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Dual effects of pre-strain on continuous and discontinuous precipitation of $L1_2$-strengthened high-entropy alloys

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Abstract

The effects of pre-strain on the continuous precipitation (CP) and discontinuous precipitation (DP) as well as mechanical properties of $L1_2$-strengthened HEAs were thoroughly studied. It is found that the pre-strain has a dual effect on the $L1_2$ precipitation behavior depending on the pre-strain level. At low pre-strains, the plastic deformation increases the dislocation density without significantly affecting the grain structure, which accelerates the CP reaction by promoting the CP nucleation and growth, leading to the CP-dominant microstructure. At high pre-strains, the server plastic deformation induces the formation of a high density of deformation bands and subgrains, the boundaries of which provide preferred nucleation sites for the DP reaction. In addition, the high stored energy induced by the cold deformation enhances the grain boundary migration, which promotes the DP growth and concurrent recrystallization. Mechanical tests further reveal that the pre-strain substantially improves the strength of the alloys, leading to the development of the strategy to design the alloys with a good combination of high strength and ductility. The contributions of dislocations, grain boundaries, and precipitates to the strengthening of the pre-strained and aged alloys were quantitatively evaluated.

Keywords: high-entropy alloy; continuous precipitation; discontinuous precipitation; pre-strain.

1. Introduction

High-entropy alloys (HEAs) have attracted considerable attention in recent years due to their outstanding mechanical and physical properties, such as excellent ductility, toughness, and corrosion resistance [1-6]. However, the strength of single-phase face-centered cubic (FCC) HEAs is generally low, which is not adequate for industrial applications. Precipitation of coherent $L1_2$ precipitates has been proved as an effective way to improve the strength of FCC HEAs while maintaining good ductility and toughness [7-13]. Continuous precipitation (CP) and discontinuous precipitation (DP) are two modes of precipitation in the $L1_2$-strengthened HEAs, which have been observed in many alloy systems [14-18]. The CP refers to the uniform precipitation of $L1_2$ nanoparticles in the grain interior, for which the solute concentration changes continuously in the FCC matrix [19, 20]. In contrast, the DP usually forms at grain boundaries and proceeds to the grain interiors via cellular growth of alternating lamellae of $L1_2$ precipitates and solute-depleted FCC matrix behind the moving grain boundaries [21-23].

Mechanical properties of $L1_2$-strengthed HEAs are highly dependent on the precipitate microstructure, including the size, morphology, and volume fraction of the precipitates. In order to optimize the mechanical properties of $L1_2$-strengthened HEAs, extensive efforts have been devoted to understanding and controlling the precipitation thermodynamics and kinetics It was found that in the CP nanoparticles strengthened HEAs, the pre-strain prior to aging could significantly affect the precipitate microstructures and hence the mechanical properties [24-26]. For example, Zheng *et al*. [25] showed that the pre-strain refines the precipitate size and increases the number density of precipitates, leading to the development of high-strength HEAs.

Nandal *et al.* [26] reported that the pre-strain significantly accelerates the precipitation kinetics of the CoCrNi-based HEAs, which is attributed to the increased dislocation density.

While most research on the pre-strain effect on the microstructure of HEAs has focused on the CP behavior, less is known about the pre-strain effect on the DP behavior. In addition, studies on other types of alloys suggest that the effect of pre-strain on the CP and DP behaviors can be very complicated and sometimes even controversial. For example, Davies *et al.* [27] reported that a small amount of pre-strain significantly increases the volume fraction of DP regions in a Ni-Co-Al alloy. In contrast, Keskar *et al.* [28] found that the pre-strain has a suppressing effect on the DP and a promoting effect on the CP in a Ni-Cr alloy. Considering the facts that the DP volume fraction in $L1_2$-strengthened HEAs is significant and that the CP and DP often occur simultaneously, it is crucial to elucidate the effect of pre-strain on the CP and DP behaviors of $L1_2$-strengthened HEAs.

