CALPHAD-aided design of high entropy alloy to achieve high strength *via* precipitate strengthening

Lin Guo¹, Ji Gu^{1*}, Xing Gong², Song Ni¹ and Min Song^{1*}

ABSTRACT Designing high entropy alloys (HEAs) with high strength and excellent ductility has attracted extensive scientific interest. In the present work, the CALPHAD (calculation of phase diagrams) method was applied to guide the design of an $(\text{FeCoNi})_{92}\text{Al}_{2.5}\text{Ti}_{5.5}$ HEA strengthened by precipitation hardening. The grain size as well as the size and volume fraction of the precipitates was tailored *via* a thermo-mechanical process to optimize the mechanical properties. The uniformly dispersed nano-precipitates are $\text{Ni}_3(\text{Al,Ti})$ -type precipitates with an $L1_2$ ordered structure presenting a fully coherent interface with the face-centered cubic (FCC) matrix. The yield strength of the alloy increases from 338.3 to 1355.9 MPa and the ultimate tensile strength increases from 759.3 to 1488.1 MPa, while the elongation maintains a reasonable value of 8.1%. The striking enhancement of strength is mainly caused by the precipitate's hardening mechanism, which is evaluated quantitatively by various analytical models. The deformation-induced microbands and the coherent precipitates sheared by dislocations are the deformation and strengthening mechanisms contributing to the superior combination of ductility and strength in the present HEA. This investigation demonstrates that the CALPHAD method is beneficial to the design and optimization of HEAs.

Keywords: high entropy alloys, CALPHAD, precipitation, mechanical properties, dislocations

INTRODUCTION

High entropy alloys (HEAs), as a new class of metallic materials, are designed based on the strategy of maximizing the mixing configurational entropy, and have attracted considerable attention due to their promising properties [1–6]. The face centered cubic (FCC) HEAs display a superb ductility but normally a low strength, which can hardly meet the demands for practical structural applications [4,6]. Therefore, designing HEAs with

both high strength and good ductility is essential. Several strengthening mechanisms, such as interstitial-solid-solution strengthening [7–9], phase-transformation strengthening [10], grain-boundary strengthening [11], and precipitations strengthening [2,4,5], have been successfully applied to strengthen the FCC-based HEAs. Second-phase intermetallic compounds (IMCs) contribute significantly to the alloy properties and offer an efficient approach to enhance the strength of HEAs [12]. Thus, developing precipitation-strengthened HEAs is a promising approach for achieving high strength with good ductility. Two different types of precipitates, including intermetallic particles (μ , σ phase) [5,13] with incoherent phase boundaries to the matrix and coherent γ' phase particles with an $L1_2$ superlattice structure [2,4], are used to develop precipitation-strengthened HEAs. The intermetallic particles strengthen the HEAs *via* the Orowan mechanism due to the hard and incoherent features, which results in high strength but low ductility [6]. On the other hand, the strengthening mechanism of the fine γ' phase is dominated by the particle shearing mechanism, and thus, the γ' phase can efficiently enhance the strength of the material without severely sacrificing its ductility [2,4]. The Ni_3Al -type γ' phase has been found to be an important strengthening phase in FCC-based HEAs, which could achieve a good balance between ductility and strength [2,4].

The key advantage of HEAs is that they provide almost infinite possibilities in designing alloys. While characterizing all candidate alloys is time-consuming and realistically impossible, the well-developed CALPHAD method offers an option to greatly accelerate the alloy designing process; for example, Zhang *et al.* [14] applied the CALPHAD method to design Nb-bearing austenitic steels with optimized contents of added C and N. The effects of alloying element, Nb, on the phase constitution

¹ State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, China

² College of Physics and Optoelectronic Engineering, Shenzhen University, Shenzhen 518060, China

* Corresponding authors (emails: guji9219@csu.edu.cn (Gu J); msong@csu.edu.cn (Song M))

in $\text{Nb}_x(\text{NbTiZr})_{100-x}$ quaternary alloy systems was also identified by the CALPHAD approach [15]. He *et al.* [16] used the CALPHAD approach to predict the phase diagram of the $(\text{CoCrFeNi})_{100-x-y}\text{Ti}_x\text{Al}_y$ (at.%) alloy system, and the predicted data agreed well with the experimental results.

