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The effect of interstitial carbon on the mechanical properties and dislocation substructure evolution in $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ high entropy alloys

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Abstract

A systematic study of the effects of up to 1.1 at. % carbon on the mechanical properties and evolution of the dislocation substructure in a series of a high entropy alloys (HEA) based on $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ is presented. Transmission electron microscopy (TEM), synchrotron X-ray diffraction (XRD) and atom probe tomography (APT) were used to show that all the alloys are single-phase f.c.c. random solid solutions. The lattice constant, determined from synchrotron XRD measurements, increases linearly with increasing carbon concentration, which leads to a linear relationship between the yield strength and the carbon concentration. The dislocation substructures, as determined by a TEM, show a transition from wavy slip to planar slip and, at higher strains, and from cell-forming structure (dislocations cells, cell blocks and dense dislocation walls) to **non-cell forming** structure (Taylor lattice, microbands and domain boundaries) with the addition of carbon, features related to the increase in lattice friction stress. **The stacking fault energy (measured via weak-beam imaging of the separation of dislocation partials) decreases with increasing carbon content, which also contributes to the transition from wavy slip to planar slip.** The formation of **non-cell forming** structure induced by carbon

leads to a high degree of strain hardening and a substantial increase in the ultimate tensile strength. The consequent postponement of necking due to the high strain hardening, along with the plasticity accommodation arising from the formation of microbands and domain boundaries, result in an increase of ductility due to the carbon addition.

Key words: High entropy alloy; Interstitial strengthening; Dislocation structures; Strain hardening; **Weak-beam imaging**.

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1. Introduction

The need for higher strength alloys at reasonable cost is an ever-present challenge. Recently, high-entropy alloys (HEAs), multicomponent alloys consisting of at least five metallic elements with amounts in the range 5-35 at. %, have seen a surge in interest due to the possibility of producing a combination of high strength, high ductility and good fracture toughness [1–4]. Solid solution *substitutional* strengthening in single-phase HEAs is usually considered to arise from the lattice distortions owing to the constituent elements having different atomic radius and modulus [3,4]. However, modeling the strengthening behavior of substitutional atoms in HEAs is problematic since it is not possible to define the solute atoms and the solvent atoms [4,5].

In addition to substitutional solid solution strengthening, interstitial strengthening offers another route to achieve improvements in mechanical properties. For example, boron added to Ni₃Al not only increased the yield strength by 242-387 MPa per atomic percent [6], but also greatly increased the ductility with an accompanying change of fracture mode from intergranular to transgranular [6]. The large change in strength was a result of the asymmetric strain field produced by boron [7], while the segregation of boron to the grain boundaries promoted the transmission of slip through the boundary and reduced the tendency for cracking, leading to the increase of ductility [8].

Regardless of the high **potential** for interstitial strengthening in HEAs, this has received little attention thus far owing to the extremely low solubility of interstitials in f.c.c. metals. However, recently Wu et al. [9] dissolved 0.5 at. % carbon in the FeNiCoCrMn HEA (the carbon content of the alloy did not appear to have been measured)

and this increased both the yield strength and the ultimate tensile strength (UTS) but, unfortunately, decreased the ductility.

Several useful strain hardening mechanisms, e.g. transformation-induced plasticity (TRIP) and twinning-induced plasticity (TWIP) [10], have been observed in multicomponent alloys with either medium or high entropy. Li et al. [11] designed dual-phase (f.c.c. and h.c.p.) $\text{Fe}_{50}\text{Mn}_{30}\text{Co}_{10}\text{Cr}_{10}$ alloys producing TRIP and achieved a UTS of ~ 880 MPa with an elongation of ~ 70 %. Nanoscale deformation twinning was observed in the single-phase f.c.c. HEA CoCrFeMnNi [12] at 77 K, producing an excellent combination of high strength (UTS of ~ 1100 MPa) and ductility (elongation of ~ 90 %). Deng et al. [13] induced twinning in single-phase f.c.c. $\text{Fe}_{40}\text{Mn}_{40}\text{Co}_{10}\text{Cr}_{10}$ alloys at room temperature by optimizing the stacking fault energy (SFE) via varying the composition, and obtained both good strength and ductility (i.e. UTS of ~ 489 MPa and elongation of ~ 58 %).

Microband-induced plasticity (MBIP) [14,15] has been proposed as a new strain hardening mechanism to account for the attractive combination of strength and ductility (i.e. UTS of 900 MPa and elongation to fracture of 100 %) in high-Mn austenitic steels. Complex dislocation substructures including microbands (MBs), a Taylor lattice (TL) and domain boundaries (DBs) were present in these Fe-Mn-Al-C steels [14].

In an earlier short note [16], we showed that the addition of 1.1 at. % carbon to a novel single-phase f.c.c. HEA $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ not only markedly increased the yield strength but also led to a 25% increase in the elongation to fracture. This unusual behavior by the addition of carbon is somewhat similar to that effect of carbon in TWIP steels [17], though the underlying mechanism was not examined. Therefore, in this paper

we present a **systematic** study of the effects of carbon on the room temperature mechanical properties and the dislocation structure evolution. The interstitial strengthening effect as a function of carbon content is discussed in terms of the lattice strain, and the strain hardening mechanisms are discussed in terms of the dislocation substructure evolution.

