Overcoming the strength-ductility trade-off via the formation of nanoscale Cr-rich precipitates in an ultrafine-grained FCC CrFeNi medium entropy alloy matrix

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ABSTRACT
FCC high- and medium-entropy alloys (HEAs and MEAs) have demonstrated high ductility and fracture toughness, but suffer from low strength. To overcome such strength-ductility trade-off, here, we present a strategy via the formation of a high density of nanoscale precipitates in an ultrafine-grained (UFG) FCC matrix. To realize this concept, we selected a cost-effective equiatomic CrFeNi MEA as our model system. The equimolar elemental powder mixture was first forced into the formation of a nanostructured supersaturated FCC solid solution, followed by densification via spark plasma sintering (SPS). During SPS, a high density of nanoscale Cr-rich precipitates were formed in the UFG FCC matrix (821 nm). Such a particular microstructure enabled the alloy to overcome the strength-ductility trade-off, with a high tensile strength of 826 MPa and elongation of 26%. Grain boundary strengthening and precipitation strengthening were found to be the main strengthening mechanisms. These results provide deep insight into the design of novel multi-principal element alloys with high strength and ductility for structural applications.

1. Introduction
Differing from the conventional alloy design strategy with only one or two principal elements, high- or medium-entropy alloys (HEAs or MEAs) with multi-principal elements offer a novel design concept to attain outstanding mechanical properties [1,2]. Among the HEAs/MEAs, the family of CoCrFeMnNi Cantor alloy with single-phase FCC structure have been widely investigated, owing to their outstanding ductility and exceptional fracture toughness at room or lower temperatures [3–6]. However, due to the limited contributions of ‘severe lattice distortion’ and the incoherent solid solution strengthening [7,8], the coarse-grained (grain size d > 1 μm) FCC HEAs/MEAs always show high ductility, but suffer from low yield strength (usually below 400 MPa [9,10]) at room temperature, which hinder their practical structural applications.

To strengthen the FCC HEAs/MEAs, various mechanisms have been developed, including phase-transformation strengthening [11,12], precipitation strengthening [13–17], heterogeneous grain structure design [18,19], grain boundaries tailoring (containing both grain size reduction and complexion engineering) [20–24], and load transfer via the introduction of strong phases [25]. These strategies indeed significantly increased the yield strength of FCC HEAs/MEAs, but are often accompanied by the reduction of ductility due to the constrained dislocation activity [21,26,27] or required complex thermo-mechanical processing routes [28–30]. Therefore, overcoming the strength-ductility trade-off of FCC HEAs/MEAs remains a great challenge.

In this context, we aim to develop a strategy to overcome the strength-ductility trade-off of FCC MEAs via the formation of nanoscale precipitates in an ultrafine-grained (UFG) FCC MEA matrix. To achieve this goal, we selected a ternary equiatomic CrFeNi MEA as our model system for the following two reasons: 1) the more costly element Co and the element Mn with a high vapor pressure were removed from the classical Cantor alloy [2]; and 2) the calculated phase diagram of CrFeNi predicted the formation of FCC + BCC binary phases [31], which can offer precipitation strengthening for the FCC matrix. The bulk CrFeNi MEA was fabricated using a combination of mechanical alloying and spark plasma sintering (SPS). The microstructure of the obtained CrFeNi MEA consisted of an UFG FCC matrix and a high
density of uniformly dispersed nanoscale Cr-rich precipitates. This particular microstructure enabled the alloy to achieve a good combination of high strength and ductility. Finally, we rationalized the formation of the hierarchical structure and quantitatively analyzed the strengthening mechanisms.

2. Experimental

2.1. Fabrication of bulk UFG CrFeNi MEA

Elemental powders of chromium, iron, and nickel were mixed with an equal atomic ratio. The mixed powder and hardened steel balls with the weight ratio of 1:5 were loaded into a hardened steel vial and subjected to high-energy ball milling (SPEX 8000D Mixer/Mill, SPEX SamplePrep LLC, USA) at room temperature (RT, 25 ± 1 °C) in an argon-filled glove box for 12 h. To investigate the forced chemical mixing of the ternary powder, a small amount of the powder was collected after ball milling for different times and analyzed using X-ray diffraction (XRD). The 12-h-milled powders were then compacted into bulk using an SPS system (SPS-211 Lx, Fujidempa Kogyo. Co., ltd., Japan) at a temperature of 1100 °C and pressure of 30 MPa in a vacuum for 5 min, producing cylinders with densities exceeding 98% of the theoretical density.