In the present work, we integrated the CALPHAD-prediction and experimental-validation approaches to design precipitation-strengthened HEAs. To optimize the strength and ductility in precipitation-strengthened HEAs, the grain size as well as the size and volume fraction of the precipitates was tailored through a thermo-mechanical process. The coherent $L1_2$ nano-precipitate is uniformly distributed in the FCC matrix after the proper thermo-mechanical process. The present work demonstrates that the CALPHAD method can aid the design of precipitation-strengthened HEAs to achieve high yield strength and ultimate tensile strength (UTS) while maintaining a reasonable ductility.

EXPERIMENTAL SECTION

In the present study, the CALPHAD method was applied to guide alloy design. The phase diagram of $(\text{FeCoNi})_{92}\text{Al}_{2.5}\text{Ti}_{5.5}$ was firstly calculated using the Thermo-Cal software with the ThermoTech Ni-based database TTNI8 to guide the thermo-mechanical process and obtain a proper number of γ' precipitates, as shown in Fig. 1. The Ni_3Al -type γ' phase was chosen as the strengthening phase. A certain amount of Fe and Co can dissolve into the Ni_3Al -type γ' phase, which help to enhance the intrinsic ductility of the γ' phase. Since Al and Ti are the γ' -phase-forming elements [4], a certain amount of Al and Ti were added to the equiatomic FeCoNi alloy to form the γ' phase.

The ingots with a nominal chemical composition of $(\text{FeCoNi})_{92}\text{Al}_{2.5}\text{Ti}_{5.5}$ (at.%) were prepared by arc-melting high purity Fe, Co, Ni, Al, and Ti (above 99.8%) under Ar atmosphere. The actual chemical composition is shown in Table 1, analyzed by inductively coupled plasma mass spectroscopy (ICP-MS). The as-cast alloy was homogenized at 1200°C for 4 h, followed by various thermo-mechanical procedures to obtain four kinds of specimens (designated as T1, T2, T3, and T4, respectively) with different grain sizes and different volume fractions and sizes of the precipitates. The T1 specimen was cold-rolled to a 60% reduction in thickness, followed by annealing at 1150°C for 10 min to obtain coarse-grained structures without precipitates. The T2 and T3 specimens were initially cold-rolled to an 85% reduction in thickness and subsequently annealed at 1150°C for 3 min. Then, the

Figure 1 Phase diagram of the $(\text{FeCoNi})_{92}\text{Al}_{2.5}\text{Ti}_{5.5}$ HEA calculated using Thermo-Cal software and the TTNI8 database.

Table 1 Chemical compositions and the basic properties of the elements [17] in $(\text{FeCoNi})_{92}\text{Al}_{2.5}\text{Ti}_{5.5}$ alloy

Element	Fe	Co	Ni	Al	Ti
at.%	33	28.8	30.3	2.5	5.4
Atomic radius (Å)	1.241	1.253	1.246	1.434	1.429
Melting temperature (°C)	1535	1495	1453	660	1660

annealed specimens were aging treated at 800 and 750°C for 1 h, respectively. The T4 specimen was initially cold-rolled to an 85% reduction in thickness and subsequently annealed at 970°C for 0.5 min. Then, the annealed specimens were aging treated at 750°C for 1 h. The detailed processing conditions and the grain size of the four specimens are shown in Table 2. All the thermo-mechanical procedures were performed in air and followed by water quenching. Doge-bone-shaped specimens with a gauge length of 24 mm were machined for the tensile tests. The surfaces of the tensile samples were grounded from 180 to 2000 grit using silicon carbide paper. The tensile tests were performed using an Instron 3369 testing machine with a strain rate of $1.4 \times 10^{-3} \text{ s}^{-1}$ at room temperature.

The phase constitution was identified by X-ray diffraction (XRD) (a Dmax 2500VB equipment) using $\text{Cu K}\alpha$ radiation. Microstructure characterizations were performed using a scanning electron microscope (SEM, FEI Helios NanoLab G3 UC) equipped with an electron backscatter diffraction (EBSD) detector and a transmission electron microscope (TEM, Tecnai G2 F20 operating at 200 kV) equipped with an X-ray energy-dispersive spectroscopy (EDS) instrument. The TSL OIMTM software was used to measure the grain size and acquire

Table 2 Grain size, yield strength, ultimate tensile strength and elongation of the alloy after different treatments processing

