of expensive elements limits the engineering applications of HEAs. To overcome this limitation, several high-performance carbon-doped single-phase, f.c.c. Fe_{40.4}Ni_{11.3}Mn_{34.8}Al_{7.5}Cr₆ HEAs with much lower cost have been designed [10]. In the present study, thermo-mechanical treatments were performed on both undoped and 1.1 at. % C-doped HEAs to further strengthen these alloys. The resulting refinement of the grain size produced a dramatic increase in strength for the thermo-mechanically-treated HEAs. It was found that the thermo-mechanical treatments also led to the formation of precipitates, which are shown to both slightly increase the yield strength and decrease the ductility. TEM studies were used to determine the dislocation substructure evolution for the HEAs, and to illuminate the deformation mechanisms. Thus, the yield strength of the HEAs was evaluated based on microstructure-related models to reveal the effectiveness of the underlying strengthening mechanisms.

2. Experimental

Approximately 65 g ingots of undoped and 1.1 at. % C-doped Fe_{40.4}Ni_{11.3}Mn_{34.8}Al_{7.5}Cr₆ HEAs were prepared by arc-melting. Details of the arc melting procedures are described in [11]. Both HEAs were subsequently cold rolled to a 70 % reduction in thickness, followed by annealing at 1073 K for 8 h, 1073 K for 30 h, and 1173 K for 8 h for the undoped HEA, and at 1073 K for 8 h, 1173 K for 8 h, 1273 K for 1 h, 1273 K for 8 h, and 1373 K for 4 h for the C-doped HEA, respectively. The higher annealing temperatures

were used for the C-doped HEA since recrystallization did not occur upon annealing at the lower temperatures of 1173 K for times up to 8 h.

X-ray diffraction (XRD) analysis was conducted on the HEAs by using a Rigaku D/MAX 2000 diffractometer with Cu-K α radiation. The operating voltage and current were 40 keV and 300 mA, respectively. A step size of 0.02° with a scanning angle (2 θ) from 30° to 100° was used. The total scanning time was approximately 70 minutes. The extrapolation function $\frac{\cos^2 \theta}{2} \left(\frac{1}{\sin \theta} + \frac{1}{\theta} \right)$ [23], where θ is the Bragg angle for each peak, was used to calculate the lattice constant of the C-doped HEA after the thermo-mechanical treatment. The X-ray wavelength is 1.5418 Å.

A FEI XL-30 field emission gun (FEG) scanning electron microscope (SEM) in backscattered electron (BSE) mode was employed to examine the microstructures of the HEAs. Specimens for SEM examination were ground using silicon carbide paper from 400 grit to 1200 grit, and then polished using a 0.3 μ m alumina suspension, before finishing in a Vibromet polishing machine using a 60 nm colloidal silica suspension. The volume fractions and sizes of precipitates in HEAs were evaluated from BSE images using Image J. The projected areas for at least 300 precipitates were measured for each heat treatment. The particle size reported is an equivalent circle diameter for a spherical particle calculated from the measured area. The grain size was determined using the linear intercept method with at least 30 intercepts.

A FEI Tecnai F20 FEG transmission electron microscope (TEM) equipped with energy dispersive X-ray spectrometry (EDS) operated at 200 kV was used to examine the microstructures and the dislocation substructure evolution of the HEAs. For TEM examination, 3 mm diameter disks with a thickness of 150 μ m were electro-

polished using a Struers Tenupol 5 in an electrolyte of 25 % nitric acid in methanol at a temperature of ~ 250 K with an applied voltage of ~ 11 V and current of ~ 80 mA.

The atomic distribution in the grain boundaries of the recrystallized 1.1 at. % C-doped HEA was characterized using atom probe tomography (APT). A dual FIB-SEM system (FEI Nova 200) was employed to prepare needle-shaped APT tips from grain boundary regions following procedures described elsewhere [24,25]. A site selective FIB liftout was used to target the grain boundary (GB). The FIB liftout was mounted to a Si microtip array, and then was thinned to a thickness of ~ 250 nm, in which the grain boundary could be clearly identified in the secondary electron image. The APT needle was fabricated such that the apex was positioned ~ 200 nm above the grain boundary. APT measurements were performed using a local electrode atom probe (CAMECA LEAP 4000X HR) with a 50 pJ laser energy, a repetition rate of 200 kHz, and a specimen temperature of 50 K [26]. IVAS 3.6.12 software (CAMECA Instruments) was used to reconstruct and analyze the resulting datasets.