2. Experimental

Six alloys **based on** the HEA $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ doped with different carbon contents were produced by melting pieces of 99.8% Fe, 99.95% Ni, 99.8% Mn, 99.8% Al, 99.8% Cr and 99% Fe_3C . An additional 5 wt. % Mn was added to compensate for the loss of Mn by evaporation during melting. The pieces were arc-melted in a water-chilled copper crucible under an argon atmosphere. Each ingot was flipped and re-melted twice in order to ensure a homogeneous mixture. The chemical compositions of the resulting ingots were measured by Chicago Spectro Service Laboratory using ASTM E1019 and ASTM E1621 test procedures.

X-ray diffraction (XRD) patterns were obtained from each of the alloys at the Advanced Photon Source (APS) at Argonne National Laboratory, using the hard X-ray microdiffraction facility at Beamline 2-ID-D [18]. The X-ray radiation was generated from a 7 GeV electron beam and APS undulator A [19] in the storage ring. 18 keV X-rays (wavelength = 0.61992 Å) were selected using a double-crystal Si <111> monochromator. The total count time was 30-50s. The position of each peak was measured on the diffractogram from which the lattice parameter was calculated. The measured lattice parameters were plotted versus $\frac{\cos^2 \vartheta}{2} \left(\frac{1}{\sin \vartheta} + \frac{1}{\vartheta} \right)$ [20], where ϑ is the

Bragg angle for each peak and the resulting graph extrapolated to zero to obtain the best value of the lattice parameter.

Atom probe tomography (APT) experiments were performed at the Center for Nanophase Materials Sciences (CNMS) within Oak Ridge National Laboratory (ORNL). The samples for APT tests were prepared using a dual FIB-SEM system (FEI Nova 200) following the procedures described in [21,22]. A local electrode atom probe (CAMECA LEAP 4000X HR) was used to perform the APT experiments with a 50 pJ laser energy, a repetition rate of 200 kHz, and a specimen temperature of 50 K [23]. The 3D volumes were reconstructed and analyzed using IVAS 3.6.12 software (CAMECA Instruments).

For examination in the scanning electron microscope (SEM), specimens were electropolished using a Struers Tenupol 5 for approximate 30 s using an electrolyte consisting of 25% nitric acid in methanol at a temperature of 250 K, an applied voltage of 11 V and a current of 100 mA. Polished and etched as-cast specimens were examined using back scattering electron (BSE) imaging and fracture surfaces were examined using secondary electron (SE) imaging on a FEI XL30 field emission gun (FEG) SEM operated at 15 kV.

Three mm diameter disks were produced for transmission electron microscope (TEM) examination by electro-discharge machining and ground to ~200 μm thickness. They were electropolished in an electrolyte of 20% nitric acid, 10% butoxyethanol and 70% methanol using a Struers Tenupol 5 at a voltage of ~10 V with a current of ~40 mA at ~250 K. The electropolished thin foils were alternately washed in ethanol and methanol for three cycles prior to a final rinse in methanol and examined using an FEI Tecnai F20 FEG TEM operated at 200 kV. Both bright field (BF) and dark field (DF) imaging were used to characterize dislocation structures. Weak beam dark field (WBDF) imaging using

$g/3g$ diffracting condition with a deviation parameter $s_g > 0.2 \text{ nm}^{-1}$ were employed to measure the separations of Shockley partial dislocations. Three measurements were made along each dislocation and two partial dislocations were measured to obtain the average partial dislocation spacing for each alloy.

The elastic modulus of the HEAs was measured from nanoindentation tests using a Hysitron Ubi-1 nanoindenter. Samples were polished with $0.05 \text{ }\mu\text{m}$ alumina powders to obtain a mirror finish followed by a light chemical etching using a solution of 4% nitric acid in water. A maximum load of 5 mN with a constant loading rate was performed in a $10 \text{ }\mu\text{m} \times 10 \text{ }\mu\text{m}$ region using a Berkovich-type diamond nanoindenter. TRIBOSCAN 7 software was used to analyze the unloading P-H curves. Details concerning the analysis of the elastic modulus can be found in [24]. At least nine measurements were conducted for each sample.

Specimens with a dog-bone shape (gauge length $\sim 10 \text{ mm}$; width $\sim 2.54 \text{ mm}$; and thickness $\sim 1.27 \text{ mm}$) were machined from the ingots for tensile tests. The tensile specimens were polished through increasingly fine grades of silicon carbide papers and finally polished using $0.3\mu\text{m}$ alumina powder. Three specimens for each alloy were tested with an initial strain rate of $5 \times 10^{-4} \text{ s}^{-1}$ at room temperature. The elongation was measured directly from the specimen after fracture using an optical microscope. The true stress-strain curves were calculated from the engineering stress-strain curves.

3. Results

3.1 Microstructures

The carbon contents of the six carbon-doped $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ ingots were

determined by atomic absorption to be 0, 0.07, 0.16, 0.30, 0.55 and 1.10 at. % (see Table 1). Both BSE and TEM observations in our earlier work [16] illustrated the single-phase nature of the carbon-doped HEA containing the highest level of carbon (1.1 at. %), i.e. no carbides were present, indicating that all the carbon is in solution. The addition of carbon has little influence on the grain size of HEAs in the as-cast state, see Fig. 1. All HEAs have average grain sizes around 110-130 μm as determined by the linear intercept method. The dark points in Fig. 1 were Al-rich nitride particles based on energy dispersive X-ray spectrometry (see insert in Figure 1(a)). These particles have little influence on mechanical properties due to their very low volume fraction.