Alloys	Treatment processing	Grain size (μm)	Yield strength (MPa)	Ultimate tensile strength (MPa)	Elongation (%)
T1	Cold rolled (60%) + annealing at 1150°C for 10 min	135.7	338.3	759.3	60.4
T2	Cold rolled (85%) + annealing at 1150°C for 3min + aging at 800°C for 60 min	93.6	576.5	1112	30.7
T3	Cold rolled (85%) + annealing at 1150°C for 3 min + aging at 750°C for 60 min	87.7	881.7	1267.7	19.8
T4	Cold rolled (85%) + annealing at 970°C for 0.5 min + aging at 750°C for 60 min	1.4	1355.9	1488.1	8.1

pseudo-colored orientation imaging microscopy (OIM) grain maps. For the SEM and EBSD observations, the specimens were electrochemically polished in a mixed solution of perchloric acid (10 vol.%) and ethanol (10 vol.%) at a direct voltage of 30 V and a temperature of -30°C . For the TEM analysis, foils with a thickness of 80 μm were initially twin-jet electropolished in a mixture of perchloric acid (5 vol.%) and ethanol (95 vol.%), at a voltage of 20 V and a temperature of -35°C , and then ion-milled for 20 min. A statistical analysis of the size of the $L1_2$ precipitates was performed for a sample of 1000 particles using the ImageJ software [18].

RESULTS

XRD and SEM analyses

Fig. 2 shows the XRD patterns of the $(\text{FeCoNi})_{92}\text{Al}_{2.5}\text{Ti}_{5.5}$ HEA after different thermo-mechanical treatments. Peaks of the FCC phase are obvious for all samples. No superlattice peak (e.g., (001)), a sign of ordered phase, was detected in the XRD patterns. Later, the TEM observa-

tions indicate the existence of ordered $L1_2$ precipitates in the T2, T3, and T4 alloys. The missing superlattice peaks are due to a relatively small scattering-factor difference between the precipitates and the matrix, which arises from the complicate atomic occupation in the ordered phase and the peak-broadening effect from nano-sized precipitates [19].

The EBSD inverse-pole-figure (IPF) maps shown in Fig. 3 demonstrate the evolution of the grain size after different thermo-mechanical treatments. The grain sizes of the alloys are listed in Table 2. The grain size was refined from 135.7 μm for the T1 alloy to 1.4 μm for the T4 alloy. Except for the fine grain structure, non-recrystallized areas exist in the T4 alloy as well. The partial recrystallized structure was further characterized by a combination of grain boundary and kernel average misorientation (KAM) maps shown in Fig. 4. Non-recrystallization regions with elongated larger grains are in the IPF map (Fig. 3d), which retains plenty of low angle boundaries (highlighted by red lines in Fig. 4b) and very high KAM values (Fig. 4a). The recovery occurs in these non-recrystallization regions during annealing, causing the formation of substructures (higher KAM values and more low-angle boundaries are evident). These substructures are formed due to the dislocation interaction and annihilation during the recovery process [20].

Fig. 5 shows the corresponding SEM micrographs for these four kinds of specimens. Only very few particles were found in the T1 alloy. In contrast, a large number of nanosized precipitates were uniformly distributed within the grain matrix in the T2, T3, and T4 alloys, as shown in Fig. 5b–d. This is consistent with the phase diagram prediction (Fig. 1). Fig. 6 shows the size distribution of the precipitates and the particle spacing in the T2, T3, and T4 alloys. The average sizes of the precipitates in the T2, T3, and T4 alloys are 33.6, 18.9, and 25.4 nm, respectively, and the precipitates' spacings in the T2, T3, and T4 alloys

Figure 2 XRD patterns of the $(\text{FeCoNi})_{92}\text{Al}_{2.5}\text{Ti}_{5.5}$ HEA after different treatments.

Figure 3 EBSD IPF maps illustrating the grain-size evolution after different thermo-mechanical processes.

Figure 4 (a) KAM map and (b) grain-boundaries map of the T4 alloy.

Figure 5 SEM micrographs of the: (a) T1, (b) T2, (c) T3, and (d) T4.

were measured to be 39.5, 13.9, and 15.0 nm, respectively. The volume fraction of the precipitates in the T2, T3, and T4 alloys are 14.9%, 20.6%, and 25.6%, respectively. The largest size and lowest volume fraction of the precipitates in the T2 alloy is due to the high temperature-aging treatment (800°C). Although the T3 and T4 alloys were submitted to the same temperature during the aging treatment (i.e., 750°C), the pre-existing dislocations (substructure) in the T4 alloy can promote the nucleation and coarsening of the precipitate, resulting in larger size and volume fraction of the precipitates in the T4 alloy.