2.2. Materials characterization

The phase formation of the ball-milled powders and the as-compact ed bulk samples were identified using XRD (Rigaku Smartlab-9 kW, Japan) in the 2θ range of 30°–90° using Cu-Kα radiation (λ=1.54056Å, 45kV, 200mA) with a step size of 0.01° and a scan rate of 10° min⁻¹. The microstructure of the as-sintered bulk CrFeNi MEA were first examined using a scanning electron microscope (SEM; MIRA 3, TESCAN, Czech Republic) in backscattered electron (BSE) imaging mode. The chemical composition was determined using energy dispersive X-ray spectroscopy (EDX; AZtec EDX system with an X-MaxN 50 mm² silicon drift detector, Oxford Instruments, UK) equipped in SEM. The grain size and phase distribution were investigated using electron backscatter diffraction (EBSD; Oxford Nordlys Max²). More detailed microstructural and chemical information were obtained using transmission electron microscopy (TEM) and high-anular dark-field scanning TEM (HAADF–STEM) with equipped EDX. All the TEM samples were prepared using the focused ion beam (FIB; Helios NanoLab™ 600i, FEI, USA) standard lift-out technique and examined using an FEI Tecnai G2 F30 TEM/STEM operated at 300 kV and an FEI Talos F200X TEM operated at 200 kV. A protective platinum strip with a thickness of ~1 μm was deposited on the surface before the FIB milling.

2.3. Mechanical testing

The strength and ductility of the as-sintered bulk CrFeNi MEA were measured using uniaxial tensile tests. Dog-bone-shaped tensile specimens with a gauge length of 4 mm, a gauge width of 2 mm, and thickness of 1 mm were cut from the as-sintered cylinders using electrical discharge machining (EDM). The tensile tests were performed at a strain rate of 1 × 10⁻⁴ s⁻¹ at RT, using a universal testing machine (CMT5105, MTS system Co., Ltd., Shanghai, China). A fine black speckle pattern was painted on a white undercoat on the test section to enable monitoring the deformation during the test using 2-D stereo Digital Image Correlation. The yield strength (σy), ultimate tensile strength (σUTS), and elongation to failure (εf) were determined from the uniaxial tensile stress-strain curves. Three samples were tested to confirm the reproducibility and a representative curve was provided.

3. Results

3.1. Phase and microstructure

The powder XRD patterns in Fig. 1 show the phase evolution that occurred during the ball milling process. After 12 h of ball milling, the characteristic reflections of BCC Cr and Fe completely vanished and the reflections of FCC Ni shifted to smaller 2θ angles, confirming that the starting equiatomic Cr, Fe, and Ni powder mixture was forced into forming an FCC CrFeNi solid solution. The lattice constant was determined to be 0.359 nm, which is slightly larger than that of pure Ni (a = 0.352 nm). This FCC solid solution powder was then consolidated into bulk using SPS.

The bulk CrFeNi alloy predominantly preserved the FCC structure, as revealed by its sharp and intense diffraction peaks (Fig. 2a). In addition to the FCC matrix, a minor amount of Cr-rich precipitates was also detected, as marked at 2θ = 39.1° and 44.2°. The backscattered (BSE) image in Fig. 2b further reveals that in addition to the FCC matrix and Cr-rich precipitates (~2.43 vol%) detected in the XRD pattern, the fabricated bulk CrFeNi MEA also contained a minor amount (~0.93 vol%) of Cr-oxide nanoparticles (dark contrast). The Cr-rich precipitates were located at both the grain boundaries and grain interior of the FCC matrix. EDX analysis (Fig. 2c) shows that the FCC matrix phase consisted of 32.2 at.% Cr, 34.7 at.% Fe and 33.1 at.% Ni, which deviates slightly from the input equiatomic ratio, and the Cr-rich phase consisted of 79.9 at% Cr, 12.9 at.% Fe and 7.2 at.% Ni. The grain size and orientation of the FCC matrix were analyzed using EBSD (Fig. 2d). Statistical measurements revealed that the FCC matrix had an average grain size (d_{50-90}) of 821 nm, with ~80% of the grains having sizes smaller than 1 μm (Fig. 3a). Twins were present in some of the FCC matrix grains because of the low stacking fault energy of FCC HEAs [32]. Note that the EBSD analysis failed to resolve the small Cr-rich precipitates and Cr-oxides because of its resolution limitation. Thus, the distribution of the Cr-rich precipitates and Cr-oxides were analyzed using TEM and HAADF–STEM with equipped EDX.