The XRD data in Fig. 2a corroborates that all the alloys were single phase with an f.c.c. structure, i.e. no non-f.c.c. peaks were observed. The lattice parameter, a , determined using an extrapolation technique from the XRD data, increases linearly with increasing carbon concentration (see Fig. 2b), which further confirms that the carbon dissolves in the interstices of the f.c.c. lattice. According to the linear fit in Fig. 2b, the increase in lattice parameter (Δa) per change in at. % carbon Δc , $\Delta a/\Delta c$, is 2.74 pm/at. %, which produces a lattice strain or fractional increase in lattice parameter per atom fraction of carbon, $\Delta a/(\Delta c \times a)$ of 0.78/at. %.

To further confirm that the carbon is in solution, APT was used to examine the HEA with the highest carbon content (1.1 at. %). As shown in Fig. 3, no nanoscale clustering or precipitation was found and all atoms exhibit a homogeneous distribution. To further evaluate the randomness, a frequency distribution analysis was performed on the atom probe data, which consists of binning the ions in groups of 100, and comparing the concentration distribution of the APT data to a binomial distribution using the chi-

squared statistical test (see the inserted table in Fig. 3). The values of the normalized chi-squared parameter, μ ($\mu=0$ indicates complete randomness and $\mu=1$ refers to complete ordering [25]), for each of the elements for the carbon-doped HEA are close to 0, showing an almost ideal homogenous distribution for all six elements.

3.2 Mechanical Properties

Fig. 4a shows engineering stress-strain curves for the as-cast $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ HEAs with different carbon contents strained under tension: the yield strength, ultimate tensile strength (UTS) and elongation to fracture are listed in Table 2. Both the yield strength and the UTS increase with the increasing carbon content, i.e., the yield strength increases from 159 ± 11 MPa for the undoped HEA to 355 ± 7 MPa for the HEA containing 1.1 at. % carbon on account of the interstitial strengthening. In addition to the improvement of yield strength in the carbon-doped $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ HEAs, the carbon results in improved elongation, i.e., the elongation increases from 40.8 ± 2.5 % for the undoped alloy to 51.6 ± 3.2 % for the alloy containing 0.07 at. % C. However, further increases in carbon content have little effect on the elongation, see Table 1. The yield stress versus carbon content is plotted in Fig. 4b. The yield strength, σ_y , measured at room temperature shows a linear increase with increasing carbon content; the increase in yield strength per at. % carbon, $\Delta\sigma_y/\Delta c$, is 184 MPa/ at. % C.

The elastic modulus (E) at room temperature for the undoped and 1.1 at. % carbon-doped HEA was determined from nanoindentation measurements, and the shear modulus (G) was calculated from $G = E/2(1+\nu)$, assuming the alloy is elastically isotropic and the value of Poisson's ratio, ν , is 0.3. Fig. 5 shows force-displacement curves of nanoindentations

for the undoped and 1.1 at. % carbon-doped HEA: the elastic modulus was calculated from these curves based on the methods outlined in [24]. The values of elastic modulus for the undoped (132 ± 4 GPa) and doped HEAs (140 ± 4 GPa) are very close, both of which are somewhat lower than FeCoCrNiMn f.c.c.-structured HEA (179 ± 4 GPa) [26] but slightly higher than the f.c.c. phase in a related FeNiMnAl alloy (122 ± 2 GPa) [24].

Fig. 6 shows both the true stress (σ_t) and the strain-hardening rate ($d\sigma_t/d\varepsilon_t$) as a function of true strain (ε_t) for each of the $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ HEAs. Both the strain hardening rate and the critical strain, where the strain-hardening rate reaches a maximum, increase with increasing carbon content. For example, at a true strain of 0.2, the strain hardening rate increases from 1236 ± 55 MPa for the undoped $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ HEA to 1895 ± 58 MPa for the 1.1 at. % carbon-doped HEA, see Fig. 6b. The maximum strain hardening coefficient for the undoped HEA is 1273 ± 82 MPa (G/40) and that for the 1.1 at. % carbon-doped HEA is 2239 ± 7 MPa (G/24). The dramatic difference in strain hardening behavior between the undoped and doped HEAs suggests an underlying change of deformation mechanism due to the addition of carbon.

Representative fracture surfaces for the undoped HEA, 0.55 at. % carbon-doped HEA and 1.1 at. % carbon-doped HEA are shown in Fig. 7. The values of elongation and reduction in area at the neck are listed on the images. Macroscopically, less necking is observed with increasing carbon content (see Fig. 7 a, c and e), e.g., significant necking occurs in the undoped HEA, while essentially no necking was observed in the 1.1 at. % carbon-doped HEA prior to failure: measurements of the reduction in area and elongation show that the elongation is far less than that of reduction in area in undoped HEA (elongation is 40.8 ± 2.5 %; reduction in area is 74.6 ± 1.7 %) while these two values are

almost the same in 1.1 at. % carbon-doped HEA (elongation is 49.5 ± 0.6 %; reduction in area is 48.3 ± 1.0 %). Fig. 7 b and d show that ductile dimples are exhibited in both undoped HEA and 0.55 at. % carbon-doped HEA. The size of dimples decreases as the carbon content increases, and ultimately in the 1.1 at. % carbon-doped HEA, no dimples exist although localized plastic flow is clearly evident on the fracture surface (see Fig. 7f).

