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A TRIP-assisted dual-phase high-entropy alloy: Grain size and phase fraction effects on deformation behavior



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ABSTRACT

We present a systematic microstructure oriented mechanical property investigation for a newly developed class of transformation-induced plasticity-assisted dual-phase high-entropy alloys (TRIP-DP-HEAs) with varying grain sizes and phase fractions. The DP-HEAs in both, as-homogenized and recrystallized states consist of a face-centered cubic (FCC) matrix containing a high-density of stacking faults and a laminate hexagonal close-packed (HCP) phase. No elemental segregation was observed in grain interiors or at interfaces even down to near-atomic resolution, as confirmed by energy-dispersive X-ray spectroscopy and atom probe tomography. The strength-ductility combinations of the recrystallized DP-HEAs (Fe₅₀Mn₃₀Co₁₀Cr₁₀) with varying FCC grain sizes and HCP phase fractions prior to deformation are superior to those of the recrystallized equiatomic single-phase Cantor reference HEA (Fe20Mn20Ni20-Co20Cr20). The multiple deformation micro-mechanisms (including strain-induced transformation from FCC to HCP phase) and dynamic strain partitioning behavior among the two phases are revealed in detail. Both, strength and ductility of the DP-HEAs increase with decreasing the average FCC matrix grain size and increasing the HCP phase fraction prior to loading (in the range of 10-35%) due to the resulting enhanced stability of the FCC matrix. These insights are used to project some future directions for designing advanced TRIP-HEAs through the adjustment of the matrix phase's stability by alloy tuning and grain size effects.

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1. Introduction

High-entropy alloys (HEAs), also known as multi-principal element materials or compositionally complex compounds, have drawn significant attention during the last decade [1–9]. In the original HEA design concept, phase separation was regarded as an undesired phenomenon as it suggested that the configurational entropy was insufficient for stabilizing a single solid solution state. Specific concerns were that phase separation would lead to the formation of brittle intermetallic compounds or that partitioned alloying elements would reduce the targeted solid solution hard-ening effect [10]. In this context, several alloys have been proposed that develop single-phase face-centered cubic (FCC; e.g., FeMnNi-CoCr [3,5] and FeNiCoCrAl_{0,3} [11]), body-centered cubic (bcc; e.g.,

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TaNbHfZrTi [12], VNbMoTaW [13], and HfMoTaTiZr [14]) and hexagonal close-packed (HCP; e.g., HoDyYGdTb [15]) crystal structures. Among these, the FeMnNiCoCr system, a typical single FCC phase solid solution HEA at room temperature that can be produced by conventional casting, has particularly excellent mechanical properties [2,16,17], including exceptional cryogenic fracture toughness [5].

However, a number of studies revealed that entropy-stabilized single-phase HEAs are often hard to realize and are also not necessarily equipped with superior properties [3,4,16,18–20]. These observations have encouraged efforts to relax the strict restrictions on HEA design regarding single-phase stability. Motivated by this, we recently developed a new class of HEAs, namely, transformation-induced plasticity-assisted dual-phase (TRIP-DP) HEA [1]. The two high-entropy phases present in this TRIP-DP-HEA (i.e., FCC γ matrix and HCP ε phases) are compositionally equivalent [1]. The new alloy design concept was realized in the four-component FeMnCoCr HEA system. The new material combines the solid-solution strengthening effect inherent in HEAs with the

TRIP effect known from certain high strength steels [21–25], resulting in improved strength and ductility compared to the above mentioned single-phase HEAs [1,2,5]. In the new TRIP-DP-HEAs, the micro-composite effect associated with its dual-phase micro-structure and the displacive phase transformation upon deformation play key roles in enhancing the strain hardening potential of the material and hence its strength and ductility. The deformation-stimulated transformation behavior is influenced by the thermo-dynamic stability of the FCC matrix phase [1], which in turn is related to the initial FCC grain size, the alloy content and elemental partitioning, the HCP phase fraction present in the matrix prior to deformation and the load partitioning among the two phases.

We observed before that grain-refinement leads to substantial improvement in both strength and ductility in these materials [1], however, the underlying mechanisms enabling such behavior were not investigated. Here, we thus address these questions including the influence of the FCC grain size on the HCP phase fraction prior to loading, the effect of the initially available HCP phase fraction on the overall deformation response and kinetics, and the influence of the FCC grain size on its phase stability. For these reasons we produced DP-HEAs with varying FCC grain sizes and initially available HCP phase fractions by corresponding thermal and grain refinement processing. In the following we present these microstructures and the associated microstructure-mechanical property relations.

2. Methodology

2.1. Alloys processing

The DP-HEA was first cast in a vacuum induction furnace using pure metals (>99.8 wt. % pure) to a predetermined composition of 50Fe-30Mn-10Co-10Cr (at. %). The as-cast ingot ($10 \times 50 \times 150 \text{ mm}^3$) was hot-rolled at 900 °C to a thickness reduction of 50%. Subsequently, the alloy sheets of 5 mm thickness were homogenized at 1200 °C for 2 h in Ar atmosphere followed by water-quenching. The exact composition (including the contents of residual elements) of the homogenized alloy was obtained by conducting a comprehensive chemical analysis and the results are listed in Table 1. The grain size of the homogenized alloy sample is nearly the largest value currently we can obtain in the alloy sample without observable chemical inhomogeneity based on the fact that the sample was heat-treated at high temperature (1200 °C) for a long time (2 h). In order to obtain samples with various grain sizes and phase fractions, the homogenized alloy was cold-rolled to a thickness reduction of 60% (thickness changed from 5 to 2 mm) and subsequently annealed at a furnace temperature of 900 $^\circ\text{C}$ in Ar atmosphere for 3, 5, 10, 15, 30 and 60 min, respectively, followed by water-quenching. Note that for the 3 min annealing, the true temperature that the sample actually reached might be lower than the furnace temperature (900 °C) due to the short annealing time. The short annealing time (3 min) was used to obtain nearly the smallest grain size value in a fully recrystallized alloy sample, and hence to ensure that we investigated the possible large range of grain sizes currently we could obtain in this new alloy.