Dog-bone shaped specimens with a gauge length of ~ 10 mm, width of ~ 2.6 mm, and thickness of ~ 1.2 mm were used for tensile tests on an Instron 5969 testing machine. Three specimens with mirror surfaces were tested for each alloy at an initial strain rate of $5 \times 10^{-4} \text{ s}^{-1}$ at room temperature. The true stress (σ_t) and true strain (ϵ_t) were calculated from the engineering stress (σ_e) and strain (ϵ_e) based on the equations $\sigma_t = (1 + \epsilon_e)\sigma_e$ and $\epsilon_t = \ln(1 + \epsilon_e)$. The elongation was determined by measuring the gauge length of specimens before and after tests using an optical microscope.

3. Results

Figure 1 shows XRD patterns from the undoped and 1.1 at. % C-doped HEAs after cold rolling and annealing for the times and temperatures shown in the legend of the figure. Previously, we have shown that both undoped and C-doped HEAs are single a f.c.c. phase in the as-cast state [11]. After cold rolling and annealing, small peaks associated with a b.c.c. structure appear in the f.c.c. matrix of the undoped HEA (see Fig. 1a). For the C-doped HEA, a b.c.c.-structured phase, $M_{23}C_6$ and M_7C_3 carbides all appear in the f.c.c. matrix after cold rolling and annealing at temperatures lower than 1273 K, whereas only $M_{23}C_6$ and M_7C_3 carbide are present after annealing at 1273 K, see Fig. 1b. Further increasing the annealing temperature to 1373 K leads to the formation of a single M_7C_3 carbide in the C-doped HEA.

Note that annealing the C-doped HEA at 1173 K for times up to 8 h did not produce the fully recrystallized material, indicating the retardation of recrystallization by the interstitial carbon. The rest of this paper discusses only material that was fully recrystallized: the microstructures of the HEAs in the fully recrystallization state are shown in Figure 2. Both the undoped and 1.1 at. % C-doped HEAs recrystallized to similar fine grain sizes with the presence of annealing twins, as illustrated in Fig. 2. Table 1 summarizes the grain size, volume fraction and size of the precipitates in both the undoped and C-doped HEAs after various thermo-mechanical treatments.

B.c.c.-structured precipitates exhibiting a light contrast were formed in the undoped HEA after annealing for 8 h at 1073 K (see Fig. 2a). Larger precipitates were present after annealing for longer times or at a higher temperature (compare Fig. 2 a, c and e), e.g., the average size of the precipitates increased from 141 nm after the 8 h anneal to 441 nm after the 30 h anneal at 1073 K. The volume fraction of precipitates

was significantly lower after the 1173 K anneal (compare Fig. 2a and 2e), i.e., after 8 h anneals at 1073K to 1173K the volume fractions of the precipitates were 13.0 % to 4.3 %, respectively.

In contrast, for the C-doped HEA, both dark, irregularly-shaped and light, roughly circular precipitates appeared upon annealing at 1273 K (see the inserted image in Fig. 2d), while only the dark, irregular precipitates occurred after annealing at 1373 K (see Fig. 2f). Combined with the XRD patterns in Fig. 1b, it can be concluded that dark, irregularly-shaped carbides are M_7C_3 and that the light, roughly circular carbides are $M_{23}C_6$. Annealing at a lower temperature and shorter time resulted in smaller grain sizes and finer precipitates for both HEAs, see Table 1.

Fig. 3a shows a bright field (BF) TEM image of a precipitate in the undoped HEA after cold rolling and annealing at 1073 K for 8 h, while the convergent beam electron diffraction (CBED) pattern in Fig. 3b demonstrates that the precipitate has a B2 (ordered b.c.c.) structure. The X-ray spectra in Fig. 3 c and d indicates that the B2 phase is enriched in Ni and Al, while the f.c.c. matrix phase is enriched in Fe, Mn and Cr, which is consistent with the phase equilibria observed in other f.c.c./B2 two-phase FeNiMnAl alloys [27,28].

A BF TEM image of carbides in the 1.1 at. % C-doped HEA cold rolled and annealed at 1273 K for 1 h is shown in Fig. 4a. Selected area diffraction (SAD) patterns in Fig. 4 b and c confirm that the irregularly-shaped carbide is M_7C_3 while the roughly circular carbide is $M_{23}C_6$. Similarly, Stepanov *et al.* [29] examined a C-doped CoCrFeNiMn HEA in which M_7C_3 and/or $M_{23}C_6$ carbides were present depending on the annealing conditions. The X-ray spectra in Fig. 4 e and f indicates that the major metallic

elements in both carbides are Cr, Fe and Mn. The element with maximum content in the $M_{23}C_6$ is Cr, while for the M_7C_3 , Mn is the most prominent element, see Table 2.