3.3 Microstructure evolution during tensile deformation

The deformation microstructures for the undoped HEA at low (1%), medium (20 %) and high (40%) strains are shown in Fig. 8. At low strain, the dislocations were arranged in bundles and loops (see Fig. 8a) and tangled dislocations resulting from the multi-slip and cross-slip were observed at the medium strain (see Fig.8b), showing that the wavy slip dominated the original deformation of the undoped HEA. Fig. 8c shows that the extensive cross-slip produced irregular dislocation cells at the high strain, and such a continuous distribution of dislocations cells produces a cell block structure. Dense dislocation walls were formed at the boundaries of the cell blocks, suggesting a typical cell-forming deformation microstructure in this undoped HEA.

The TEM images presented in Fig. 9 show the evolution of the deformation structure for the 1.1 at. % carbon-doped HEA from low to high strains. At low strain (1 % strain), dislocations in linear arrays were observed in the bright field (BF) TEM image (see Fig. 9a). At a strain of 24 %, extended pile-ups were seen in Fig. 9b, indicating planar slip. This is widely observed in binary f.c.c. solid solutions [27], f.c.c. HEAs [12,28] and high-Mn austenitic steels [15]. Such parallel sets of dislocations along the glide plane, with the existence of less uniform distribution of dislocations, constitute the structure of the so-

called Taylor lattice. At the high strain (48 %), both single-wall structured domain boundaries and microbands with a plate-like zone structure intersecting each other, forming Taylor lattice domains resulting from grain subdivision. The intersections of microbands have been associated with large shear strains in [29–31]. The higher magnification image displayed in Fig. 9d shows the structures of well-developed microbands with a thickness of ~200 nm. The slip trace shows that the microbands are parallel to the trace of the $\{111\}$ glide plane, which is consistent with previous observations in other metals and alloys [31,32]. The selected area diffraction pattern in Fig. 9d confirms the absence of any twinning.

APT was performed on the 1.1 at. % carbon-doped HEA strained to 10 % in order to determine whether any segregation to dislocations occurred. **At this level of strain**, pile-ups of dislocations on single slip planes were observed in the carbon-doped HEA (see Fig. 10). Fig. 10 shows that all the elements distribute homogenously based on the frequency distribution analysis, indicating that neither short-range order nor the segregation of carbon atoms to dislocations occurs.

The microstructures at different strain levels for the 0.07 at. % carbon-doped HEA are presented in Fig. 11 for comparison. Both cross-slip and linear arrays of dislocations were seen at low to medium strains (see Fig. 11 a and b), indicating the tendency of a transition from wavy slip to planar slip for this HEA with the lowest carbon content. The intersections between domain boundaries and microbands were found at high strain, and the dislocation cells can also be seen in Fig. 11c, which shows a mixed structure of cell-forming and none cell-forming features. The dark field (DF) image for the microbands in Fig. 11d illustrates that the interior microbands contain a high density of dislocations.

Fig. 12 shows WBDF images of $\mathbf{a}/2\langle 110 \rangle$ dislocations that are clearly dissociated into $\mathbf{a}/6\langle 211 \rangle$ Shockley partials viewed perpendicular to the $\{111\}$ slip plane for the undoped, 0.07 at. % carbon-doped, and 1.1 at. % carbon-doped HEAs. When the diffraction conditions for visibility for both partial dislocations are satisfied, the Burgers vector of the perfect dislocation ($\mathbf{b}_T$) is parallel to the $\mathbf{g}$ -vector, as shown in Fig. 12. The separations of the partial dislocations were measured from the WBDF images (see Fig. 12), and a minor correction was performed to determine the actual partial dislocation separation because of the asymmetrical strain fields between partial dislocations [33]. The stacking fault energy (γ) can be calculated from the corrected partial dislocation spacing (d_c) based on the following equation [34]:

$$\gamma = \frac{Gb_p^2}{8\pi d_c} \frac{2-v}{1-v} \left(1 - \frac{2v \cos 2\beta}{2-v} \right) \quad (1)$$

where G is the shear modulus, b_p is the magnitude of the Burgers vector of the partial dislocations ($b_p = a/6\langle 112 \rangle$, a is a lattice constant), v is the Poisson's ratio, and β is the dislocation character angle (angle between the Burgers vector of the perfect dislocation and the dislocation line). The measured values of shear modulus for undoped and 1.1 at. % carbon-doped HEA are 51 ± 2 GPa and 54 ± 1 GPa, respectively (see earlier). The value of shear modulus for undoped HEA was used to calculate the SFE for the 0.07 at. % carbon-doped HEA, since such a low carbon content has negligible influence on the shear modulus. The corrected partial dislocation spacing (d_c) and the dislocation character angle (β) are listed in Table 3. Thus, the calculated values of the stacking fault energy are 22.2 ± 1.9 mJ/m² for undoped HEA, 20.1 ± 1.0 mJ/m² for 0.07 at. % carbon-doped HEA, and 10.2 ± 0.9 mJ/m² for 1.1 at. % carbon-doped HEA, respectively, indicating that the carbon additions reduce the stacking fault energy of this HEA.