The purpose of this study is to gain insight into how the pre-strain affects the CP and DP behaviors and associated mechanical properties of the $L1_2$-strengthened HEAs. Specifically, the CP and DP microstructures of an $L1_2$-strengthened $(FeCoCrNi)_{94}Al_3Ti_3$ alloy with the pre-strains ranging from 0 to 70% were thoroughly investigated through a combination of scanning electron microscopy (SEM), electron backscatter diffraction (EBSD), and atom probe tomography (APT). We show that the pre-strain has a dual effect on the precipitation behavior of the $L1_2$-strengthened HEAs depending on the pre-strain level. Particular attention was paid to elucidating mechanisms of the dual effects of pre-strain on the CP and DP behaviors of the $L1_2$-strengthened HEAs.

2. Experimental

The alloy with a nominal composition of $(FeCoCrNi)_{94}Al_3Ti_3$ (at.%) was prepared by the arc-melting method under a protective argon atmosphere. Alloy ingots were flipped and melted five times to ensure chemical homogeneity and then drop-cast into a water-cooled copper mold with a dimension of 50 × 15 × 3 mm^3. The as-cast ingots were solution-treated for 2 h at 1150 °C and then cold-rolled with a total reduction of approximately 70%. The rolled sheets were subjected to recrystallization for 3 min at 1150 °C, followed by water quenching. To figure out the pre-strain effect on the CP and DP behavior, the recrystallized samples were then subjected to strains of 5%, 10%, 20%, 30%, 40%, 50%, 60%, and 70%, respectively. After that, the unstrained and 5-70% strained samples were aged at 800 °C for 1 h (hereafter denoted as the 0%SA, 5%SA, 10%SA, 20%SA, 30%SA, 40%SA, 50%SA, 60%SA, and 70%SA samples, respectively). The schematic diagram of the processing procedure is shown in Fig. 1. Crystal structures were examined by X-ray diffraction (XRD) with Cu Kα radiation scanning from 20° to 100° in 2θ with a scanning rate of 5 °/min. SEM, EBSD, and APT were used to characterize the resulting microstructures. SEM and EBSD samples were mechanically polished and then electrochemically polished with a solution of HNO_3 (25%) and C_2H_5OH (75%) at -40 °C for 10 s at 5 V and 1 min at 20 V, respectively. The EBSD characterizations were performed at a step size of 0.5 μm, and the obtained EBSD data were analyzed by using an open Matlab toolbox MTEX 5.7 [29]. Needle-shaped APT samples were prepared by the lift-out technique using FEI Scios focused ion beam/scanning electron microscope (FIB/SEM). The APT characterizations were performed in a CAMECA Instruments LEAP 5000XR local electrode atom probe. The samples were analyzed in voltage mode, at a temperature of 70 K, a pulse repetition rate of 200 kHz, a pulse fraction of 0.2, and an ion collection rate of 0.5% ions per field evaporation pulse. Imago Visualization and Analysis Software version 3.8 was used for the 3D reconstruction and data analysis. Dog-bone-shaped tensile specimens with a gauge length of 12.5 mm and a width of 4 mm were cut using electrical-discharge machining. Room-temperature tensile tests were performed on an MTS mechanical testing system at a strain rate of 10^{-3} s^{-1}, and the resulting fracture surfaces were examined by SEM.

3. Results

3.1 Microstructures in the initial as-strained states

Representative EBSD inverse pole figure (IPF) maps of the $(FeCoCrNi)_{94}Al_3Ti_3$ alloy under different strains are shown in Fig. 2. Prior to strain (Fig. 2a), the microstructure consists of a uniform distribution of equiaxed grains, where a number of annealing twins are present. When the strain is applied, the grains become elongated along the strain direction, and their morphologies change from equiaxed to elongated structures, which is accompanied by the formation of deformation bands. At the strain of less than 40% (Figs. 2a-c), the grain orientation changes to become close to the <101> direction, whereas the grain shape does not change significantly. When the strain increases to 40% (Fig. 2d), the grain becomes elongated along the strain direction, and a few deformation bands were detected in some areas. When the strain increases to 50% (Fig. 2e), the shear bands become more visible and intense. At the 70% strain (Fig. 2f), the grain orientation is mainly along the <111> and <101> directions, and the deformation bands are spread over the entire microstructure.