Table 1

Composition (including the contents of possible residual elements) of the homogenized TRIP-DP-HEA (wt. %).

Elements	Fe	Mn	Со	Cr	Cu	Ni	Мо
	Bal.	28.5	11.1	9.77	0.333	0.0114	< 0.002
Elements	Sb <0.001	Sn <0.01	C 0.0064	N 0.0077	O 0.025	P <0.001	S 0.0063

2.2. Analysis

The microstructures of the alloys were analyzed using multiple techniques. Electron backscatter diffraction (EBSD) measurements were carried out using a Zeiss-Crossbeam XB 1540 FIB scanning electron microscope (SEM) with a Hikari camera and the TSL OIM data collection software. Back-scattered electron imaging (BSEI) and electron channeling contrast imaging (ECCI) analyses [26] were performed in a Zeiss-Merlin instrument. The elemental distribution in the grain-refined TRIP-DP-HEA samples was investigated using energy-dispersive X-ray spectroscopy (EDS) and atom probe tomography (APT) (LEAP 3000X HR, Cameca Inc.). Site-specific liftout of APT tips was performed from the regions including phase and grain boundaries (revealed by a prior EBSD scan) using the focused ion beam (FIB) technique (FEI Helios Nanolab 600i) [27–29].

Rectangular dog-bone-shaped tensile specimens, with a thickness of 1 mm, were sectioned from the alloys by electrical discharge machining (EDM). The gage length and width of the tensile specimens were 10 and 2.5 mm, respectively. Uniaxial tensile tests were carried out at ambient temperature using a Kammrath & Weiss tensile stage at an initial strain rate of $1 \times 10^{-3} \text{ s}^{-1}$. To confirm reproducibility, three tensile specimens for each alloy were tensile tested. The evolution of local strain during tensile testing was determined by digital image correlation (DIC) method using Aramis system (GOM GmbH) [30–32].

The deformation mechanisms in the DP-HEAs were investigated by EBSD and ECCI at different regions of the fractured tensile samples with different local strain levels [33–35]. XRD measurements were performed on different regions of the tensile samples using the X-ray equipment ISO-DEBYEFLEX 3003 in conjunction with Co K_{α1} ($\lambda = 1.788965$ Å) radiation operating at 40 kV and 30 mA between 40 and 130 deg (2 θ) at a step size ($\Delta 2\theta$) of 0.05 deg and a counting time of 20 s per step. The X-ray beam shape was in point focus with a beam size of 1.5 mm. Phase fractions were also obtained by Rietveld analysis of XRD patterns using the software MAUD (version 2.53).

Prior to the above EBSD, ECCI and XRD measurements, the sample surfaces were first ground using silicon carbide paper from 600 to 4000 granulation, followed by polishing with 3 and 1 μ m diamond suspensions. Fine polishing was performed using an oxide suspension (OPS) with silica particle size around 50 nm for more than half an hour to effectively remove the deformation layer caused by mechanical grinding. The sample surfaces were finally polished with ethanol to remove the nano-silica particles.

3. Results

3.1. Microstructure prior to deformation

3.1.1. Microstructure in the as-homogenized coarse-grained (CG) dual-phase HEA

Fig. 1 shows a typical analysis of the microstructure of the homogenized CG DP-HEA. Fig. 1a–c gives the BSE, ECCI and EBSD images. These data reveals that the alloy consists of two phases, namely, FCC γ matrix and HCP ε phase. The HCP ε phase is formed within the FCC γ matrix and mainly exhibits laminate morphology. According to the calculation from multiple BSE images and EBSD maps, the γ matrix has an average grain size of approximately 45 µm while the thickness of the ε laminate is varying between the submicron scale to more than 10 µm. From EBSD analysis, the average fractions of the FCC γ and HCP ε phases are approximately 72% and 28%, respectively. High angle grain boundaries (HAGBs, misorientation greater than 15°) prevail in the homogenized alloy. They occupy a fraction of more than 80%, while the fraction of low



Fig. 1. Combined EBSD and ECCI analysis on the homogenized DP-HEA after water-quenching without plastic deformation: (**a**) BSE image with relatively low magnification; (**b**) ECC image of the marked square region in (a); (**c**) EBSD IQ and phase map of the identical sample region in (b); (**d**) EBSD IPF map corresponding to (c); (**e**) ECC image with relatively high magnification showing stacking faults in various sizes; (**f**) stereographic projection of the orientations; (**g**) simulated electron channeling pattern for the applied diffraction during ECCI analysis. IQ: Image quality; IPF: Inverse pole figure.

angle grain boundaries (LAGBs, misorientation less than 15°) is lower than 20%. Note that, in Fig. 1c and d, HCP ε laminates with widths below 50 nm, as shown in Fig. 1b, are not captured in the EBSD phase and associated inverse pole figure (IPF) maps (except for a slight decrease in IQ), since ECCI has higher lateral resolution than EBSD [26].