APT was performed on the 1.1 at. % C-doped HEA after cold-rolling and annealing at 1273 K for 1 h in order to reveal the atomic distributions along the grain boundary. The elemental maps and the concentration profile in Fig. 5 show that a clear compositional variation between the grain boundary and matrix occurs with segregation of C and Mn to the grain boundary. Similar C and Mn segregation to the grain boundaries has been reported in an austenitic steel [30,31].

Fig. 6 presents typical engineering stress-strain curves for the undoped and 1.1 at. % C-doped HEAs with different grain sizes produced by different anneals following cold rolling. The variations of the yield strength, ultimate tensile strength (UTS) and elongation to fracture as a function of grain size are shown in Fig. 7. An increase in yield strength and UTS for the HEAs, along with a decrease in elongation to fracture, was observed with a decrease of grain size. For HEAs with similar grain sizes, the C-doped HEA exhibited both higher yield strength and UTS than those for the undoped HEA due to both the interstitial carbon strengthening and the higher strain hardening rate from the interstitial carbon.

Fig. 8 shows plots of the true stress-strain curves and strain hardening rate as a function of true strain for both the undoped (Fig. 8 a and c) and 1.1 at. % C-doped (Fig. 8 b and d) HEAs with different grain sizes. The strain hardening rate of the C-doped HEA is higher than that of undoped HEAs at a similar grain size, which is consistent with the observations of a prior study [11]. For the early stages of deformation ($< 10\%$ strain), the strain hardening rate increases with decreasing grain size for both undoped and C-doped

HEAs, as indicated by the dark arrow in Fig. 8 c and d. As the deformation proceeds, however, the strain hardening rate of HEA with fine grain sizes, i.e., 5 μm and 7 μm for undoped, and 5 μm and 8 μm C-doped HEAs, drops sharply, and, ultimately, the strain hardening rate of the fine grain-sized HEAs is lower than that of the same HEAs with larger grain sizes at high strains (see the yellow arrow in Fig. 8 c and d).

Fig. 9 displays the major microstructural features of the 19 μm grain-sized (Fig. 9 a1, a2 and a3) and 5 μm grain-sized (Fig. 9 b1, b2 and b3) undoped HEAs at low, medium and high strains. At a low strain (1 %), dislocation cross-slip was found in both 19 μm and 5 μm grain-sized HEAs, i.e. the same behavior that was previously observed in the 122 μm grain-sized HEA [11]. As the strain increased, cross-slip occurred and tangled dislocations were seen in the 19 μm grain-sized HEA (see Fig. 9a2), whereas the dislocation cross-slip was hindered by B2-structured precipitates in the 5 μm grain-sized HEA and dislocations accumulated around the precipitates (see Fig. 9b2). Fig. 9a3 shows that a dislocation cell structure had formed in the 19 μm grain-sized HEA at high strain, suggesting a similar dislocation substructure evolution in undoped HEAs with the grain size of 19 μm and 123 μm [11]. In contrast, in the 5 μm grain-sized HEA, high densities of dislocations were observed around the precipitates but a dislocation cell structure did not form, see Fig. 9b3.

The evolution of the deformation structure from low to high strains for the 23 μm grain-sized and 5 μm grain-sized C-doped HEAs are illustrated in Fig, 10. As demonstrated in Fig.10 a1 and b1, dislocations in linear arrays are observed in both 23 μm grain-sized and 5 μm grain-sized HEAs, indicating a planar slip mode for the C-doped material at the early stages of deformation. A stacking fault is also seen in 23 μm

grain-sized at a low strain (see Fig. 10a1), which is a common feature for f.c.c. alloys with a relatively low stacking fault energy [32,33]. As deformation proceeds in the 23 μm grain-sized HEA, a Taylor lattice with parallel sets of dislocations along the glide plane is formed (Fig. 9a2) and microbands are formed at high strain (Fig. 9a3), the same behavior as that observed in the non-cell forming microstructure present in the C-doped HEA with a 118 μm grain size [11]. However, the planar slip was impeded by both the carbides and the grain boundaries in the 5 μm grain-sized HEA, and dislocations clustered in some local areas, see the white arrow in Fig. 10b2. At high strain, only irregular dislocation configurations, rather than the Taylor lattice and microband structure, can be observed in the 5 μm grain-sized C-doped HEA, i.e., randomly distributed dislocation clusters in localized areas were present, as shown in Fig. 10b3.