3.2 Microstructures in the pre-strained and aged conditions

The strained samples were subjected to aging for 1 h at 800 °C, and the resultant microstructures are shown in Fig. 3, in which the DP region exhibits a bright contrast compared with the CP region. The unstrained sample was also aged in the same condition, and the microstructure is included for comparison. It is evident that the pre-strain has a significant impact on the CP and DP microstructure. The volume fractions of the DP colonies in the pre-strained and aged samples are illustrated in Fig. 4 as a function of pre-strain. The 0%SA sample exhibits a mixed microstructure consisting of 54% CP and 46% DP (Fig.3a). A high-resolution SEM image of the CP and DP regions of the 0%SA sample is shown in Fig. 3b. It is seen that the CP region shows an even distribution of spherical nanoparticles in the grain interior, whereas the DP region is composed of parallel precipitates with a lamellar structure near the grain boundary. With a small pre-strain (<10%), the volume fraction of DP regions decreases drastically, reaching a valley of 20% ± 1% in the 10% pre-strained sample. Further increasing the pre-strain results in an increase in the volume fraction of DP regions, which reaches 56% ± 3% at the 40% pre-strain, 72% ± 2% at the 50% pre-strain, and 91% ± 2% at the 60% pre-strain. Finally, the DP regions occupy almost the entire microstructure at the 70% pre-strain. Therefore, the variation of the volume fraction of DP regions is not monotonous with the increased pre-strain; rather, there is an obvious decrease-to-increase transition in the volume fraction of DP regions at the 10% pre-strain condition.

The phase structures of the pre-strained and aged samples were examined by XRD, and the corresponding patterns are shown in Fig. 5. The samples with different pre-strains exhibit a similar pattern consisting of FCC and $L1_2$ peaks, validating that the precipitates in the CP and DP regions have the same crystal structure and no other phases form after the strain and aging processes. In the 0%SA sample, the (111) plane shows the strongest intensity. With the pre-strain, the peak intensity of the (220) plane becomes pronounced, indicating that the deformation texture is formed after the pre-strain. In particular, the (220) peak becomes dominant in the 40%SA and 50%SA samples. Further increasing the pre-strain results in a decrease in the intensity of the (220) peak and an increase in the (111) peak, suggesting that recrystallization occurs in these two severely deformed and aged samples.

3.3 Mechanical properties

Room-temperature tensile tests were performed to investigate the effect of pre-strain on the age hardening of the $L1_2$-strengthened HEA. The engineering stress-strain curves of the pre-strained and aged samples are depicted in Fig. 6a. For comparison, the engineering stress-strain curves of the unstrained alloy at the solid solution state are also included. Before aging, the unstrained sample exhibits a yield strength of 270 ± 12 MPa, an ultimate tensile strength of

670 ± 10 MPa, and an elongation to failure of 77 ± 1%. After aging for 1 h at 800 °C, the yield and ultimate tensile strengths increase drastically to 522 ± 10 and 1012 ± 13 MPa, respectively, demonstrating a moderate age hardening response in the unstrained condition. As the pre-strain increases from 0 to 40%, the yield strength increases gradually from 522 ± 10 to 987 ± 10 MPa, which is accompanied by a slight decrease in the ductility. But the 40%SA sample is still very ductile, with an elongation to failure of 22 ± 2 %, showing a good combination of high strength and ductility. Further increasing the pre-strain results in no significant changes in the mechanical property. The yield strengths of the samples with 40-70% pre-strains are all around 990 MPa, and their ductilities are approximately 20-22%. The fracture surfaces of the pre-strained and aged samples were examined by SEM. Representative fracture surfaces of the 0%SA and 70%SA samples are presented in Figs. 6b and c, respectively. Both samples reveal plenty of fine dimples, which is a characteristic mode of a ductile fracture. In addition, the dimple size of the 70%SA sample is smaller than that of the 10%SA sample, which is likely attributed to the microstructure refinement.

4. Discussion

From the aforementioned results, it is seen that the CP and DP reactions are competitive under different pre-strains. The CP is dominant under the low pre-strains, whereas the DP is prevalent under the high pre-strains. In the following sections, the effects of pre-strain on the CP and DP as well as mechanical properties of the $L1_2$-strengthened HEAs will be analyzed and discussed in detail.