To reveal the crystal defects more clearly, Fig. 1e presents a highmagnification ECCI analysis of the microstructure tilted into twobeam conditions corresponding to the square region denoted in Fig. 1b–d. The stereographic projection of the orientations and simulated electron channeling pattern for the applied diffraction are shown in Fig. 1f and g, respectively. Under two-beam condition, the perfect crystal appears dark in the ECCI analysis. Regions of dislocation and stacking fault modulate the crystal's coherence appear bright due to the backscattering effect [26,36]. Fig. 1e shows some stacking faults and dislocations. The density of dislocations and stacking faults are calculated to be 1.9 (\pm 0.3) \times 10¹³ m⁻² and 4.5 (±0.5) × 10¹³ m⁻², respectively, using multiple ECC images and the method described in Ref. [37]. In summary, the ECCI analysis in combination with EBSD data, confirms the dual-phase (FCC and HCP) microstructure, with stacking faults and dislocations present even in the as-homogenized state of the FCC γ matrix.

3.1.2. Microstructure and chemical homogeneity following grain refinement

To refine grain size in the homogenized CG DP-HEA, further cold-rolling and recrystallization annealing followed by waterquenching were performed at 900 °C for 3, 5, 10, 15, 30, 60 min, respectively. Fig. 2 shows typical resulting microstructures of the recrystallized DP-HEAs for annealing times of 3, 5 and 30 min, respectively. All of the recrystallized DP-HEAs show co-existence of FCC γ and HCP ε with various respective fractions and sizes (Fig. 2a₁, 2b₁ and 2c₁). The ECCI analysis with relatively low magnification in Fig. 2a₂, 2b₂ and 2c₂ confirms the lath-shaped morphology of the

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Fig. 2. Typical EBSD phase maps (a₁, b₁ and c₁) and ECC images (a₂₋₃, b₂₋₃ and c₂₋₃) of the TRIP-DP-HEAs following annealing at 900 °C for different time: (a₁₋₃) 3 min; (b₁₋₃) 5 min and (c₁₋₃) 30 min.

HCP ε phase formed within the FCC γ grains. Accordingly, the high magnification ECCI analysis in Fig. 2a₃, 2b₃ and 2c₃ shows that there are a number of stacking faults developed within the FCC γ grains in all of the recrystallized DP-HEAs.

The variations in FCC grain size and HCP phase fraction with increasing annealing time are summarized in Fig. 3. Note that the value of FCC grain size refers to the size of the whole matrix grain which may contain HCP laminate phase, while the value of HCP phase fraction indicates the fraction of HCP laminate within the matrix grains, as schematically illustrated by the inset in Fig. 3. The sample annealed for only 3 min at 900 °C was fully recrystallized



Fig. 3. Variations of FCC grain size and HCP phase fraction in the TRIP-DP-HEAs with increasing the annealing time. The inset schematically showing that the calculation of FCC grain size is based on the whole matrix grain which may contain HCP laminate phase.

with average FCC grain size of ~4.5 μ m and HCP phase fraction of ~32% (Figs. 2a₁₋₂ and 3). Interestingly, the increase of the annealing time to 5 min results in the increase of the average FCC grain size to ~6.0 μ m, but HCP phase fraction drops to ~14%. With further increasing the annealing time to 10, 15, 30 and 60 min, the average FCC grain size increases to ~8.5, ~12.5, ~15 and ~17.5 μ m, respectively, while the average fraction of HCP phase also gradually increases to ~16%, ~30%, ~31% and 36% according to EBSD analyses, respectively. The underlying mechanisms for the evolution of FCC grain size and HCP phase fraction in the DP-HEAs as well as their effects on deformation behavior will be discussed in the following sections.

All chemical elements in the as-homogenized CG DP-HEA are uniformly distributed, even at the phase boundaries [1]. To rule out the possibility of elemental segregation during the grainrefinement process [38], multiple types of probes, including BSEI, EBSD, EDS and APT, were performed on the grain-refined DP-HEAs. Fig. 4 shows the typical results corresponding to the DP-HEA with annealing time of 5 min. The BSE image, EBSD phase and IPF maps corresponding to a representative region (Fig. 4a) show the typical morphology of the dual-phase structure. The EDS maps for this region (Fig. 4b) show that there is no notable elemental partitioning at the grain-scale in the dual-phase structure.

To reveal the elemental distribution at nanometer scale, APT tips were lifted out from the boundary region as denoted in Fig. 4a [39,40]. The 3D atom maps of all elements (Fe, Mn, Co and Cr) in a typical tip (Fig. 4c) show that there is no apparent elemental segregation in the investigated volume. Furthermore, the frequency distribution analysis (Fig. 4d) shows that the binomial curves obtained from experiment match the curves obtained from a binomial simulation which corresponds to a random distribution. Several parameters were used to quantify the quality of the fit, as shown in the insert table in Fig. 4d. Specifically, the values of the normalized



Fig. 4. Elemental distribution in the grained-refined DP-HEA with annealing time of 5 min: (a) BSE image, EBSD phase and IPF maps with the same sample region. (b) EDS maps of all the elements with the identical region in (a). (c) 3D atom maps of all elements in a typical tip taken from the region marked in (a). (d) Frequency distribution analysis obtained both from observed experiment results and from binomial simulation. (e) 1D concentration profiles taken along the length direction of the tip shown in the inset.

homogenization parameter μ for all the four elements are close to 0, confirming the random distribution of elements [41]. Fig. 4e shows the 1D concentration of elements across the whole tip [42]. This profile analysis also shows a uniform distribution of all elements across the tip. The analysis further reveals that the tip has an overall composition of Fe_{49,45}Mn_{27,93}Co_{11.72}Cr_{10.90} (all in at. %), showing acceptable match to the bulk composition obtained from wetchemical analysis.