4. Discussion

4.1 Grain boundary segregation and recrystallization

As listed in Table 1, the grain size of the undoped HEA is 5 μm after cold rolling and annealing at 1073 K, while the 1.1 at. % C-doped HEA exhibits a similar grain size of 5 μm after annealing at 1273 K. The delay of recrystallization in the C-doped HEA is not surprising since solute drag in solid solutions during recrystallization has been widely reported [34,35]. Desrayaud *et al.* [35] found that the grain boundary mobility in α -iron alloys decreased due to the segregation of carbon atoms. The migration rate of a grain boundary is generally assumed to be proportional to the driving force [36]. The APT results in Fig. 5 show that carbon atoms strongly segregated to the grain boundaries, which may have occurred by sweeping up the interstitial carbon atoms from the lattice

into the grain boundary during recrystallization [37]. The segregation of carbon atoms in grain boundaries exerts a strong drag force, leading to retardation of recrystallization and grain growth in the C-doped HEA.

4.2 Yield strength and strengthening mechanisms

The thermo-mechanical treatments produced a substantial increase in strength for both undoped and 1.1 at. % C-doped HEAs with little compromise in the ductility. As shown in Fig. 11, the mechanical properties of 1.1 at. % C-doped HEAs are superior to those of most advanced steels. In order to understand the strengthening mechanisms in the HEAs, the yield strength can be evaluated by employing microstructure-related models. The yield strength (σ_y) for the HEAs arises from a number of different contributions, i.e.

$$\sigma_y = \sigma_{fr} + \sigma_{ss} + \sigma_{dis} + \sigma_{gb} + \sigma_{ppt} \quad (1)$$

where σ_{fr} is the lattice friction stress, σ_{ss} , σ_{dis} , σ_{gb} and σ_{ppt} are the strengthening contributions from solid solutions, dislocations, grain boundaries, and precipitates, respectively. The constituent atoms are randomly distributed in the f.c.c. lattice, and in HEAs which are solvent and which are solute atoms cannot be defined. Thus, the substitutional solid solution strengthening term is commonly subsumed into the lattice friction stress term (σ_{fr}) in multi-component alloys [38,39]. The carbon solute results in a strong interstitial strengthening in HEAs, which can be folded into the lattice friction stress as well. TEM images (Fig. 3 and Fig. 4) show that the recrystallized HEAs are well annealed and very few dislocations can be seen, suggesting that the strengthening contribution from dislocations (σ_{dis}) is negligible. Therefore, the expression for yield strength in the present study can be simplified to:

$$\sigma_y = \sigma_{fr} + \sigma_{gb} + \sigma_{ppt} \quad (2)$$

Because of the large precipitate size, a model for particulate-reinforced metal matrix composite is employed to calculate the strengthening effect. Equation (3) incorporates a modified shear lag model and the Orowan strengthening effect [40,41]:

$$\sigma_y = \sigma'_y(1+0.5f)(1+\frac{\Delta\sigma_{Orowan}}{\sigma'_y}), \quad (3)$$

where σ'_y is the reduced yield strength, arising from lattice friction and grain boundary strengthening of the f.c.c. matrix, f is the volume fraction of precipitates, and $\Delta\sigma_{Orowan}$ is the strengthening contribution from the Orowan mechanism. The Orowan strengthening is due to the resistance of passing dislocations from the very hard precipitates (the B2 phase or carbides), which can be calculated by the Ashby-Orowan equation [42,43]:

$$\Delta\sigma_{Orowan}=(0.538 \cdot Gb f^{0.5}/D)\ln(D/2b) \quad (4)$$

where G is the shear modulus, b is the Burgers vector, f is the volume fraction of precipitates, and D is the real spatial diameter of precipitates. Values of the shear modulus for the undoped and 1.1 at. % C-doped HEA are 51 GPa and 53 GPa, respectively [11]. The magnitude of the Burgers vector is given by $b=a_0/\sqrt{2}=0.26$ nm, where a_0 is the lattice constant of the HEAs [11]. The real spatial diameter of the precipitates (D) can be calculated from the average diameter of the precipitates (D_0) measured from the intersection plane based on the equation of $D=(3/2)^{1/2}D_0$. Table 1 presents the volume fraction and average diameter of precipitates in all HEAs. The calculated results for a reduced yield strength (σ'_y) are shown in Table 3. The precipitate strengthening part (σ_{ppt}) is obtained by subtracting the reduced yield strength (σ'_y) from the yield stress (σ_y), as listed in Table 3. As expected, contributions from precipitation

strengthening to the yield strength are relatively small, as a result of the large size and low volume fraction of precipitates.