To illustrate the microstructure in detail, particularly the size and distribution of Cr-rich precipitates and Cr-oxides, we also performed TEM and HAADF–STEM characterization of the bulk CrFeNi MEA (Fig. 4). Statistical size measurements over 480 Cr-rich precipitates from several HAADF–STEM and BSE images indicated that the size of the Cr-rich precipitates ranged from several nanometers to submicron...
scale with an average size of 69 nm and ~75% of the precipitates had sizes smaller than 20 nm (Fig. 3b). The intergranular Cr-oxide particles exhibited a much larger average size of 210 nm, with sizes ranging from 50 to 530 nm (Fig. 3c). The EDX elemental maps in Fig. 4c clearly confirmed the composition of the Cr-oxides. Quantitative EDX analysis confirmed that the Cr-oxides were Cr$_2$O$_3$. A schematic illustration of the microstructure of the bulk CrFeNi MEA is presented in Fig. 4d, which shows that hierarchical structure of the alloy consisting of a submicron-scale FCC matrix, a high density of nanoscale Cr-rich precipitates, and a minor amount of intergranular Cr-oxide nanoparticles.

### 3.2. Mechanical properties

Fig. 5 a–b present a representative tensile stress-strain curve and corresponding fractograph at RT, respectively. The fabricated UFG CrFeNi MEA exhibited high yield strength ($\sigma_y$) of 640 MPa, ultimate tensile strength ($\sigma_{UTS}$) of 826 MPa, tensile ductility (strain to failure, $\varepsilon_f$) of 26%, and Young’s modulus of 180 GPa. The fracture surface reveals ductile dimpled fracture by submicron-void coalescence. The average size of the voids was 630 nm. Inside the voids of the fracture surface, Cr-oxide particles with an average size of ~200 nm were observed. These Cr-oxide particles acted as initiation sites for the submicron voids. This observation is in line with the fractographs of CoCrFeMnNi HEA [3] and CrCoNi MEA [6], which exhibit exceptional damage-tolerance at cryogenic temperatures. The hardness of the as-fabricated alloy was determined to be 267.0 (± 3.9) HV.