3.2. Mechanical behavior of dual-phase HEAs with various grain sizes and phase fractions

Fig. 5a shows the representative tensile stress-strain curves of the DP-HEAs with various FCC grain sizes and initial HCP phase fractions at room temperature. Fig. 5b presents the corresponding strain hardening response with respect to true strain. For comparison, the curves for recrystallized equiatomic $Fe_{20}Mn_{20}Ni_{20}$. $Co_{20}Cr_{20}$ HEA with single FCC phase reported in Ref. [2] are also shown in Fig. 5.

The ultimate tensile strength (σ_u) values of all the DP-HEAs with various grain sizes are significantly higher than those corresponding to the grain-refined equiatomic Fe₂₀Mn₂₀Ni₂₀Co₂₀Cr₂₀ HEA with single-phase FCC structure (Fig. 5a), although the later one shows a slightly higher yield strength (σ_y) value due to smaller grain size. Specifically, the σ_u and σ_y values of the as-homogenized DP-HEA with grain size of ~45 µm (and HCP phase fraction of ~28%) are ~730 and ~250 MPa, respectively. As the grain size was refined to ~15 µm (with initially available HCP phase fraction of ~31%), the average σ_u and σ_y values are ~830 and ~305 MPa, respectively, showing the expected improvement as compared to those of the

as-homogenized CG DP-HEA. The elongation to fracture is also improved from ~50% to ~63%.

Interestingly, as the grain size was refined to ~6 μ m, although the σ_y value was enhanced slightly, the σ_u value of the DP-HEA did not show any increase. This is related to the decrease of HCP phase fraction prior to deformation (to ~14%) and will be discussed later. As the average grain size was further refined to ~4.5 μ m (with initially available HCP phase fraction of ~32%), the σ_u value of the DP-HEA increased to 870 MPa. Simultaneously the elongation to fracture was enhanced to ~75%.

Fig. 5b shows the true stress and strain-hardening curves with respect to true stain. This analysis reveals that the improvements in strength discussed above correspond indeed to the higher strain-hardening capability of the DP-HEAs, particularly after the grain refinement. The as-homogenized CG DP-HEA exhibits significantly higher strain-hardening rate than the grain-refined equiatomic single FCC phase HEA over the entire plastic loading regime. Moreover, the strain-hardening rate of the DP-HEA is further substantially improved by grain refinement (Fig. 5b). The notable increase of strain-hardening ability in the DP-HEAs after grain refinement is related to the grain size dependence of the FCC phase stability and will be discussed below.

3.3. Microstructural evolution in dual-phase HEAs upon deformation

3.3.1. Microstructural evolution in as-homogenized coarse-grained dual-phase HEAs

The evolution of the deformation microstructure in the homogenized DP-HEA was investigated by XRD, EBSD and ECCI at four



Fig. 5. (a) Typical tensile stress-strain curves of the DP-HEAs with various FCC grain sizes and initially available HCP phase fractions. (b) True stress and strain-hardening rate with respect to true strain corresponding to the engineering stress-strain curves shown in (a).

deformation stages corresponding to local strain level of 10%, 30%, 45% (uniform deformation stages) and 65% (post-necking deformation regime), respectively.

Fig. 6 shows the analysis on different regions of the tensile tested sample carried out by XRD. In all regions, two phases are observed, i.e., FCC γ and HCP ϵ phases. Increasing strain leads to changes in the diffraction intensities, indicating a variation in phase volume fractions. Zoom-in images in Fig. 6b and c shows that with increasing strain, the intensities of $\gamma(111)$ and $\gamma(311)$ peaks decreased, while those of the $\epsilon(0002), \epsilon(10\bar{1}1)$ and $\epsilon(2\bar{1}12)$ peaks increased significantly, suggesting that the volume fraction of HCP ϵ phase increased at the expense of FCC γ phase during the deformation.

Quantitative information for the evolution of phases and other microstructural characteristics (e.g., LAGBs and twin boundaries) in the DP-HEA was obtained by EBSD. Fig. 7 shows the phase and 3rd nearest-neighbor kernel average misorientation (KAM) maps for regions with different local strain levels. The corresponding variations of fractions for phases, LAGBs and twin boundaries are summarized in Fig. 8, where the standard deviations were calculated based on the analysis of at least 3 EBSD mappings on the regions with identical local strain levels. The phase fractions obtained by XRD (see Fig. 6) are also summarized in Fig. 8. The trends of the phase fractions obtained by EBSD and XRD are consistent to each other (see Fig. 8).

With increasing local strain from 0 to 10%, the average fraction



Fig. 6. XRD analysis of the tensile tested DP-HEA: (a) XRD patterns for different regions with various local strain levels; (b) and (c) are zoom-in images qualitatively showing the phase transformation with increasing the local strain.