Thus, the classical Hall-Petch relationship can be applied to describe the reduced yield strength [44,45]:

$$\sigma'_y = \sigma_{fr} + k \cdot d^{-1/2} \quad (5)$$

where d is the grain size and k is the Hall-Petch slope. However, due to the formation of carbides, the carbon content in the f.c.c. matrix is decreased in the thermo-mechanically treated C-doped HEAs, which leads to a significant reduction in the lattice friction stress. Our earlier work showed that a linear relationship exists between the carbon content and the change in lattice parameter, and between carbon content and the yield strength [11]. Thus, the decrease of yield strength in the C-doped HEAs, which results from the reduction of the lattice friction stress, can be determined once the lattice constant is known. The lattice constant for the f.c.c. matrix was calculated based on XRD patterns in Fig. 1b. These gave 3.6575 Å for the 5 µm grain-sized HEA, 3.6584 Å for the 8 µm grain-sized HEA, and 3.6625 Å for the 23 µm grain-sized HEA, which correspond to carbon contents of 0.80 at. %, 0.83 at. %, and 0.98 at. % in the f.c.c. matrix, respectively. Thus, based on these values, the reduction in interstitial carbon can be estimated and the resulting reduction in lattice friction ($\Delta\sigma_{fr}$) of the HEAs under different thermo-mechanical treatments can be calculated, as listed in Table 3.

After compensating for the decrease in the lattice friction stress, the reduced yield strength was plotted versus $d^{-1/2}$ with correlation coefficient R^2 of 0.98 for both undoped and C-doped HEAs (see Fig. 12), which suggests an almost perfect fit to the of Hall-Petch relationship. The fitting in Fig. 12 provides similar values of the Hall-Petch

slope of $534 \text{ MPa} \cdot \mu\text{m}^{-0.5}$ for the undoped HEA and $574 \text{ MPa} \cdot \mu\text{m}^{-0.5}$ for the C-doped HEA: these values are also similar to the value for the CoFeNiMnCr f.c.c. structure HEA of $494 \text{ MPa} \cdot \mu\text{m}^{-0.5}$ [5]. The lattice friction stress of the C-doped HEA (313 MPa) is much higher than that of the undoped HEA (102 MPa), which is mainly due to the interstitial solid solution strengthening from the carbon atoms.

4.3 Dislocation substructures evolution

At the early stage of tensile deformation, wavy slip is exhibited in the undoped HEA and planar slip is seen in the C-doped HEA, irrespective of grain size, as shown in Fig. 9 (a1 and b1) and Fig. 10 (a1 and b1). Planar slip is favored in a f.c.c. material with a low stacking fault energy (SFE) [46], a high lattice friction stress [47,48], and the presence of short range order [49,50]. Our previous study revealed that the addition of interstitial carbon lowers the SFE and increases the lattice friction stress in HEAs, both of which can inhibit the cross slip of dislocations and, thus, lead to planar slip [11].

At large strains, typical cell-forming structures were found in the $122 \mu\text{m}$ grain-sized [11] and $19 \mu\text{m}$ grain-sized (see Fig. 9a3) undoped HEA, while localized dislocation clusters were seen in the $5 \mu\text{m}$ grain-sized undoped HEA (see Fig. 9b3); indicating that the dislocation substructure evolution is strongly influenced by the grain size and the precipitates. The occurrence of cell-forming structure relies on the subdivision of grains, i.e., an individual grain breaks into small volume elements with different orientations [51]. Adjacent volume elements, known as cell blocks, deform collectively to fulfill simultaneous operations of at least five independent slip systems in Taylor's model [52–55]. As strain increases, the subdivision of grains occurs

continuously by forming new cell blocks in initial cell blocks [51]. Yet a lower degree of grain subdivision was observed in the alloy with a smaller grain size [56]. In the current 5 μm grain-sized undoped HEA, the grain subdivision is largely inhibited by the very fine distribution of grain boundaries and the B2 precipitates, as seen in Fig. 9 b2 and b3. Without the grain subdivision, the cell-forming structure is unable to form. Instead, irregular dislocation configurations are exhibited.