TEM characterization

The dark-field TEM image of the T2 alloy in Fig. 7a

Figure 6 Particle-size and spacing distributions of the L_{12} ordered precipitates in the (a, d) T2, (b, e) T3, and (c, f) T4 samples.

clearly shows the uniformly distributed nanosized precipitates in the FCC matrix. The corresponding selected area electron diffraction (SAED) pattern (inset in Fig. 7a)

demonstrates that these precipitates have an ordered L_{12} structure. Fig. 7b shows a high-resolution TEM (HRTEM) image of a precipitate in the T2 alloy, taken

Figure 7 TEM characterizations of the T2: (a) TEM dark-field image and corresponding SAED pattern, (b) HRTEM image of the precipitates and corresponding FFT pattern (the superlattice spots are outlined by red arrows), (c) HAADF STEM image and (c1) corresponding elemental mapping in the red-square region in (c).

along the $[011]_{\text{FCC}}$ crystallographic direction. Fast Fourier transformation (FFT) patterns from the red and yellow square regions in Fig. 7b confirm the structure of FCC and $L1_2$, respectively. Besides, the precipitate and the matrix present a fully coherent interface. The lattice parameters of the FCC structure and the ordered $L1_2$ structure are 0.359 and 0.360 nm, respectively, calculated from the distance between two $\{111\}$ planes in the HRTEM-filtered image. The lattice parameter mismatch between the matrix and the precipitate is only 0.28%, and such a low value accounts for the formation of a coherent interface [21]. This also explains why the superlattice spots cannot be detected by XRD. Fig. 7c shows a high-angle annular dark-field (HAADF) scanning TEM (STEM) image of the T2 and the corresponding elemental mapping from the red square region. Ti and Ni elements are preferentially segregated in the $L1_2$ precipitates. The matrix is enriched in Fe and Co. The TEM images (Fig. 7 and Fig. S1) and the elemental distribution indicate that the precipitates are the $\text{Ni}_3(\text{Ti,Al})$ -type $L1_2$ phase.

Mechanical properties at room temperature

Fig. 8 shows representative engineering strain–stress curves for the four specimens at room temperature. The corresponding values of the yield strength, UTS, and tensile elongation are listed in Table 2. Owing to its single-phase structure and coarse grain size, the T1 exhibits the lowest yield strength (338.3 MPa) and UTS (759.3 MPa) but the highest elongation (60.4%) compared with other specimens. The alloys with finer grain sizes and precipitates show a higher yield strength and UTS. As a result, the T4 exhibits a striking enhancement in the mechanical properties; for example, the yield strength increases from 338.3 to 1355.9 MPa and the UTS increases from 759.3 to 1488.1 MPa, due to the high density and uniformly dispersed precipitates as well as the fine grains (1.4 μm). The superior combination of yield strength (1355.9 MPa), UTS (1488.1 MPa), and ductility (tensile elongation of 8.1%) of the T4 is mainly ascribed to grain boundary strengthening and precipitates strengthening.

Microstructural evolution during tensile deformation

Fig. 9 shows the deformation microstructures of the T1 at low (2%), medium (30%), and high (60%) strains. Pile-up dislocations gliding along the primary crystallographic direction were detected at a low strain of 2% (Fig. 9a), which was a representative planar glide configuration. When the sample was deformed to about 30%, as shown in Fig. 9b, planar dislocation arrays appeared in the dense

Figure 8 Engineering strain–stress curves of the four specimens tensile-deformed at room temperature.

dislocation networks due to the activation of two non-coplanar slip systems. Such a dislocation configuration is the so-called Taylor lattice (TL) structure, a kind of low energy dislocation structure against dislocation cells formed by a wavy glide [22–24]. These dislocation configurations indicate the pronounced planar glide in the T1. At a high strain (~60%), well-developed microbands (MBs) were observed, as seen in Fig. 9c. Moreover, well-refined nanograins were also observed near the MB region. This is revealed by the corresponding SAED pattern, which shows a set of distinctive continuous rings. As the strain increases, the TLs rotate to activate different slip systems for accommodating the strain [23]. Then, more MBs will be formed and refined for compensating the geometrical requirement caused by this resultant rotation [23]. Since the MBs preferentially end at low energy location, such as at grain boundaries and other MBs, the grains will be subdivided by their intersections at a high strain, resulting in the formation of nanograins (Fig. 9c) [23,25]. The grain subdivisions and refinement formed by dislocation substructure at a high strain can enhance the strength by the dynamic Hall–Petch effect.