Fig. 7. EBSD (a₁-e₁) phase and (a₂-e₂) KAM maps showing microstructure evolution in the homogenized CG DP-HEA with increasing local strain level (0, 10%, 30%, 45%, and 65%) during tensile deformation. Mt, Md and TD refer to thermally induced martensite, deformation induced martensite, and tensile direction, respectively.

of the HCP ε phase obtained from EBSD increased from 28% to 46% (35–51 vol % according to XRD analysis). The average fraction of LAGBs in the FCC γ phase increased from 19% to 76%, while that for the HCP ε phase increased from 13% to 68%. The fraction of {111} annealing twin boundaries in the FCC γ phase decreased from 3.5% to 1.4%, while { $\overline{1210}$ } tensile twin boundaries (axis angle of 94.8°) with a fraction of approximately 1% appeared in the HCP ε phase. The 3rd nearest-neighbor KAM maps in Fig. 7a₂ and 7b₂ reveal that the KAM values increased throughout the early uniform deformation regime, preferably at internal interfaces inside and adjacent to the FCC γ phase regions. This suggests that plastic strain and lattice curvature was preferentially accommodated inside the FCC γ phase at this stage [43,44].

The trends continue upon further deformation to 30%. The KAM maps reveal increased average misorientation throughout the microstructure, suggesting that a larger portion of the microstructure contributes to plastic accommodation processes (Fig. 7c₂). The average fraction of HCP ε phase reached 70% (Figs. 7c₁ and 8); the average fraction of FCC LAGBs increased to 95%, while that for HCP ε phase increased to 80%. EBSD could not measure any FCC {111} twin boundaries anymore, whereas in the HCP phase { $\overline{1210}$ } tensile twin boundaries (~2%) and { $\overline{1210}$ } compression twin

boundaries (axis angle of 57°) (~1%) were detected. The observed high density of nano-twins and stacking faults in the HCP ε phase are clearly shown by ECC images (see Fig. 4b in Ref. [1]).

With further increasing local strain from 30% to 45%, the average fraction of HCP ε phase increased to 74% (Figs. 7d₁ and 8). Interestingly, the average fraction of LAGBs in the FCC γ phase did not increase, and in fact a slight decrease from 95% to 93% was observed (Fig. 8). The average fraction of LAGBs in the HCP ε phase decreased to 75%. This suggests that a certain part of LAGBs which formed during the early stages of deformation gradually evolved into HAGBs during the later uniform deformation stage. The average fraction of $\{\overline{1}2\overline{1}0\}$ tensile twin boundaries in the HCP ε phase increased to 3.1%, while the $\{\overline{1}2\overline{1}0\}$ compression twin boundaries did not show notable increase. The 3rd nearest-neighbor KAM map in Fig. 7d₂ shows further increase in misorientation, with only a small part of regions with relatively low KAM value in the map (as denoted as "Mt" in Fig. 7d₂). In the HCP ε phase at this stage, there are a number of slip lines caused by slip bands (where dislocations glide in the form of narrow microbands on the same or closely neighbored lattice planes), and a certain number of stacking faults and dislocations formed in the slip bands, as shown in Fig. 4b in Ref. [1].



Fig. 8. Evolutions of phase and boundary fractions in the homogenized CG DP-HEA obtained by EBSD analysis at different local strain levels.

With further increasing strain to 65%, localized necking occurred (see Extended Data Fig. 2 in Ref. [1]), yet, still approximately 19% FCC phase was retained (Figs. 7e₁ and 8). The average fraction of LAGBs in the retained FCC γ phase decreased to 90%, while that for the HCP ε phase decreased to 67% (Fig. 8). The average fractions of tensile and compression twin boundaries in the HCP ε phase did not notably increase. As shown in Fig. 4b in Ref. [1], a large number of slip lines and stacking faults in the HCP ε phase at this stage can be observed. The slip lines and stacking faults exhibit similar appearance, however, they can be distinguished by the feature that the sharp edge side of slip lines does not show the same pronounced contrast as the stacking faults do [26,45].

3.3.2. Microstructural evolution in grain-refined dual-phase HEAs

Fig. 9 shows the representative EBSD phase maps corresponding to various local strain levels in grain-refined DP-HEAs. Evidently the transformation from FCC to HCP phase is the primary deformation mechanism in all of the grain-refined DP-HEAs, which is similar to the case of as-homogenized CG DP-HEA described above. However, the values observed for the retained FCC phase fraction at a certain local strain level in different alloys differ, suggesting deviations in FCC phase stability among the different DP-HEAs. Fig. 10 summarizes the variations in the values of the retained FCC phase fractions with increasing local strain levels ($\varepsilon_{loc} = 0$, 40, 70 and 150%) in the various grain-refined DP-HEAs. It is worth noting that the local strains of 40% and 70% in the grain-refined DP-HEAs are corresponding to uniform deformation stages, while the local strain of 150% corresponds to the plastically instable stage which is characterized by the onset of necking, as shown in the inset in Fig. 10.

Fig. 11 shows the representative ECCI analysis results of grainrefined DP-HEAs at the local strain level of 40%. All of the grainrefined DP-HEAs show a high amount of deformation-induced HCP ε phase in laminate morphology, consistent with the EBSD results. The thicknesses of a large fraction of the HCP ε laminates are below 100 nm and their lengths generally can reach the size of their host FCC matrix grains. The formation mechanism of these HCP ε laminates in the grain-refined DP-HEAs is similar to that in the case of as-homogenized CG DP-HEA, which is related to the overlap of stacking faults [1].