4.1 Dual effects of pre-strain on the CP and DP behaviors

4.1.1 At low pre-strains

The SEM results reveal that the samples with 0-30% pre-strains exhibit the CP-dominant microstructure. Particularly, as the pre-strain increases from 0 to 10%, the volume fraction of CP regions increases, whereas that of DP regions decreases. To understand the effects of pre-strain on the CP behaviors, the CP microstructures of the 0%SA and 10%SA samples were comparatively investigated through SEM and APT. Figures 7a and d show the high-resolution SEM microstructure of the 0%SA and 10%SA samples, both exhibiting evenly distributed spherical nanoparticles. The APT microstructures of the two samples are displayed in Figs. 7b and e, the required tips for which were obtained from the CP region by using the site-specific FIB lift-out technique. The 12% (Al + Ti) concentration isosurfaces were used to visualize the precipitates. A high number density of nanoparticles can be readily detected in both samples. The proximity histograms of the 0%SA and 10%SA samples are depicted in Figs. 7c and f, respectively. The partitioning of Ni, Ti, and Al to the precipitates and Co, Cr, and Fe to the matrix is evident. Based on the APT composition, the volume fraction of the CP nanoparticles in the two samples was estimated by using the lever rule [30]. The volume fraction of CP nanoparticles increases from 6.6% in the 0%SA sample to 7.6% in the 10%SA sample, indicating that the pre-strain substantially promotes the CP reaction in the pre-strained sample.

The effect of pre-strain on promoting the CP reaction can be explained in terms of precipitate nucleation and growth. Figure 8 shows the geometrically necessary dislocations (GNDs) density distribution of the 0 – 20% strained samples before aging. It can be seen that the low pre-strains drastically increase the dislocation density without significantly altering the grain structure. Increasing the dislocation density can promote the CP in two manners. On the one hand, dislocations can serve as heterogeneous nucleation sites for the $L1_2$ precipitates, and thus, the enhanced dislocation density by pre-strains can promote the $L1_2$ nucleation. On the other hand, dislocations can act as fast paths for diffusing atoms. The increased dislocation density facilities the rapid growth of precipitates. Because of the enhanced nucleation and growth of $L1_2$ precipitates in the CP region, the volume fraction of CP nanoparticles is increased in the pre-strained samples. As a result, a higher volume fraction of CP nanoparticles was observed in the 10%SA sample than in the 0%SA sample.

In addition, the accelerated CP reaction would inhibit the DP reaction. From the thermodynamic point of view, the concentration difference of solutes across the migrating grain boundary functions as a chemical driving force for the DP growth. The fast nucleation and growth of the CP quickly decrease the supersaturation of the FCC matrix, which reduces the solute concentration gradient across the migrating grain boundary and hence the chemical driving force for the DP reaction. Moreover, the CP nanoparticles with coarse sizes have a pining effect on the grain boundary migration, which kinetically retards the DP growth. Therefore, the DP growth is significantly suppressed, leading to the formation of the CP-dominant microstructure at the low pre-strains.

4.1.2 At high pre-strains

The DP structure is prevalent in the samples with 40-70% pre-strains, and the volume fraction of DP regions increases with increasing pre-strain, indicating that the large pre-strain promotes the DP reaction. The plastic deformation of crystalline alloys proceeds via heterogeneous formation, movement, annihilation, and/or storage of dislocations [31]. A large pre-strain can introduce a high density of dislocations, the accumulation of which can evolve into planar defects, thereby affecting the DP formation. First, the FeCoNiCr-based HEA is known to have a low stacking fault energy, which facilitates the planar slip of dislocations. The accumulation of planner dislocation slips in a narrow zone results in the formation of deformation bands (Figs. 2e and f). The high local lattice curvature of the deformation bands facilitates the DP nucleation at their walls. Second, internal energy minimization makes the dislocations arrange themselves into energetically favorable configurations, such as dislocation walls. With further deformation, the dislocation walls transform into subgrain boundaries inside the grains and cause a break in the boundaries of the original grains, thereby producing ultrafine grains. This is similar to the grain refinement mechanism observed in severe plastic deformation for various metals. It is known that both the subgrain boundaries and walls of deformation bands are preferred nucleation sites for the DP reaction. Therefore, increasing the strain levels provides more nucleation sites for the DP and hence promotes the DP reaction.