Fig. 10 shows the deformation microstructure of the T2 at different strains. At a low strain (~2%), the dislocation band observed in Fig. 10a indicates a planar glide of dislocations. Since uniformly dispersed nano-precipitates with an atomically ordered structure are beneficial to the planar glide of dislocations, a similar dislocation configuration is often observed in precipitate-strengthening FCC alloys [21,26]. The microstructure of the specimen deformed to fracture (~28%) presents well-developed MBs. Mechanical twinning and transformation induced martensite were not detected in this alloy, which is similar to the T1.

Figure 9 TEM micrographs showing the microstructures of the T1 at different strains: (a) 2%, (b) 30%, and (c) 60%.

Figure 10 TEM micrographs showing the microstructures of the T2 alloy at different strains: (a) 2% and (b) 28%.

The interaction between precipitates and the dislocation observed at a tensile strain of about 28% were further analyzed by HRTEM, as shown in Fig. 11. The precipitates–matrix interface was identified by the corresponding FFT patterns of the four regions (A, B, C, D) in Fig. 11a, outlined by a yellow dashed line. Regions A and B are confirmed to be the FCC matrix, while regions C and D are determined to be the $L1_2$ ordered structure.

The irregular interface indicates the occurrence of dislocation cutting through the precipitates. Fig. 11b shows the HRTEM-filtered image. The corresponding inverse-FFT (IFFT) patterns for the (11-1) and (1-11) planes are shown in Fig. 11c and d, respectively. Numerous dislocations—denoted as “T”—are found at the interface and inside precipitates, which demonstrate dislocation shearing of the precipitates during deformation.

DISCUSSION

Phase constitution

In general, the formation of multi-component solid-solution phases in HEAs should satisfy the empirical criteria, that is, $\delta \leq 6.6\%$ and $\Omega \geq 1.1$, where Ω is an integrated parameter referring to ΔS_{mix} (entropy of mixing), T_m (melting point), and ΔH_{mix} (enthalpy of mixing), and δ is the atomic-size difference of the constituent elements [27]. δ , Ω , ΔS_{mix} , and ΔH_{mix} are defined as follows [27]:

$$\delta = \sqrt{\sum_{i=1}^n c_i (1 - r_i / r_{\text{avg}})^2}, \quad r_{\text{avg}} = \sum_{i=1}^n c_i r_i, \quad (1)$$

Figure 11 (a) HRTEM image of the T2 tensile-deformed to fracture (with a total strain of about 28%), with the interface between the matrix and the precipitate being identified by the corresponding FFT pattern A, B, C, and D (the superlattice spots are outlined by red arrows), (b) HRTEM-filtered image of the precipitate–matrix interface, and (c, d) corresponding IFFT images of the HRTEM shown in (b) for the (11-1) and (1-11) planes.

$$\Omega = \frac{T_m \Delta S_{\text{mix}}}{|\Delta H_{\text{mix}}|}, \quad (2)$$

$$\Delta S_{\text{mix}} = -R \sum_{i=1}^n (c_i \ln c_i), \sum_{i=1}^n c_i = 1, \quad (3)$$

$$\Delta H_{\text{mix}} = \sum_{i=1, i \neq j}^n 4H_{ij}^{\text{mix}} c_i c_j, \quad (4)$$

$$T_m = \sum_{i=1}^n c_i (T_m)_i, \sum_{i=1}^n c_i = 1, \quad (5)$$

where r_i and $(T_m)_i$ are the atomic radius and melting point of the i th component, respectively, H_{ij}^{mix} is the enthalpy of mixing of the i th and j th components, calculated by Miedema model, and $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ is the gas constant. When Ω is infinitely close to the critical value 1.1, coherent precipitates can form in the matrix [28]. The enthalpy of mixing (H_{ij}^{mix}), atomic radius, and melting points of the five elements are shown in Tables 1 and 3 [29]. The values of δ and Ω are 3.8% and 1.179, respectively, derived from the above equations. The enthalpy of mixing for the atom pair Al/Ti is the most negative one (-30 kJ mol^{-1}), which indicates their good affinity for

Table 3 The values of chemical mixing enthalpy, ΔH_{mix} (kJ mol^{-1}), of atomic pairs between elements Fe, Co, Ni, Al, and Ti [29]

Element	Fe	Co	Ni	Al	Ti
Fe	0	−1	−2	−11	−17
Co		0	0	−19	−28
Ni			0	−22	−35
Al				0	−30

each other. In addition, Al and Ti preferentially form intermetallic phases with Fe, Ni, and Co because they exhibit negative enthalpies of mixing for different atom pairs, including pairs with Fe, Co, and Ni, as seen in Table 3. A small amount of Al and Ti benefit the formation of a strong γ' phase ($L1_2$) in FeCoCrNi HEAs [2,4]. According to the above analysis, a solid-solution phase and coherent precipitates can be formed in the present alloy system. The experimental results are in good agreement with the values predicted by the CALPHAD method. The γ' ($L1_2$) phase precipitates within the FCC matrix when the alloy is annealed at 750 and 800°C. In addition, the experimental results show that the volume fraction of the $L1_2$ phase decreases with increasing an-

nealing temperature, consistent with the predicted results. Although there is a small deviation between the experimental data and the predicted results in the volume fraction of the precipitates, the CALPHAD method is a reliable tool to evaluate the phase constitution and stability in multicomponent alloy systems.