For the C-doped HEA, microbands are formed in the 23 μm grain-sized HEA, which is similar to the dislocation substructure in the C-doped HEA with a coarse grain size of 118 μm [11]. In the 5 μm grain-sized C-doped HEA, however, randomly-distributed dislocation clusters replaced the microbands, see Fig. 10b3, suggesting that the sizes of grains and the precipitates are also crucial for the formation of microbands. A microband is plate-like structure with a high dislocation density, which is aligned along $\{111\}$ planes in a f.c.c. metal [19,57,58]. In the C-doped HEA, the microband is proposed to form via a dislocation boundary splitting mechanism [11], as observed in a Ni-Co alloy [59], an Al-Mg alloy [21] and in an Austenitic high-Mn steel [12]. The grain subdivides into misorientated domains in order to accommodate the macroscopic plastic strain with fewer slip systems than the requirements of Taylor's model. Double-wall dislocation structures were gradually formed in domain boundaries via a multi-slip process to shield the stress, which leads to the occurrence of microbands.

Welsch *et al.* [17] recently proposed a different mechanism for the formation of microbands in a high-Mn lightweight steel during tensile deformation. At the onset of plastic deformation, planar slip is promoted by glide plane softening due to the presence of either short-range order or long-range order. The newly-activated dislocations

propagate within the glide plane, leading to the formation of the initial slip bands. Slip bands go through the grain and eventually reach grain boundaries. The occurrence of piled-up dislocations increased the back stresses, which further produces more dislocations emitted inside the slip bands. As a result, a fully developed slip band referred to as a microband is formed. New sources of dislocations are then produced by the mutual shearing of slip bands [60], dislocation cross slip [61], or the activation of existing dislocations with smaller segment length [62] so as to accommodate further plastic strain. This results in the formation of even more microbands.

According to Welsch *et al.*'s model [17], microbands develop from slip bands filled with dislocations. The pile-up of dislocations at grain boundaries or carbides should lead to the occurrence of microbands at even earlier stages of deformation. As seen in Cu-Al₂O₃ [63], microbands form at lower strains than those in the pure Cu due to the greater dislocation density in the material with particles. However, in this study, microbands disappeared when the grain size decreased to 5 μm and very fine precipitates were present, in which a random distribution of dislocation clusters was occurred instead, see Fig 10b3. Therefore, grain subdivision plays a key role for the formation of microbands and the dislocation boundary splitting model appears to be a more plausible mechanism in the present case. In the 5 μm grain-sized C-doped HEA, grain subdivision is inhibited by the very fine distribution of precipitates and grain boundaries as the strain increases. Without the grain subdivision to accommodate the plastic strain, dislocation clusters were formed in localized areas (see Fig. 10b2) and, eventually, these evolved to irregular dislocation configurations (see Fig. 10b3).

4.4 Strain hardening behavior

The strain hardening behavior and the corresponding dislocation substructure evolution during tensile deformation for both undoped and C-doped HEAs are shown schematically in Fig. 13. The strain hardening behavior of HEAs is closely related to the dislocation substructure evolution during deformation. Fig. 8 c and d show how the strain hardening rate increases with decreasing grain size for both the undoped and C-doped HEAs at the initial stages of deformation. Precipitates and grain boundaries are able to impede the motion of dislocations during slip, resulting in the pile-up of dislocations at both grain boundaries and precipitates, as illustrated in Fig. 9 and Fig. 10. More dislocation pile-ups occur in a HEA with a smaller grain size and more precipitates, which thus, produces a greater strain hardening during deformation. Therefore, the strain hardening rate curves shift upwards monotonically with a reduction of grain size. In this dislocation slip regime, for example at the true strain of 0.1, the strain hardening rate of our HEAs varies in the range of $G/18$ to $G/42$, which are slightly higher than those of the $4.4\text{ }\mu\text{m}$ grain-sized f.c.c. CrMnCoFeNi HEA ($G/43$) [5], but substantially higher than those of typical f.c.c. metals ($G/200$) [64] in the similar deformation regime.

The formation of regular dislocation configurations at high strains (i.e., dislocations cell structures for the undoped HEA and microbands for the C-doped HEA) is able to accommodate the plastic strain and stabilize the deformation, which further enhances the ductility of the HEAs. The arrangement of dislocation cell structures minimizes the elastic energy per unit length of dislocation line based on the mesh-length theory of strain hardening [65], and the cell size decreases during deformation for further strain accommodation [66]. The refinement of the microband spacing occurs as strain

continuously proceeds, which increases the passing stress acting on microbands and thus, promotes strain hardening [17]. However, without the formation of such regular dislocation configurations of dislocation cells and microbands, the densities of dislocations increase sharply in localized areas as strain increases, which leads to the onset of dynamic recovery [67]. Thus, the strain hardening rate drops very rapidly and the unstable deformation occurs at a smaller strain, as shown in Fig. 8d.