### 4. Discussion

#### 4.1. Formation of the hierarchical structure

We first rationalized the formation of the hierarchical structure of the present UFG MEA CrFeNi. It is generally difficult to predict the phase selection in HEAs using the theoretical equilibrium thermodynamic method [33]. However, based on Hume–Rothery rules and thermodynamic parameters used to predict solid-solution phase formation in HEAs, the following empirical rules have been developed to understand the phase stability of HEAs [34,35]: 1) atomic size difference ($\delta_r \leq 6.6\%$); 2) average valence electron concentration (VEC ≥ 8 for FCC); 3) mixing enthalpy ($-15 \text{kJ/mol} < \Delta H_{\text{mix}} < 5 \text{kJ/mol}$); and 4) the parameter $\Omega$ expressed by $T_m \Delta S_{\text{mix}}/|\Delta H_{\text{mix}}|$ ($T_m$ is the average melting temperature and $\Delta S_{\text{mix}}$ is mixing enthalpy) ($\Omega \geq 1.1$). For the
The present equiatomic CrFeNi alloy, $\delta_c$, VEC, $\Delta H_{\text{mix}}$, and $\Omega$ are 0.267%, 8, $-4.4 \text{ kJ/mol}$, and 3.36, respectively, which appear to fulfill the empirical criteria for solid-solution phase formation. However, Guo et al. [35] also pointed out that at the boundary VEC = 8.0, sometimes BCC phases also form but are minor phases. Both the experimentally determined and calculated equilibrium phase diagrams of the Cr–Fe–Ni ternary system indicate the presence of a single FCC phase between 927 °C and 1400 °C, below which FCC + BCC coexist [31,36,37]. A systematic investigation of the phase stability of the subsystems of the Cantor alloy also revealed that the cast equiatomic CrFeNi MEA after homogenization at 1200 °C followed by water quenching contains only the single-phase FCC solid solution; however, after cold rolling and annealing, an additional BCC phase was present [38]. In this study, severe plastic deformation (SPD) during high-energy ball milling drove the system far from equilibrium and led to the formation of a nanocrystalline supersaturated solid solution. At the sintering temperature of 1100 °C, the single-phase FCC solid solution should be present. However, during cooling, when the temperature was decreased below 927 °C, solutes (mainly Cr) precipitated to reduce the total free energy of the system. The formation of BCC Cr-rich precipitates was also observed in the annealed Cantor alloy after SPD [21] and in annealed CrFeNi fabricated by casting [39]. Precipitation at grain boundaries occurs preferentially compared with that within grains because of the reduced energy barrier for heterogeneous nucleation and higher self-diffusion coefficient at the grain boundaries [40]. However, because of the fast cooling rate of SPS (approximately 100 °C/min) and sluggish diffusion in MEA, the primary FCC phase was preserved and Cr-rich precipitates were also formed inside the FCC-matrix grains. Oxide nanoparticles are typically formed when alloys contain reactive elements such as Cr, V, Mn and Ti, even in cast HEAs [3,6,41].

### 4.2. Strengthening mechanism

The FCC HEAs often exhibit high ductility but suffer from low strength. However, a comparison with other reported subsystems of the Cantor alloy [4,6,10,25] and CrFeNi-related MEAs/HEAs [25,42–47] (Fig. 6) indicates that our present UFG MEA CrFeNi offers an excellent combination of tensile strength and ductility. We then analyzed the origin for this excellent combination of high tensile strength and ductility combination. In general, these properties arise from the hierarchical structure produced by mechanical alloying and SPS. Specifically, the yield stress ($\sigma_y$) of the present CrFeNi alloy should include the intrinsic lattice friction stress to dislocation motion ($\sigma_0$) and incremental contributions from the solid solution strengthening of the

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**Fig. 4.** Microstructure of as-fabricated bulk CrFeNi MEA. (a) and (b) are bright-field TEM and corresponding HAADF–STEM images, respectively; (c) EDX elemental maps of the representative oxide particle in (b), with scale bar of 100 nm; (d) a schematic diagram demonstrating the hierarchical structure of the alloy.

**Fig. 5.** A representative tensile stress–strain curve (a) and corresponding fractograph (b) of CrFeNi MEA.
equiatomic elements ($\Delta \sigma_{ss}$), ultrafine grains (grain boundary strengthening, $\Delta \sigma_{gb}$), Cr-rich precipitates ($\Delta \sigma_{p}$) and Cr-oxides strengthening ($\Delta \sigma_{o}$).

$$\sigma_f = \sigma_0 + \Delta \sigma_{ss} + \Delta \sigma_{gb} + \Delta \sigma_{p} + \Delta \sigma_{o}$$  \hspace{1cm} (1)

The measurement of solid solution strengthening is limited to the traditional dilute alloy system, where dislocation motion is impeded by the strain field arising from the mismatch between the solute and solvent [15]. However, for the present equiatomic MEA, the 'solute' lattice and 'solute' atoms are indistinguishable, assuming that the constituent atoms in the matrix are randomly arranged in the FCC lattice. Thus, the equiatomic alloys are more akin to a stoichiometric compound with fixed atomic ratio, albeit disordered, than a traditional dilute solid solution [10]. Taking this view, it is reasonable to fold the solid solution strengthening term ($\Delta \sigma_{ss}$) in Eq. (1) into the lattice friction term ($\sigma_0$), and then the new lattice friction stress ($\sigma_f$) represents some 'average' resistance offered by all the constituent atoms rather than a single type of solvent atom. According to the classical Hall–Petch equation, the third term, grain boundary strengthening can be expressed by $\Delta \sigma_{gb} = k d^{-1/2}$, where $k$ is the strengthening coefficient (Hall–Petch slope) and $d$ is the average grain size. Then, Eq. (1) can be revised to:

$$\sigma_f = \sigma_0 + k d^{-1/2} + \Delta \sigma_{p} + \Delta \sigma_{o}$$  \hspace{1cm} (2)