The DP region grows with the grain boundary migration, and its growth rate is highly dependent on the grain boundary mobility. In the pre-strained samples, the stored energy induced by cold work would activate the recrystallization, during which the subgrains tend to grow through grain boundary migration. Therefore, the pre-strained sample with high stored energies would have a high grain boundary mobility. The fast migration of the grain boundaries sweeps the solute in their path resulting in the accumulation of solutes at the grain boundary, which enhances the DP growth. As shown in Figs. 9a and b, the 70%SA sample shows fully recrystallized grains with a full DP microstructure. In addition, the grain structure of the 70%SA sample is greatly refined with an average grain size of 2 μm, as revealed by the EBSD IPF map (Fig. 9c). Therefore, the aging of the heavily pre-strained samples results in the mutual promotion of the DP and recrystallization, leading to the formation of fine-sized recrystallized grains with a DP-dominant microstructure.

Meanwhile, there is a strong sweep of CP nanoparticles by the DP front, because the DP process is closer to the equilibrium state as compared with the CP process. With the high pre-strain, the DP process is significantly enhanced, which consumes the supersaturated matrix quickly in the early stage of aging. Thus, the concentration difference across the migrating grain boundary between the CP and DP regions is large, providing a high driving force for the sweep of metastable CP nanoparticles by the DP process. As a result, the DP colonies invade the CP region and eventually occupy the entire microstructure of the alloys.

4.1.3 Summary of the dual effects of pre-strain

On the basis of the aforementioned discussion, it is clear that the effect of pre-strain on the CP and DP of the $L1_2$-strengthened HEA is not a simple phenomenon, but rather a complex one depending on the amount of pre-strain. The effect of pre-strain on the microstructural evolution of the $L1_2$-strengthened HEA is schematically illustrated in Fig. 10.

I) For the sample without pre-strain, the CP and DP occur simultaneously upon aging. The CP leads to the formation of spherical nanoparticles with a uniform distribution in the grain interior. In contrast, the DP initiates at grain boundaries and grows into the grain interior through a cellular reaction, leading to the formation of rod- or lamellar-like precipitates. The simultaneous development of the two modes of precipitation results in a mixed microstructure consisting of both CP and DP regions.

II) When a low pre-strain is applied, the near-uniform deformation occurs, which increases the dislocation density without significantly affecting the grain morphology. The high-density dislocations not only serve as heterogeneous sites for the CP nucleation but also act as fast paths for diffusion atoms, which significantly increase the CP nucleation and growth rates, thereby promoting the CP reaction. Meanwhile, the fast CP reaction quickly decreases the supersaturation of the matrix ahead of the migrating grain boundaries of the DP, which reduces the chemical driving force for the DP reaction. In addition, the pre-formed CP nanoparticles retard the migration of grain boundaries, which kinetically inhibits the DP growth. As a result, the CP reaction is significantly promoted, while the DP reaction is greatly suppressed, leading to the CP-dominant microstructure.

III) At high pre-strain levels, the severe plastic deformation induces the formation of deformation bands and breaks the original grains into subgrains. The boundaries of the deformation bands and subgrains can serve as the preferred sites for the DP nucleation. In addition, the stored energy induced by the pre-strain facilitates the grain boundary migration, which enhances the DP growth, leading to the concurrent recrystallization and DP reaction. The fast growth of the DP sweeps the metastable CP nanoparticles, thereby forming a DP-dominant microstructure within fine-sized grains.