4. Discussion

4.1 Effect of carbon on Yield Strength

In the absence of precipitates, the yield strength (σ_y) for well-annealed HEAs can be described by

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

where σ_{fr} is the lattice friction stress and $\Delta\sigma_{gb}$ is the strengthening contribution from grain boundaries. We noted earlier that the grain size is similar for all HEAs, indicating similar grain boundary strengthening ($\Delta\sigma_{gb}$) contributions to yield strength. Since the grain sizes are quite large, the grain boundary strengthening effect is **negligible**. Thus, the majority of the increase in yield strength results from the increase in lattice friction stress due to the interstitial strengthening from the solute carbon, as proposed in our preliminary work [16].

As noted earlier, carbon is almost insoluble in most metallic elements at room temperature [35], and thus, it is difficult to compare interstitial carbon behavior in the f.c.c. $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ HEAs to the effect of carbon in f.c.c. metals. Interestingly, carbon is soluble, up to possibly 0.5 at. % in the f.c.c. HEA FeNiCoCrMn [9] (the actual carbon content of the alloy was not measured) and up to 5.5 at. % in TWIP steels, which have a f.c.c. Fe-Mn matrix [36]. Therefore, the effects of carbon solute on lattice parameters and yield strength in the $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ HEA have been compared with those in boron-doped Ni_3Al and FeAl , and in carbon-containing TWIP steels.

The increase in the lattice parameter per change in at. % carbon ($\Delta a/\Delta c$) for a series of boron-doped cast specimens, with boron concentrations up to 1.12 at. %, of the ordered face-centered cubic compound Ni_3Al was measured to be 0.47 pm/at. % boron producing

a value of the lattice strain ε (0.13/at. %) that is much smaller than that measured for the $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ HEA (0.78/at. %) [7]. The values of ε of 0.78/at. % for carbon doping of the HEA is also substantially larger than the value of 0.26/at. % measured for both boron [37] and carbon [38] doping of melt-spun Ni_3Al ribbons, but comparable to that for the ordered body-centered cubic compound FeAl , which ranges from 1-1.55/at.%, depending on the Fe:Al ratio [39].

The increase in yield strength (σ_y) per at. % carbon (Δc) in HEAs, $\Delta\sigma_y/\Delta c$, of 184 MPa/ at. % C, is significantly higher than carbon strengthening of 26-42 MPa/ at. % C in TWIP steels [17,40], yet is less than the values reported for the boron strengthening effect in Ni_3Al of 387-420 MPa/at. % [41,42]. Although classical models of solute strengthening typically predict a $c^{1/2}$ [43] or $c^{2/3}$ of dependence of σ_y [44,45], in practice a linear dependence of σ_y on the concentration is often observed [46]: a model producing linear dependence of yield strength on concentration was proposed by Mott and Nabarro [47]. For carbon-doped $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$, both the yield strength and fractional increase in lattice parameter ($\Delta a/a$) show a linear dependence on the carbon concentration, and the yield strength is also linearly related to the $\Delta a/a$. Thus, relating the strength simply to the lattice strain is reasonable for a small concentration of interstitial atoms, since the other parameter that can influence the strength, i.e., the change in the elastic modulus, was shown to be very small.

4.2 Evolution of dislocation substructure

4.2.1 Wavy Slip vs. Planar Slip

Two different slip modes have been found in the $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ HEAs at the

early stages of deformation, i.e., wavy slip occurs in the undoped HEA and planar slip in 1.1 at. % carbon-doped HEA. Planar slip can occur due to short range ordering (SRO), a low stacking fault energy (SFE) or a large friction stress [27,48]. The possibility of SRO has been ruled out in this series of HEAs since APT results showed that the atoms are distributed randomly in both the as-cast (Fig. 3) and 10 % strained states (Fig. 10). On the other hand, a decrease in SFE (see Figure 12) and an increase of lattice friction stress was observed in the carbon-doped HEAs. Therefore, the presence of planar slip in the carbon-doped HEAs can be attributed to a combination of lower SFE and increase of lattice friction stress.

The lattice friction stress increased sharply in the carbon-doped HEAs, along with the reduction of SFE; producing the transition from wavy slip in the undoped HEA to planar slip in the carbon-doped HEA. With a reduction of SFE, cross slip is inhibited so that the Shockley partial dislocations are more separated on the slip plane [49], although planar slip has been observed in some solid solutions with high SFEs [50,51]. Carbon in f.c.c. metals has also found to inhibit dislocation cross-slip because of the increase of lattice friction stress [52]. Hong and Laird [48] proposed that edge components are included in the dissociated partials of a screw dislocation, which can be influenced by the presence of solute atoms. In order to achieve cross slip, the dissociated partials have to join together by overcoming the friction stress. The presence of solute atoms imposes additional friction stress and thus, hinders the formation of cross slip.