Wu et al. [38] investigated the Hall–Petch slopes of various equiatomic subsystems of the Cantor alloy, and their results indicated that $k$ was in range of 110–200 MPa ($\mu$m)$^{-1/2}$. The present CrFeNi MEA has an UFG microstructure with $d = 0.821 \mu$m, which may lead to an increase of 100–180 MPa in the yield strength. Precipitation strengthening occurs by shearing or the Orowan bypass mechanism, depending on the precipitate size, coherency, antiphase boundary energy, strength, and modulus of the precipitates. The shearing mechanism dominates when the precipitates are small and coherent to matrix, whereas the Orowan mechanism dominates when the precipitates are incoherent [48]. In this study, the size of the Cr-rich precipitates was scattered over a wide range and we observed that the nanoscale Cr-rich precipitates showed no appreciable coherency, thus, Orowan mechanism should dominate in the present system. The Orowan strengthening can be calculated using the Ashby-Orowan equation [49]:

$$\Delta \sigma_{p} = 0.538 \frac{G b \rho^{0.5}}{D_p} \left( \frac{D_p}{2 b} \right)$$  \hspace{1cm} (3)

where $G$ and $b$ are the shear modulus and Burgers vector of the alloy matrix, respectively, and $D_p$ and $\rho$ are the size and volume fraction of the precipitates, respectively.

$$\Delta \sigma_{gb} = \frac{G b}{2 \pi} \frac{d_0}{h} \ln \frac{d_0}{2 b} \left( \frac{d}{d_0} \right)^{5/2}$$

To calculate $\Delta \sigma_{gb}$, the average diameter of the precipitates ($D_0 = 69 \text{nm}$) measured from the intersection plane using the equation $D_p = (3/2)^{1/2} D_0$.

To calculate the incremental contribution from the precipitation strengthening $\Delta \sigma_{p} = \sim 89 \text{MPa}$. The load-bearing strength increase resulting the presence of the large intergranular oxide particles was calculated using a simple model for particulate-reinforced metal matrix composite [50,51]:

$$\Delta \sigma_{p} = 0.5 f_p \sigma_m$$

where $f_p$ is the volume fraction of the oxide particles ($=0.93\%$) and $\sigma_m$ is the yield strength of the matrix which is equal to the sum of the first two terms in Eq. (2). The estimated incremental contribution from Cr-oxide strengthening, $\Delta \sigma_{o}$, is only $\sim 2 \text{MPa}$. Note that the strengthening effect induced by thermal expansion mismatch between the particle and matrix is negligible because high-temperature densification via SPS has removed most of the mismatch dislocations. The above quantitative analysis demonstrated that the high tensile yield strength mainly originated from the UFG microstructure of the matrix and the uniformly dispersed high density of nanoscale Cr-rich precipitates.

5. Conclusions

We have demonstrated a strategy via the formation of nanoscale precipitates in an ultrafine-grained (UFG) FCC matrix to overcome the strength-ductility trade-off. The starting equiatomic Cr, Fe, and Ni powder mixture was forced into the formation of a single-phase FCC CrFeNi supersaturated solid solution after 12 h of ball milling. The 12 h-ball milled powder was then spark plasma sintered into bulk alloy. The fabricated bulk CrFeNi MEA consisted of an UFG FCC matrix with a high density of nanoscale Cr-rich precipitates ($\sim 2.43 \text{vol}\%$) and a minor amount of intergranular Cr-oxide nanoparticles ($\sim 0.93 \text{vol}\%$). The formation of the hierarchical structure was discussed. The alloy with this particular microstructure showed an excellent combination of high tensile strength of 826 MPa and elongation of 26%. The strengthening mechanisms were quantitatively analyzed and the results showed that grain boundary strengthening and precipitation strengthening were the two main contributions to the obtained yield strength. The present cost-effective CrFeNi MEA with an excellent combination of high tensile strength and ductility could be a promising candidate for structural applications.

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Appendix A. Supplementary data

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References