Evolution of deformation microstructure

As shown in Figs 9 and 10, no distinct cell structures, mechanical twinning or transformation induced martensite are in the present HEAs, and their absence is due to the high stacking fault energies of the matrix alloy [30]. Furthermore, the formation of nano-precipitates can enhance the resolved stress for twinning, resulting in the retardation of twinning [12,31]. In contrast, well-developed MBs were obtained at high strains. At the onset of plastic deformation, it is beneficial to activating the planar slip due to the presence of a short- or long-range ordered phase ($L1_2$), resulting in glide-plane softening [21,32,33]. Due to the dislocation propagating throughout the glide plane, initial slip bands are formed, which will further go through the grain. Upon increasing the strain, dislocation pile-ups occur, which increases the back stress. Thus, more dislocations are produced and emitted inside the slip bands [32]. Consequently, a well-developed slip band referred to as a MB is formed. The MBs formed by planar glide are similar to the low-angle grain boundaries and provide an additional work-hardening source to accommodate the imposed strain at high strain, which stabilizes the plastic deformation [23,34,35]. The nano-precipitates produce hardening through either the Orowan bowing or the dislocation-shearing mechanism, depending on the interaction between precipitates and moving dislocations [36,37]. The precipitates are sufficiently small and coherent, causing a dislocation-shearing mechanism (Fig. 11). In the present alloy, the precipitates have an average size of about 30 nm and are coherent with the matrix. The results of the HRTEM analysis (Fig. 11) indicate that the precipitation hardening in the present alloy is dominated by the dislocation-shearing mechanism.

Strengthening mechanisms

Compared with the matrix alloy (i.e., T1 without precipitates), the pronounced increase in the yield strength ($\Delta\sigma_{0.2}$) for the T2, T3, and T4 (with precipitates) is mainly due to grain-boundaries hardening ($\Delta\sigma_G$), precipitation hardening ($\Delta\sigma_p$), and dislocation hardening ($\Delta\sigma_{dis}$). Therefore, the increase in the yield strengths of T2, T3, and T4 can be derived from a simple function including

the individual contributions, which can be expressed as [8,38]:

$$\Delta\sigma_{0.2} = \Delta\sigma_G + \Delta\sigma_p + \Delta\sigma_{dis}. \quad (6)$$

Based on the classical Hall-Petch equation, $\Delta\sigma_{0.2} = \sigma_0 + kd^{1/2}$, where σ_0 is the lattice friction, k is the strengthening coefficient, and d is the average grain size [2]. Thus, the increase in yield strength caused by the grain boundaries can be expressed as:

$$\Delta\sigma_G = k(d_2^{-1/2} - d_1^{-1/2}), \quad (7)$$

where d_1 and d_2 represent the different grain sizes. In the present study, the value of $k=226 \text{ MPa } \mu\text{m}^{1/2}$ is adopted from the FeCoNiCrMn system [39]. Therefore, the $\Delta\sigma_G$ for the T2, T3, and T4 were calculated to be 0.8, 0.9, and 159.8 MPa, respectively.

The strengthening caused by ordered coherent precipitates ($\Delta\sigma_0$) is due to dislocation shearing in the ordered precipitates and the creation of an antiphase boundary (APB) on their glide plane, which impede the movement of dislocations [40]. Dislocation shearing of the precipitates was observed in the present study (Fig. 11). Therefore, three contributing factors for precipitation hardening should be considered, namely, particle-matrix coherency $\Delta\sigma_{CS}$, modulus mismatch $\Delta\sigma_{MS}$, and atomic ordering $\Delta\sigma_{OS}$. The former two take place prior to the dislocation-shearing process whereas the latter one occurs during shearing. In principle, the precipitation hardening is determined by the larger of the two values between $\Delta\sigma_{CS} + \Delta\sigma_{MS}$ and $\Delta\sigma_{OS}$. $\Delta\sigma_{CS}$, $\Delta\sigma_{MS}$, and $\Delta\sigma_{OS}$ can be expressed as [41]:

$$\Delta\sigma_{CS} = M \cdot \alpha_\epsilon (G \cdot \epsilon)^{3/2} \left(\frac{rf}{0.5Gb} \right)^{1/2}, \quad (8)$$

$$\Delta G_{MS} = M \cdot 0.0055 \cdot (\Delta G)^{3/2} \left(\frac{2f}{G} \right)^{1/2} \left(\frac{r}{b} \right)^{3m/2-1}, \quad (9)$$

$$\Delta\sigma_{OS} = M \cdot 0.81 \frac{\gamma_{APB}}{2b} \left(\frac{3\pi f}{8} \right)^{1/2}, \quad (10)$$

where M is the Taylor factor (3.06 for the FCC matrix), $\alpha_\epsilon=2.6$ for the FCC structure, $\epsilon=2/3 \cdot (\Delta a/a)$ represents the matrix-precipitate misfit (with Δa being the difference in lattice constant between the matrix and the precipitates and a representing the lattice constant of the matrix), $m=0.85$, ΔG is the different shear modulus between the precipitates and the matrix, f is the volume fraction of the ordered precipitates, r is the precipitate's radius, b is the Burgers vector ($b = a_0 / \sqrt{2}$, with a_0 as the lattice constant of the ordered precipitates), and γ_{APB} is the APB energy [2]. The values of $\Delta G=4 \text{ MPa}$ and $\gamma_{APB}=0.2 \text{ J m}^{-2}$ adopted

in present study were borrowed from the Ni₃Al precipitates in Ni-based superalloys [2,42]. According to the above equations, the particle–matrix coherencies in the T2, T3, and T4 were calculated as 207.2, 184.3, and 240 MPa, respectively. The modulus mismatches in the T2, T3, and T4 were calculated to be 27.1, 64.4, and 85.2 MPa, respectively. The calculated $\Delta\sigma_{OS}$ are 407.5, 479, and 534 MPa, respectively. Since the contributions from $\Delta\sigma_{CS}$ and $\Delta\sigma_{MS}$ are smaller than that from $\Delta\sigma_{OS}$, the ordering strengthening determines the resultant contribution of precipitation hardening.

In the case of the T4, the non-recrystallized region has a high KAM value and a large number of low angle boundary misorientations, which indicates that the dislocations are not completely eliminated during the annealing process. The dislocations then interact with each other and impede their motion during deformation. The increment in dislocation hardening can be expressed using the Bailey–Hirsch formula [2]:

$$\Delta\sigma_{dis} = M\alpha Gb\rho^{1/2}, \quad (11)$$

where α is a constant for FCC metals ($\alpha=0.2$), ρ represents the dislocation density, and $G=74$ GPa is the shear modulus adopted from the FeCoNiCrMn system. The dislocation density was roughly estimated using the Williamson–Hall method, which can be expressed as [43]:

$$\beta\cos\theta = k\lambda / D + (4\sin\theta) \cdot \varepsilon, \quad (12)$$

where β is the peak broadening determined from the XRD data, k is a constant (~ 0.9), λ is the wavelength of Cu K α radiation (0.15405 nm), D represents the crystallite size, ε stands for the microstrain, and θ is the Bragg angle of a certain diffraction peak. The linear fit of $\beta\cos\theta-4\sin\theta$ is shown in Fig. S2. The slope stands for the ε parameter, which has a value of 0.13513. The dislocation density (ρ) can be derived from the following equation [44]:

$$\rho = 2\sqrt{3} \cdot \varepsilon / (Db). \quad (13)$$

Using this equation, the dislocation density was calculated to be $1.31 \times 10^{15} \text{ m}^{-2}$. Hence, taking this value into Equation (11), the yield-strength increment in the T4 caused by dislocation hardening is determined to be 401 MPa. The T1, T2, and T3 present a fully recrystallized structure and the TEM bright-field image of the T2 (Fig. S3) shows very few dislocations. Therefore, the strengthening contribution by dislocation can be negligible in the T1, T2, and T3.