4. Discussion

4.1. Micro-mechanisms and strain partitioning upon deformation

We first discuss the mechanisms of deformation in detail and also provide insights into the evolution of strain partitioning among the FCC and HCP phases at different deformation stages during room temperature tensile deformation. The CG DP-HEA in the ashomogenized state was selected as the representative case considering that the CG structure is more favorable for presenting the microstructural characteristics. This is also based on the observation that the basic sequence of microstructural evolution for DP-HEAs with different grain sizes is similar.

As shown above, the microstructure in the un-deformed CG DP-HEA consists of the FCC γ phase and HCP ε phase, where the specific fraction of the FCC γ phase is approximately three times of that corresponding to HCP ε phase. The CG DP-HEA was water-quenched after homogenization at 1200 °C, which suggests that the HCP ε phase was formed by thermally induced martensitic transformation during cooling. Moreover, a certain number of stacking faults, dislocations and annealing twins are present in the FCC γ phase as revealed by the ECCI analysis.

At the early stages of uniform deformation (e.g., local strain of 10%), regions with or adjacent to the FCC γ phase exhibit higher KAM values (Fig. 7b₂); whereas HCP ε phase regions showed less notable KAM values. Since the KAM value is associated with the density of geometrically necessary dislocations (GNDs) in the detected region [46], higher KAM values of the FCC γ phase regions suggests higher density of GNDs and more plastic strains in these zones. The above findings suggest that the plastic strain at this deformation stage was primarily accommodated by the FCC γ phase. EBSD analysis also reveals that the mechanically-induced transformation from FCC γ to HCP ε acts as the primary deformation mechanism (Figs. 7 and 8). Since the stacking faults are nuclei for the formation of the HCP ε phase as discussed above, a large number of stacking faults are supposed to have formed inside the FCC phase to realize the transformation from FCC to HCP phase at this stage. The reduction in the fraction of {111} annealing twin boundaries (can be referred to as de-twinning, see the inset in Fig. 8) at this stage is likely to be controlled by the kinetics of twin partial nucleation or shear transformation mediated by collective motion of twin partials during deformation [47].

With increasing strain (e.g., local strains of 30% and 45%), the strain driven transformation from FCC γ to HCP ε remains a prevalent deformation mechanism (Fig. 7c). Deformation induced twinning inside the HCP ε phase is also an important deformation mechanism during these loading stages (Fig. 8), and contributes to the work hardening of the alloy. Dislocations and stacking faults, often occurring in the form of slip bands inside the HCP ε phase, were also observed during the late uniform deformation stage as



Fig. 9. Representative EBSD phase maps showing the microstructure evolution with increasing local strain (ϵ_{loc}) in DP-HEAs with different FCC grain sizes and initially available HCP phase fractions: (**a**₁₋₄) 4.5 µm/32%; (**b**₁₋₄) 6 µm/14% and (**c**₁₋₄) 15 µm/31%.



Fig. 10. Variations of the values of retained FCC phase fractions with increasing local strain levels in the DP-HEAs with different FCC grain sizes and initially available HCP phase fractions. The standard deviations were calculated based on 3 large-area EBSD mappings on the regions with identical local strain levels. The inset shows the typical local strain distribution in a grain-refined DP-HEA sample at the stage prior to fracture.

revealed by ECCI (see Fig. 4b in Ref. [1]). These observations suggest that the deformation mechanisms in the HCP ε phase played an important role in the plastic deformation and inter-phase strain

accommodation of the alloy at the late uniform deformation stages. In terms of strain partitioning behavior at the medium and late uniform deformation stages, not only the FCC γ phase regions have higher KAM value, but most HCP phase regions also exhibits higher KAM values compared to the early uniform deformation stage (Fig. $7a_2-d_2$). This observation suggests that not only the FCC γ phase partitions the plastic strain but the HCP ε phase also accommodates a certain part of the applied load at these stages via the multiple deformation mechanisms discussed above. We find that a small fraction (<10%) of HCP ε phase did not show notable KAM values as revealed by the mark "Mt" in Fig. 7c₂ and 7d₂. These regions were observed to be the inner regions of large HCP ε grains formed during the water-quenching process prior to deformation. Generally the HCP phase is harder and less deformable than FCC phase as revealed in other alloys [48]. This explains that GND arrays are harder to form in the inner regions of large HCP ε grains.

After onset of necking (e.g., at a local strain of 65%), phase transformation from FCC γ to HCP ε proceeded further, leading to a relatively small fraction of retained FCC γ phase. In the HCP ε phase, except for deformation induced twinning and stacking faults, a high density of dislocations and slip lines in most regions of the HCP ε phase were observed by ECCI (see Fig. 4b in Ref. [1]). This means that the HCP ε phase was capable of accommodating further plastic straining through its multiple deformation mechanisms also at elevated strains. Similar to the medium and late uniform deformation stages, it was also observed that a small portion of HCP ε phase did not show significantly increased KAM values, as denoted by "Mt" in Fig. 7e₂. This suggests that GNDs did not extensively form in such spatially confined regions even in the post-necking deformation regime.

These observations show that the DP-HEA can accommodate loads through a set of deformation mechanisms, varying in contribution through the different deformation stages. During the early deformation stages, straining proceeds by transformation from FCC γ to HCP ε and the formation of stacking faults and



Fig. 11. Representative ECC images showing microstructures with local strain of 40% in DP-HEAs with various FCC grain sizes and HCP phase fractions prior to loading: (a₁₋₂) 4.5 µm/ 32%; (b₁₋₂) 6 µm/14% and (c₁₋₂) 15 µm/31%.

dislocation slip primarily inside the FCC γ phase. At later stages of deformation, mechanical twinning, dislocation slip and formation of stacking faults in the HCP ε phase are also activated. The evolution of these deformation mechanisms with increasing load leads to a dynamic strain partitioning behavior among the FCC and HCP phases at the different deformation stages. While the plastic strain is accommodated primarily by the FCC γ phase during the early straining stages; the HCP ε phase also carries a part of the applied strain at the later stages of deformation.