4.2 Strengthening mechanisms

The mechanical results reveal that the pre-strain can significantly affect the mechanical properties of the HEA, which is accompanied by a change in the microstructure features, including the dislocation density, grain size, and volume fraction of CP and DP regions. To gain a basic understanding of the pre-strain effect on the strength of the $L1_2$-strengthened HEA, the strengthening mechanism of the pre-strained samples was modeled. Considering that the 70%SA sample exhibits a uniform grain structure and has a good combination of high strength and ductility, this sample was selected as the representative to investigate the strengthening mechanism. The yield strength, $\sigma_{0.2}$, can be expressed by:

$$\sigma_{0.2} = \sigma_0 + \Delta\sigma_{ss} + \Delta\sigma_d + \Delta\sigma_{gb} + \Delta\sigma_p \tag{1}$$

where σ_0 is the intrinsic strength or so-called lattice friction strength, and $\Delta\sigma_{ss}$, $\Delta\sigma_d$, $\Delta\sigma_{gb}$, and $\Delta\sigma_p$ are the strengthening contributions from the solid solution, dislocations, grain boundaries, and precipitates, respectively.

Because the solvent and solute are not distinguishable in the HEAs, the traditional dilute solid solution model is not precise for the perdition of solid solution hardening. In this study, the sum of the intrinsic strength and solid-solution hardening (σ_0 + $\Delta\sigma_{ss}$) was experimentally determined by the yield strength of the $(FeCoCrNi)_{94}Al_3Ti_3$ alloy in the solid-solution state, which was measured to be 270 MPa.

Plastic deformation results in the movement of mobile dislocations, which interact with each other and impede their own motion. The dislocation strengthening can be estimated by the Bailey–Hirsch formula [32]:

$$\Delta\sigma_d = M\alpha Gb\rho^{1/2} \tag{2}$$

where $M = 3.06$ is the Taylor factor [33], $\alpha = 0.2$ is a constant for FCC metals, $G = 78.5$ GPa is the shear modulus for the matrix [14], $b = 0.255$ nm is the burger vector for the FCC structure [14], and ρ stands for the dislocation density, which can be estimated from the EBSD. The average GND density is approximately 9.2×10^{13} m^{-2}. Putting these values into Eq. 2, the contribution of dislocation strengthening to yield strength was evaluated to be 118 MPa.

The contribution from grain-boundary strengthening can be estimated by the Hall-Petch equation [34]:

$$\Delta\sigma_{gb} = k_{HP} \big/ \sqrt{d} \tag{3}$$

where $k_{HP} = \sim 516\ \mathrm{MPa}\ \mu\mathrm{m}^{0.5}$ is the Hall-Petch coefficient, which is obtained from the FeCoNiCr-based alloy system with a similar composition [35], and $d = 2$ μm is the average grain size. The contribution of grain-boundary strengthening was calculated to be 364 MPa.

Considering the small diameter of the $L1_2$ precipitates (< 40 nm), the precipitate shearing mechanism is expected to be operative. Previous studies have indicated that the order strengthening plays a dominant role in the $L1_2$ strengthening in HEAs. The equation for the order strengthening is expressed by [36]:

$$\Delta\sigma_p = 0.81M\frac{\gamma_{APB}}{2b}\left(\frac{3\pi f}{8}\right)^{1/2} \tag{4}$$

where f is the volume fraction of the precipitates, and $\gamma_{APB} = 0.19$ J/m^2 is the anti-phase boundary energy of the $L1_2$ precipitates [37]. The volume fraction of the $L1_2$ precipitates was estimated to be approximately 8%. With the input of the obtained data into Eq. 4, the strengthening contribution of the $L1_2$ precipitates was estimated as 283 MPa.

Based on the abovementioned analysis, the sum of the intrinsic strength and solid solution hardening, dislocation hardening, grain-boundary strengthening, and precipitation hardening are summarized in Fig. 11. It shows that the precipitation hardening and grain-boundary strengthening play a major role in strengthening the alloy. The theoretical yield strength of the 70%SA sample is calculated to be 1035 MPa, which is reasonably consistent with the experimental results (990 ± 16 MPa) within experimental uncertainties. In addition, it is worthy to point out that the concurrence of recrystallization and DP growth leads to a fine-grained microstructure consisting fully of nanoscale DP colonies, which can greatly enhance the mechanical properties of the $L1_2$-strengthened HEAs.