Based on the above analysis, the yield strengths in the T2, T3, and T4 are calculated as 746.6, 818.2, and 1433.1 MPa, respectively. For clarity, a column chart is shown in Fig. 12, which indicates that the calculated va-

Figure 12 A column chart characterizing the strengthening contributions of different mechanisms, where $\Delta\sigma_p$, $\Delta\sigma_G$, and $\Delta\sigma_{dis}$ represent the precipitation hardening, grain-boundaries hardening, and dislocation hardening, respectively.

lues are in reasonable agreement with the experimentally determined ones (marked by the red, green, and blue dots, respectively). It should be noted that these estimations of the contributions of the individual hardening mechanisms cannot be absolutely accurate because the relevant parameters (e.g., the strengthening coefficient k , APB energy, and shear modulus) are either roughly estimated or adopted from superalloys. Nevertheless, these estimates can provide a reasonable reference for analyzing the contributions of the individual hardening mechanisms. According to the results, precipitation hardening plays a dominant role in the increment of the yield strength.

CONCLUSION

In the present study, the CALPHAD method was applied to guide the design of the (FeCoNi)₉₂Al_{2.5}Ti_{5.5} HEA strengthened by precipitation hardening. The phase-precipitation, microstructural-evolution, and strengthening mechanisms were discussed. The following conclusions can be drawn:

(1) Uniformly dispersed precipitates having an $L1_2$ ordered structure and forming a fully coherent interface with the FCC matrix were obtained by a proper aging treatment. The experimental results agree well with the CALPHAD-predicted results.

(2) Compared with the single-phase T1, the yield strength increases from 338.3 to 1355.9 MPa and the ultimate tensile strength increases from 759.3 to 1488.1 MPa upon tailoring the size and volume fraction of the precipitates, as well as the size of the grains, while the elongation maintains a reasonable value of 8.1%. The

impressive enhancement of the strength is mainly due to precipitate hardening. The strengthening contributions by precipitation in the T2, T3, and T4 are 407.5, 479, and 534 MPa, respectively.

(3) A pronounced planar glide and well-developed MBs were observed in both alloys without and with precipitates at low and high strain, respectively. The deformation-induced MBs and the coherent precipitates sheared by dislocations correspond to the deformation and strengthening mechanisms, which contribute to the combination of good ductility and high strength in the present alloy.

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Author contributions Song M designed the project. Guo L and Gong X produced the materials and performed the mechanical testing. Guo L, Gu J, and Ni S conducted the microstructural characterization. Guo L, Gu J and Song M wrote the manuscript. All authors contributed to the discussion of the results and commented on the manuscript.

Conflict of interest The authors declare no conflict of interest.

Supplementary information Supporting data are available in the online version of this paper.

Lin Guo is currently a PhD candidate at Powder Metallurgy Research Institute, Central South University, China. His current research focuses on HEAs designing and microstructural evolution.

Ji Gu is a lecturer of Powder Metallurgy Research Institute, Central South University, China. He received his PhD degree in material science and engineering in 2019 under the supervision of Prof. Min Song. His current research focuses on exploring the mechanical behaviour, deformation mechanism and structure-property relationship of HEAs and gradient structure materials.

Min Song is a Professor and Vice Dean of Powder Metallurgy Research Institute at Central South University. He serves as Associate Editor of “*Materials Characterization*”. He received his PhD degree in 2005 at Dartmouth College, USA. His current research interests involve deformation mechanisms of metallic materials, including: metals and alloys, bulk nanocrystalline materials, metallic glasses, HEAs and metal matrix composites.

CALPHAD辅助设计高强度沉淀强化型高熵合金

郭林¹, 顾及^{1*}, 龚星², 倪颂¹, 宋皎^{1*}

摘要 近年来,设计具有高强度和优异延展性的高熵合金(HEAs)引起了人们的广泛兴趣.在本文中,我们采用CALPHAD方法来设计沉淀强化型 $(\text{FeCoNi})_{92}\text{Al}_{2.5}\text{Ti}_{5.5}$ 高熵合金.通过热机械处理过程来调控合金晶粒尺寸、析出相大小及体积分数,从而优化合金力学性能.在一定温度时效后,具有 L1_2 有序结构的 $\text{Ni}_3(\text{Al,Ti})$ 型第二相在面心立方(FCC)基体中均匀析出,并与FCC基体共格.通过热机械处理过程,合金的屈服强度从338.3 MPa增加到1355.9 MPa,抗拉强度从759.3 MPa增加到1488.1 MPa,而伸长率仍然保持在8.1%.基于分析模型定量评估屈服强度的增加,结果表明屈服强度的显著增加主要是由沉淀强化机制引起的.变形引起的微观条带和位错切过析出相是该合金的变形机制和强化机制,有助于该合金同时具有优异的延展性和高强度.本研究表明,CALPHAD方法可以为高熵合金的设计和优化提供借鉴.