4.2. Grain size and phase fraction effects on mechanical behavior

We first discuss the grain size effect on the thermally induced HCP phase fraction during the grain refinement process. As shown in a former section, the FCC grain size gets gradually reduced with decreasing annealing time. However, the variation in the HCP phase fraction corresponding to the reduction of the FCC grain size was not monotonic, suggesting additional factors that influence the relationship between the FCC grain size and the thermally induced HCP phase fraction: First, since FCC grain boundaries have been known as the prime nucleating sites for HCP ε phase in other alloys [49,50], an increase in grain boundary area due to the decrease in FCC grain size increases the density of nucleation sites for the martensitic transformation from the FCC γ matrix to HCP ε phase. On the other hand, grain boundaries are relatively stable and hence the growth of HCP ε phase within an FCC γ grain would be restricted by the grain boundaries when the size of the HCP ϵ plate reaches a critical value [50]. In addition, the decrease in grain size is likely to result in an increase in back-stress [51], which may severely limit the growth of HCP ε nuclei [52]. These different aspects suggest that the specific effect of the FCC grain size on the martensitic transformation during quenching depends on a variety of mechanisms. According to the present study, the blocking effects of grain boundaries and back-stresses acting against the growth of HCP $\boldsymbol{\epsilon}$ plates are mainly responsible for the decrease of the average HCP phase fraction from 36 to 14% with decreasing average FCC grain size from 18 to 6 μ m, respectively (Fig. 3). Correspondingly, the promoting effect of the higher FCC grain boundary density on the nucleation of HCP ε martensite plays a key role for the increase of the HCP phase fraction with the decrease of the FCC grain size density (Fig. 3).

We next discuss the effects of grain size and initially available HCP phase fraction on the mechanical behavior of the DP-HEAs. First we reflect on the grain size effect: when the HCP phase fractions prior to loading are similar (e.g., around 30%), all tensile properties, namely, yield strength (σ_y), ultimate tensile strength (σ_u) and elongation to fracture gradually increase with decreasing the average grain size from 45 to 15 and further to 4.5 µm (Fig. 5a). The finer FCC grain size results in higher grain boundary strengthening as can be explained by the Hall-Petch effect [53,54]. This effect leads to the increase of the σ_y values. On the other hand, the decrease of the FCC grain size when maintaining similar HCP phase fractions prior to loading leads to the enhancement of the stability of the FCC matrix phase (as shown in Section 3.3.2), causing an increase in work hardening (Fig. 5b). This further leads to the increase of the σ_u values and of the elongation to fracture (ductility).

Second we discuss the effect of the initial HCP phase fraction prior to loading: when the average FCC grain sizes are similar (e.g., $4.5-6\,\mu$ m), both the strength and ductility grow with increasing the initially available HCP phase fraction from 14 to 32% (Fig. 5a). In fact, the increase of the initial HCP phase fraction when maintaining similar FCC grain size would also lead to the increase of the stability of the FCC matrix phase (see Section 3.3.2), thereby resulting in the increase of the work hardening capability (Fig. 5b) hence improving strength and ductility. Interestingly, the two alloys with average FCC grain sizes of 15 and 6 μ m, respectively, did not reveal significant differences in mechanical properties, although the later alloy shows much smaller grain size than the former one. This is due to the fact that the later alloy has an obviously lower HCP phase fraction prior to loading, which is consistent to the preceding discussion.

4.3. Insights for the design of strong and ductile HEAs

Since the first emergence of the HEA design concept [6,7], the majority of the research efforts in this field have focused on achieving single-phase solid solution HEAs and examining their microstructural characteristics as well as their mechanical properties [3,5,11–13,15–17]. The present work on mechanical behavior and corresponding deformation mechanisms of the recently introduced TRIP-DP-HEAs demonstrates the huge potential of dualphase (or controlled multiple-phase) microstructure design for the improvement in mechanical properties of HEAs. One particularly essential aspect in this context is not only the presence of more than one massive solid solution phase prior to deformation but also

the relative stability of these phases against athermal phase transformations which are stimulated by mechanical loading.

The corresponding insights obtained in this work can hence be understood by comparing the deformation behavior of the novel DP-HEA alloy class to that of single-phase HEAs previously investigated. Taking the typical five-component equiatomic FeMnNiCoCr Cantor HEA as a reference, the plastic deformation of this singlephase FCC HEA at room temperature is governed by the planar glide of 1/2110 dislocations and characterized by the formation of dislocation cell structures at higher strains [2,5]. Similar deformation mechanisms and structure evolution are also dominant in the non-equiatomic Fe37Mn45Co9Cr9 HEA with single FCC structure [18]. The similarity of the active deformation mechanisms in these single-phase HEAs limits their strain hardening capacity at large strains as well as the attainable strength-ductility combinations as shown in previous studies [2,5,18]. This is attributed to the fact, that high ductility of strong metallic FCC structured alloys can be obtained when different deformation mechanisms are sequentially activated during ongoing loading such as the additional activation of twinning at higher deformations in TWIP steels [33,55,56]. Such additional strain hardening mechanisms compensate at larger deformation for geometrical softening and for the exhaustion of the preceding prevalent dislocation strain hardening. Similar argumentation holds for the transformation induced plasticity effect (TRIP) [24,57,58]. Both phenomena, i.e. TWIP and TRIP, can be actually best tuned not by achieving the highest possible entropydriven thermodynamic stability of the host FCC phase but instead by its instability, rendering it amenable for athermal transformation mechanisms [59-62].