5. Summary and conclusions

The microstructures and mechanical properties of undoped and 1.1 at. % C-doped HEAs after thermo-mechanical treatments have been studied. TEM images of the dislocation substructure evolution after tensile straining revealed the effects of varying grain size and on the precipitates present on the deformation mechanisms. The main conclusions are:

1. The grain size is refined via thermo-mechanical treatments for both undoped and C-doped HEAs. Segregation of carbon to the grain boundaries delays the recrystallization of the C-doped HEA.
2. Thermo-mechanical treatments led to the presence of B2 precipitates in the undoped HEA, and the formation of B2 precipitates, M_7C_3 and $M_{23}C_6$ carbides in the C-doped HEA depending on the annealing conditions.
3. The refinement of grain size and the occurrence of precipitates after thermo-mechanical treatments result in a remarkable increase in strength in both undoped and C-doped HEAs with an acceptable reduction in ductility.
4. At an early stage of deformation, wavy slip is exhibited in the undoped HEA and planar slip is observed in the C-doped HEA, irrespective of the grain size and the

presence of precipitates. At high strains, the dislocation substructures transform from a regular configuration, i.e., dislocations cells for the 19 μm grain-sized undoped HEA and microbands for the 23 μm grain-sized C-doped HEA, to irregular configurations, i.e., localized dislocation clusters for both the 5 μm grain-sized undoped and C-doped HEAs, since grain subdivision is inhibited by the very fine distribution of grain boundaries and precipitates.

5. At a low strain, the strain-hardening rate increases with decreasing grain size for both undoped and C-doped HEAs due to stronger impediment to dislocation motion from the finer distribution of grain boundaries and precipitates. The transformation from regular to irregular dislocation configurations at high strains results in a significant decrease in the strain hardening rate, which leads to the decrease in ductility.

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Table 1 Grain size, precipitate size and volume fraction of the undoped and 1.1 at. % C-doped HEAs after 70% cold rolling and annealing at the temperatures shown. The $M_{23}C_6$ and M_7C_3 carbides are counted together since they have the same strengthening effects.

Alloy	Annealing condition	Grain size (μm)	Precipitate diameter (nm)	Precipitate fraction (%)
Undoped	1073 K, 8h	5	141	13.0
	1073 K, 30h	7	441	14.3
	1173 K, 8h	19	884	4.3
1.1 at. % C-doped	1273 K, 1h	5	600	13.4
	1273 K, 30h	8	929	11.3
	1373 K, 4h	23	1928	2.9

Table 2 Chemical compositions of phases determined by EDS (in at. %) from TEM specimens in undoped and 1.1 at. C-doped HEAs after 70% cold rolling and annealing at 1073 K for the undoped HEA and 1273 K for the C-doped HEA. The error bars indicate the average of five measurements

Alloy Phase	Undoped		1.1 at. % C-doped		
	f.c.c.	B2	f.c.c.	M ₂₃ C ₆	M ₇ C ₃
Fe	47.0 ± 1.2	4.5 ± 0.2	42.5 ± 0.2	23.0 ± 0.8	14.3 ± 0.7
Ni	7.3 ± 1.0	36.4 ± 1.1	11.2 ± 0.2	1.6 ± 0.1	0.8 ± 0.1
Mn	34.1 ± 0.7	16.1 ± 0.6	34.5 ± 0.5	31.1 ± 0.6	25.7 ± 0.9
Al	5.7 ± 0.6	42.3 ± 0.5	8.5 ± 0.4	1.2 ± 0.2	0.7 ± 0.3
Cr	5.8 ± 0.1	0.7 ± 0.1	3.3 ± 0.2	24.8 ± 0.6	33.4 ± 0.9
C	--	--	--	18.4 ± 1.5	25.2 ± 2.2

Table 3 The yield strength (σ_y), precipitation strength (σ_{ppt}), reduced yield strength (σ'_y), reduction in lattice friction stress ($\Delta\sigma_{fr}$), lattice friction stress (σ_{fr}), and Hall-Petch slope (k) for undoped and 1.1 at. % C-doped HEAs with various grain size (d).