4.2.2 Cell-Forming vs. Non-Cell Forming

At high strains, cell blocks composed of dislocations cells were formed in the undoped

HEA with the boundaries of the cell blocks delineated by dense dislocation walls. Based on Taylor's model [53], the simultaneous operations of at least five independent slip systems are required to achieve the uniform slip for polycrystals. However, plastic deformation with a reduced number of slip systems is energetically favorable, since a lower flow stress is required for further deformation due to the decrease of intersecting jogs [54,55]. When a smaller number of slip systems is involved in the deformation of polycrystals, each grain subdivides into various volume elements named cell blocks with adjacent cell blocks deforming in order to jointly fulfill the Taylor criterion. The orientation of neighboring cell blocks deviates increasingly with the continuing deformation, leading to the formation of dense dislocation walls in boundaries of cell blocks. Dense dislocation walls can further split and then form a microband as deformation proceeds, as found in the cold-rolled microstructure of Ni [56], Cu [57] and Al [58]. However, microbands were not observed in the undoped HEA, possibly because fracture occurs at a tensile strain of 40 %, which was not large enough to activate the splitting of dense dislocation walls.

A Non-cell forming deformation structure is observed in the 1.1 at. % carbon-doped HEA, of which Taylor lattice structure is formed at the medium strain and further evolves to the Taylor lattice domain with boundaries delineated by the intersection of microbands and domain boundaries. Hughes [32] proposed that microbands were developed from single-walled domain boundaries during the evolutionary deformation progression. In order to fulfill the strain accommodation in fewer slip systems, the grain subdivided into domain boundaries consisting of misoriented Taylor **lattice** in a similar way to that in cell-forming metals. Initially, single dislocation walls occurred in domain boundaries,

and double dislocation walls were formed to shield the stress relating to the domain boundaries. The development of secondary slip induced by wall-like dislocation structures in regions between the double walls eventually produced plate-like microbands [31]. As the strain increases, further grain subdivision occurred to accommodate growing lattice rotations, causing the formation of new domain boundaries and microbands within the Taylor lattice.

The dislocation structures of the cell-forming and **non-cell forming** situations are shown schematically in Fig. 13. The interstitial carbon atoms in the HEAs triggers the transition from cell-forming to **non-cell** forming, since the increase of friction stress arising from the carbon solute in the HEAs hinders the cell formation, and further promotes the formation of microbands, as seen in 6061 Al [31] and Al-Mg alloys [32]. The solute carbon was also found to promote the formation of the Taylor lattice in TWIP steels [52]. Yoo and Park [15] found that the formation of microbands in a Mn-Al-C steel with a relative high stacking fault energy ($\sim 90 \text{ mJ/m}^2$) (SFE). However, Huang and Gary [31] proposed that the formation of microbands is more likely to be independent of SFE. In the present study, **microbands were observed in the HEAs with a relative low SFE (10-20 mJ/m²), validating Huang and Gary's viewpoint [31] that the SFE is unable to dominate the formation of microbands.**

4.3 Strain Hardening and Ductility

Most conventional strengthening mechanisms lead to a reduction in ductility; whereas the opposite is observed here: a simultaneous increase in strain hardening rate and ductility, which is similar to HEAs that undergo a martensitic transformation [11] or deformation

twinning [12]. The highest work-hardening rate was observed at a true strain of 0.35 for the HEA with 1.1 at. % carbon of 2239 ± 7 MPa or G/24, which is a value in the range of those for TWIP steels (G/20-G/40 [52,59–61]) and is substantially higher than those for common f.c.c. metals (G/200) [62,63]. Yet the microbands in carbon-doped HEAs can hardly produce remarkable strain hardening effects [52,55]. Such a high strain hardening rate for the 1.1 at. % carbon-doped HEA is largely related to the formation of Taylor lattice domains with increasing lattice friction stress. The further increase of strain hardening with increasing strain in carbon-doped HEAs, as shown in Fig. 6b, results from the size refinement of Taylor lattice domains as the deformation proceeds.

The formation of microbands (microband-induced plasticity, MBIP) was proposed to be responsible for the excellent ductility in the Fe-Mn-Al-C steel [15]. However, the improvement of ductility in our carbon-doped HEAs cannot be simply ascribed to the formation of microbands. Instead, the increase in strain hardening for carbon-doped HEAs postpones the onset of necking, and thus, stabilizes the plastic deformation, as seen in f.c.c. materials that exhibit TRIP and TWIP behavior [5,11,12]. This is also consistent with the observations of the fracture surfaces (see Fig. 7), which show that less necking occurs as the carbon content increases. In addition, the occurrence of Taylor lattice domains accompanying the intersections of microbands and domain boundaries relaxes the plastic localization and enables extra accommodation of plasticity, which further enhances the ductility.

5 Summary and conclusions

The mechanical properties of the $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ HEA doped with six levels of carbon have been investigated. The dislocation substructure evolution corresponding to the strain hardening behavior during tensile deformation has been studied for both undoped and 1.1 at. % carbon-doped HEAs. The main conclusions are:

1. A linear relationship was found between the carbon content and the change in lattice parameter, and between the carbon content and the yield strength. Carbon additions produce a lattice strain of 0.78/at. % and yield strength increase of 184 MPa/at. %.
2. The addition of carbon both **lowers the stacking fault energy** and increases the lattice friction stress, and further leads to the transition from wavy slip for undoped HEA to planar slip for the carbon-doped HEAs.
3. At high strains, the undoped HEA forms a cell structure, whereas a non-cell forming structure was found in carbon-doped HEAs as a consequence of the increase in the lattice friction stress.
4. The formation of the **non-cell** forming structure composed of the Taylor lattice, domain boundaries and microbands leads to the increase of both ductility and strain hardening in carbon-doped HEAs. The increase of strain hardening in carbon-doped HEAs delays the onset of necking, which further enhances the ductility. Additionally, the transition of dislocation substructures to the non-cell forming structure accommodates the plasticity due to the relaxation of local strain.