Indeed, in the present study, the dual-phase structure of the $Fe_{50}Mn_{30}Co_{10}Cr_{10}$ HEA introduces the TRIP effect and other associated multiple deformation mechanisms (as discussed in Section 4.1), which enables a significant improvement of the strain-hardening capacity and strength-ductility combinations. Therefore, we suggest that the introduction of multiple deformation mechanisms which are activated gradually or respectively sequentially during loading is a future key route for the design of HEAs with advanced mechanical properties. Such design concept can include dual- or multi-phase alloys with multiple principle elements, rather than being restricted artificially to one single massive solid solution phase material.

It should be emphasized that to form such a DP-HEA, the constituent elements should best be uniformly partitioned in the dualor multi-phase structure (see Fig. 4 for example) or be at least partitioned in such a way that all phases have a high solid solution content. This was not achieved in former studies where multiphase structures were rather formed by elemental segregation and precipitation which finally led to the occurrence of undesired brittle intermetallic compounds [8,63]. From this point of view, the partial athermal deformation-driven phase transformation without associated chemical gradients across phase boundaries as observed in this study is likely to be a well suited approach for producing "genuine" multi-phase HEAs with uniformly distributed multiple principle elements.

In this regard, except for the TRIP effect and other multiple deformation mechanisms which can be employed to improve the strain-hardening capacity and strength-ductility combinations in dual- or multi-phase HEA, the solid solution strengthening effect is also worth noting when considering the strength of the material [64]. According to the study by Remy et al. [65], the room temperature yield strength of Fe-30Mn (at.%) binary alloy processed by homogenization and water-quenching is approximately 120 MPa; whereas the value corresponding to the homogenized Fe₅₀Mn₃₀. Co₁₀Cr₁₀ DP-HEA studied herein with the identical processes and grain size is approximately 230 MPa. This significantly improved

yield strength in the present HEA confirms the importance of solid solution strengthening through the effect of the alloying elements Co and Cr. In the future design of HEAs, alloying systems exhibiting higher solid solution strengthening effects may also be explored. On the other hand, when studying HEA systems with significant solid solution strengthening effects, alloying cost is also an important factor to be considered when addressing practical applications. It is evident that the non-equiatomic Fe₅₀Mn₃₀Co₁₀Cr₁₀ HEA studied herein has lower alloying cost compared to the typical five-component equiatomic Cantor-type FeMnNiCoCr HEAs. Therefore, the design concept of non-equiatomic HEAs is also promising for exploring HEAs at reduced alloying costs.

Furthermore, as discussed above, grain size and phase fraction show significant effects on the deformation behavior [66] and substantial improvements in strength and ductility can be simultaneously achieved through grain-refined DP-HEAs compared to their CG as-homogenized counterparts (Fig. 5a). This suggests that microstructural design of strong and ductile DP-HEAs can be further improved through adequate thermo-mechanical processing.

5. Conclusions

In this work, systematic microstructural-mechanical investigations of the newly designed TRIP-DP-HEAs with various FCC matrix grain sizes and initially available HCP phase fractions were presented. Deformation mechanisms and strain partitioning behavior in the DP-HEAs during room temperature tensile deformation were revealed in detail. The effects of FCC matrix grain size and HCP phase fraction prior to loading on the mechanical behavior were discussed. The main conclusions are as follows:

- (1) Both, in as-homogenized and grain-refined state, the newly developed $Fe_{50}Mn_{30}Co_{10}Cr_{10}$ HEA consists of two phases (namely, FCC γ matrix and laminate HCP ε phase) with a high density of stacking faults in the FCC matrix. Prior to and following grain refinement, no apparent elemental segregation was observed both at grain scale and near-atomic scale as revealed by EDS and APT, respectively.
- (2) The DP-HEA exhibits multiple deformation mechanisms and dynamic strain partitioning behavior. At early stages of deformation, the plastic strain is accommodated primarily by the softer and less confined FCC γ matrix. The corresponding deformation mechanisms include displacive transformation from FCC γ to HCP ε , formation of stacking faults and dislocation slip in the FCC γ phase. At later stages of deformation, additional mechanical twinning, dislocation slip and formation of stacking faults in HCP ε phase are also activated as important deformation mechanisms. This shows that the HCP ε phase also partitions a certain portion of the imposed load.
- (3) The strength-ductility combinations of the DP-HEAs with various FCC grain sizes and initially available HCP phase fractions are superior to that of the grain-refined equiatomic single-phase Cantor-type Fe₂₀Mn₂₀Ni₂₀Co₂₀Cr₂₀ HEA. Mainly due to the improvement of the stability of the FCC matrix, both strength and ductility of the DP-HEAs increase with decreasing the average grain size when retaining a similar HCP phase fractions prior to loading. Both properties simultaneously improve with increasing the initially available HCP phase fraction at similar average FCC grain sizes.
- (4) Future HEAs design concepts can be extended to dual- or multi-phase alloys where each of the coexisting phases consists of multiple non-equiatomic principle elements. Microstructural design for a given composition through

thermal-mechanical processing is promising for further improvement of mechanical properties.

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