Compared with the 70%SA alloy with relatively uniform and fully recrystallized microstructure, it is worth noting that the microstructures of the 40%-60%SA alloys are heterogenous due to the partial recrystallization, which consists of the coarse-sized and fine-scale grains. CP nanoparticles form in the coarse size grains, whereas DP rods form in the fine-scale grains. This heterogeneous microstructure has a hetero-deformation induced strengthening effect, which can greatly increase the strength of the alloy [38-40]. With the increase of the pre-strain, the degree of the recrystallization increases and the hetero-deformation induced strengthening becomes less effective, replaced by the grain boundary strengthening effect. Therefore, with the changes in the microstructure from partially recrystallized to fully recrystallized, there is a transition of the dominant strengthening effect from the hetero-deformation induced strengthening to the grain boundary strengthening, which can explain why the mechanical properties are quite similar for the 40%-70%SA samples.

5. Conclusions

In this study, the effects of pre-strain on the CP and DP behavior of the $L1_2$-strengthed $(FeCoCrNi)_{94}Al_3Ti_3$ alloy were thoroughly investigated, and the following conclusions are drawn:

1. The effect of pre-strain on the CP and DP in the $L1_2$-strengthened HEA is not a simple phenomenon, but rather a complex one depending on the amount of pre-strain.
2. At low pre-strains, the plastic deformation increases the dislocation density without significantly affecting the grain structure. The increased dislocation density accelerates the CP reaction by promoting the CP nucleation and growth. The accelerated CP reaction quickly consumes the supersaturation of the matrix, which decreases the chemical driving force for the DP reaction. In addition, the pre-formed CP nanoparticles retard the migrating grain boundaries, which kinetically inhibits the DP growth. Therefore, the low pre-strains lead to the CP-dominant microstructure.
3. At high pre-strains, the server plastic deformation induces the formation of a high density of deformation bands and subgrains, the boundaries of which provide preferred nucleation sites for the DP reaction. In addition, the high stored energy induced by the cold deformation enhances the grain boundary migration, which promotes the DP growth and concurrent recrystallization. Meanwhile, the metastable CP nanoparticles are swept by the fast-migrating DP front. As a result, the large pre-strains result in the formation of the fine-grained and DP-dominate microstructure.
4. The 40-70% pre-strained samples exhibit a yield strength of 990 MPa, an ultimate tensile strength of 1260 MPa, and an elongation of 20-22 %, indicating a good combination of high strength and ductility. The strength modeling indicates that the grain-boundary and precipitation strengthening plays a major role in strengthening the alloy.

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Figure captions

Fig. 1. Schematic diagram of the heat treatment process.

Fig. 2. EBSD IPF maps of the $(FeCoCrNi)_{94}Al_3Ti_3$ samples with different pre-strains.

Fig. 3. Representative SEM micrographs of the aged $(FeCoCrNi)_{94}Al_3Ti_3$ samples with different pre-strains.

Fig. 4. The variation of volume fraction of DP regions versus pre-strain.

Fig. 5. XRD profiles of the aged $(FeCoCrNi)_{94}Al_3Ti_3$ samples under different pre-strains.

Fig. 6. (a) Engineering tensile stress-strain curves of the samples with different pre-strains, and fracture surface of the (b) 0%SA and (c) 70%SA samples. SS state: solid solution state.

Fig. 7. (a, d) High-resolution SEM images, (b, e) APT nanostructures, and (c, f) proximity histograms of the samples with different pre-strains: (a-c) 0%SA and (d-f) 10%SA.

Fig. 8. GND density distribution map of the $(FeCoCrNi)_{94}Al_3Ti_3$ samples under different pre-strains before aging: (a) unstrained, (b) 10%, and (c) 20%.

Fig. 9. (a) SEM microstructure, (b) high-resolution micrograph of precipitates and grains, (c) EBSD IPF map, and (d) the grain size distribution of the 70%SA sample.

Fig. 10. Schematic diagram showing the precipitation mechanism of $L1_2$-strengthened HEAs under different pre-strains.

Fig. 11. Contributions of the solid solution, dislocations, grain boundaries, and precipitates to the yield strength of the 70%SA sample.