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Table 1 Chemical composition of as-cast carbon-doped Fe_{40.4}Ni_{11.3}Mn_{34.8}Al_{7.5}Cr₆ HEAs (denoted as C_x, where x is the carbon concentration) determined using ASTM E1019 and ASTM E1621 test procedures by Chicago Spectro Service Laboratory, Inc, Chicago, IL (in at. %).

Alloys	Fe	Ni	Mn	Al	Cr	C
C_{0.07}	41.83	10.13	35.25	7.20	5.52	0.07
C_{0.16}	40.6	11.58	35.55	7.10	5.01	0.16
C_{0.30}	44.85	10.05	32.25	7.35	5.20	0.30
C_{0.55}	41.08	10.21	35.46	7.39	5.31	0.55
C_{1.1}	39.93	10.35	35.67	7.40	5.55	1.1.

Table 2 Yield stress, ultimate tensile stress (UTS), elongation to fracture and strain hardening rate (SHR) for Fe_{40.4}Ni_{11.3}Mn_{34.8}Al_{7.5}Cr₆ HEAs with the various amounts of carbon (denoted as C_x, where x is the carbon concentration) are shown. The error bars indicate the standard deviation calculated from three tests.

Alloys	C₀	C_{0.07}	C_{0.16}	C_{0.30}	C_{0.55}	C_{1.10}
Yield stress (MPa)	159 ± 11	171 ± 3	181 ± 4	208 ± 6	274 ± 12	355 ± 7
UTS (MPa)	535 ± 21	674 ± 26	713 ± 7	762 ± 27	960 ± 66	1174 ± 19
Elongation (%)	40.8 ± 2.5	51.6 ± 3.2	52.2 ± 2.0	48.2 ± 0.9	52.3 ± 4.7	49.5 ± 0.6
SHR (MPa) @ strain = 0.2	1236 ± 55	1313 ± 14	1360 ± 31	1506 ± 68	1542 ± 32	1895 ± 58
Max. SHR (MPa)	1273 ± 82	1350 ± 27	1400 ± 24	1591 ± 39	1854 ± 45	2239 ± 7

Table 3 The corrected partial dislocation spacing (d_c) and the dislocation character angle (β) of the undoped, 0.07 at. % carbon-doped and 1.1 at. % carbon-doped HEAs based on measurements from WBDF images.

Alloy	Corrected partial dislocation spacing (nm)	Dislocation character angle
Undoped HEA	6.0 ± 0.3	62°
	7.2 ± 0.6	82°
0.07 at. % carbon-doped HEA	7.5 ± 0.2	71°
	6.7 ± 0.4	62°
1.1 at. % carbon-doped HEA	14.9 ± 1.0	84°
	15.6 ± 1.8	77°

Figure Captions

Figure 1 BSE images of as-cast $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ HEAs with (a) 0 at. % carbon, (b) 0.16 at. % carbon and (c) 1.1 at. % carbon. The inserted X-ray spectra in (a) shows the dark points are Al-rich nitride particles.

Figure 2 (a) Synchrotron XRD patterns from carbon-doped $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ HEAs. The at. % of carbon is shown on each curve, all of which are single phase f.c.c.. (b) Lattice parameter versus carbon content for $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ HEAs.

Figure 3 Atom probe tomography (APT) elemental maps and frequency distribution analysis for the as-cast 1.1 at. % carbon-doped $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ HEA. The value of μ indicates the degree of atomic segregation, where 0 is a complete random distribution and 1 is a fully ordered distribution [25].

Figure 4 (a) Typical engineering stress-strain curves for carbon-doped $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ HEAs, and (b) Yield strength versus carbon content for $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ HEAs.

Figure 5 Force-displacement curves of (a) undoped and (b) 1.1 at. % carbon-doped $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ HEAs loading by nanoindents.

Figure 6 (a) Typical true stress and (b) Strain hardening rate as a function of true strain for carbon-doped $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ HEAs. The at. % of carbon is shown on each curve.

Figure 7 Fracture surfaces of (a, b) undoped HEA, (c, d) 0.55 at. % carbon-doped HEA and (e, f) 1.1 at. % carbon-doped HEA at low and high magnification. The black dotted line in (a), (c) and (e) indicates the contour of fracture surfaces. The values of reduction in area (RA) and elongation to fracture (EG) for each specimen are listed in (a), (c) and (e).

Figure 8 BF TEM micrographs of the undoped $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ HEA after (a) 1 % strain, (b) 20 % strain and (c) 40 % strain. The dislocations cells (DCs) and dense dislocation walls (DDWs) are seen in (c).