Alloy	d (μm)	σ_y (MPa)	σ_{ppt} (MPa)	σ'_y (MPa)	$\Delta\sigma_{fr}$ (MPa)	σ_{fr} (MPa)	k (MPa $\cdot \mu\text{m}^{-0.5}$)
Undoped	5 μm	416	76	340	--		
	7 μm	361	47	314	--	102	534
	19 μm	219	12	207	--		
1.1 at. % C-doped	5 μm	557	54	503	67		
	8 μm	488	38	450	61	313	574
	23 μm	405	9	396	33		

Figure Captions

Figure 1 X-ray diffraction patterns of (a) the undoped and (b) the 1.1 at. % C-doped HEAs after cold-rolling and annealing for the times and temperatures shown.

Figure 2 BSE images of the undoped HEA after cold-rolling and annealing at (a) 1073 K for 8 h, (c) 1073 K for 30 h, and (e) 1173 K for 8 h; and 1.1 at. % C-doped HEA after cold-rolling and annealing at (b) 1273 K for 1 h, (d) 1273 K for 8 h, and (f) 1373 K for 4 h. The inserted image with higher magnification in (d) shows the shape and contrast of M_7C_3 and $M_{23}C_6$ carbides.

Figure 3 (a) BF TEM images of the undoped HEA after cold-rolling and annealing at 1073 K for 8 h, and (b) The (010) superlattice diffraction spot in the CBED pattern shows that the particle has a B2 structure. (c) and (d) X-ray spectra from the f.c.c. matrix and B2 precipitate, respectively.

Figure 4 (a) BF TEM image of the C-doped HEA after cold-rolling and annealing at 1273 K for 1 h; (b) and (c) SAD patterns from the $M_{23}C_6$ and M_7C_3 carbides. (d), (e) and (f) X-ray spectra from the f.c.c. matrix, $M_{23}C_6$ and M_7C_3 carbides, respectively. An annealing twin is also visible in (a).

Figure 5. APT atom maps and a 1D concentration profile along the grain boundary (GB) for the 1.1 at. % C-doped HEA after cold-rolling and annealing at 1273 K for 1h.

Figure 6 Typical engineering stress-strain curves of (a) the undoped HEA and (b) the 1.1 at. % C-doped HEA with different grain sizes.

Figure 7 The variation of (a) yield strength, (b) UTS, and (c) elongation to fracture for the undoped HEA and the 1.1 at. % C-doped HEA with different grain sizes.

Figure 8 True stress-true strain curves and strain-hardening rate curves for (a, c) the undoped and (b, d) the 1.1 at. % C-doped HEA with different grain sizes. With the decrease of grain sizes, the strain hardening rate increases at the early stage of deformation as indicated by the dark arrow, while the strain hardening rate decreases at large strains as indicated by the yellow arrow.

Figure 9 BF TEM micrographs of dislocation substructures in the (a1-a3) 19 μm grain-sized and (b1-b3) 5 μm grain-sized undoped HEAs after low, medium and high strains. The grain boundary (GB), B2 phase, and dislocation cell structures (DCs) are marked in the images.

Figure 10 BF TEM micrographs of dislocation substructures in the (a1-a3) 23 μm grain-sized and (b1-b3) 5 μm grain-sized 1.1 at. % C-doped HEAs after low, medium and high strains. Stacking faults (SF) and microbands (MBs) are marked on the images. The white arrow in (b2) points out the early stage of dislocation clusters.

Figure 11 Ductility versus ultimate tensile strength at room temperature for steels and HEAs. The mechanical properties of 1.1 at. % C-doped HEAs with various grain sizes are indicated for comparison. Properties of steels are from [68] and the CoCrFeMnNi HEA with a grain size of 4.7 μm are from [5].

Figure 12 Plot of reduced yield strength versus inverse square root of grain size for undoped and 1.1 at. % C-doped HEAs.

Fig 13 Schematic illustration of the dislocation substructure evolution and strain hardening curves for the undoped (a) and C-doped (b) HEAs. The dark and red curves indicate the strain-hardening rate of relatively coarse and fine grain-sized HEAs, respectively. The carbon solute in HEAs induces a transition from wavy slip to planar

slip during initial deformation, and from cell-forming structures (e.g., dislocation cells) to non-cell forming structure (e.g., microbands) at higher strains. With decreasing grain size, regular dislocation configurations consisting of dislocation cells and microbands transforms to irregular dislocation configurations consisting of dislocation clusters at higher strains, leading to the reduction of strain hardening.

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