Figure 9 BF TEM micrographs of 1.1 at. % carbon-doped $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ HEA after (a) 1% strain, (b) 24% strain; and (c) and (d) 48 % strain. The solid line and dotted line in (c) are domain boundary and microband, respectively. Domain boundaries (DBs) define the single dislocation boundaries for the Taylor lattice, and microbands (MBs) indicate the plate-like zones [32]. The trace of $\{111\}$ in (d) shows that microband orient along $\{111\}$ plane.

Figure 10 Atom probe tomography (APT) elemental maps and frequency distribution analysis of the 1.1 at. % carbon-doped $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ HEA after 10 % strain. The inserted BF TEM image shows the pile-up of dislocations. The value of μ indicates the degree of atomic segregation, where 0 is a complete random distribution and 1 is a fully ordered distribution [25].

Figure 11 TEM micrographs of 0.07 at. % carbon-doped $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ HEA after (a) 1% strain, (b) 24% strain; and (c) and (d) 52 % strain. The black arrows in (a) and (b) indicate linear arrays of dislocations. The solid line and dotted line in (c) are the domain boundary (DB) and microband (MB), respectively. The dislocation cells (DCs) are seen in (c). (d) DF image for a microband.

Figure 12 WBDF images of a dissociated dislocation in (a) undoped HEA, (b) 0.07 at. % carbon-doped HEA, and (c) 1.1 at. % carbon-doped HEA at 1 % strain. The inserted SAD pattern in (a) shows the $\mathbf{g}/3\mathbf{g}$ diffracting condition. A representative separation measurement is shown for each image.

Figure 13 Schematic images of dislocation substructure for (a) cell-forming and (b) **non-cell forming** structure.

Figure 1 BSE images of as-cast Fe_{40.4}Ni_{11.3}Mn_{34.8}Al_{7.5}Cr₆ HEAs with (a) 0 at. % carbon, (b) 0.16 at. % carbon and (c) 1.1 at. % carbon. The inserted X-ray spectra in (a) shows the dark points are Al-rich nitride particles.

Figure 2 (a) Synchrotron XRD patterns from carbon-doped $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ HEAs. The at. % of carbon is shown on each curve, all of which are single phase f.c.c.. (b) Lattice parameter versus carbon content for $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ HEAs.

Figure 3 Atom probe tomography (APT) elemental maps and frequency distribution analysis for the as-cast 1.1 at. % carbon-doped $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ HEA. The value of μ indicates the degree of atomic segregation, where 0 is a complete random distribution and 1 is a fully ordered distribution [25].

Figure 4 (a) Typical engineering stress-strain curves for carbon-doped $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ HEAs, and (b) Yield strength versus carbon content for $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ HEAs.

Figure 5 Force-displacement curves of (a) undoped and (b) 1.1 at. % carbon-doped $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ HEAs loading by nanoindents.

Figure 6 (a) Typical true stress and (b) Strain hardening rate as a function of true strain for carbon-doped $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ HEAs. The at. % of carbon is shown on each curve.

Figure 7 Fracture surfaces of (a, b) undoped HEA, (c, d) 0.55 at. % carbon-doped HEA and (e, f) 1.1 at. % carbon-doped HEA at low and high magnification. The black dotted line in (a), (c) and (e) indicates the contour of fracture surfaces. The values of reduction in area (RA) and elongation to fracture (EG) for each specimen are listed in (a), (c) and (e).

Figure 8 BF TEM micrographs of the undoped $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ HEA after (a) 1 % strain, (b) 20 % strain and (c) 40 % strain. The dislocations cells (DCs) and dense dislocation walls (DDWs) are seen in (c).

Figure 9 BF TEM micrographs of 1.1 at. % carbon-doped $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ HEA after (a) 1% strain, (b) 24% strain; and (c) and (d) 48 % strain. The solid line and dotted line in (c) are domain boundary and microband, respectively. Domain boundaries (DBs) define the single dislocation boundaries for the Taylor lattice, and microbands (MBs) indicate the plate-like zones [32]. The trace of $\{111\}$ in (d) shows that microband orient along $\{111\}$ plane.

Figure 10 Atom probe tomography (APT) elemental maps and frequency distribution analysis of the 1.1 at. % carbon-doped $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ HEA after 10 % strain. The inserted BF TEM image shows the pile-up of dislocations. The value of μ indicates the degree of atomic segregation, where 0 is a complete random distribution and 1 is a fully ordered distribution [25].

Figure 11 TEM micrographs of 0.07 at. % carbon-doped $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ HEA after (a) 1% strain, (b) 24% strain; and (c) and (d) 52 % strain. The black arrows in (a) and (b) indicate linear arrays of dislocations. The solid line and dotted line in (c) are the domain boundary (DB) and microband (MB), respectively. The dislocation cells (DCs) are seen in (c). (d) DF image for a microband.

Figure 12 WBDF images of a dissociated dislocation in (a) undoped HEA, (b) 0.07 at. % carbon-doped HEA, and (c) 1.1 at. % carbon-doped HEA at 1 % strain. The inserted SAD pattern in (a) shows the $g/3g$ diffracting condition. A representative separation measurement is shown for each image.

(a) Cell-forming

(b) Non-cell forming

Figure 13 Schematic images of dislocation substructure for (a) cell-forming and (b) **non-cell** forming structure.