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Competition between continuous and discontinuous precipitation in L1$_2$-strengthened high-entropy alloys

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Abstract

Understanding of the competition between continuous precipitation (CP) and discontinuous precipitation (DP) is crucial for tailoring the microstructure and mechanical properties of precipitation-strengthened high-entropy alloys (HEAs). In this study, the effects of aging temperature, aging time, and grain size on the CP and DP behaviors of L1$_2$-strengthened HEAs were systematically investigated. Our results reveal that low temperatures favor the DP reaction while high temperatures facilitate the CP reaction, which is related to the nucleation site and diffusion path of the two precipitation modes. At intermediate temperatures, both the CP and DP occur simultaneously and compete with each other, and the solute concentration difference across the boundaries between the two precipitation regions serves as the driving force for the sweeping of the CP regions by the DP reaction. In addition, grain size refinement can promote the DP reaction by providing more nucleation sites and more fast diffusion paths, leading to the formation of the DP-dominant microstructure. This study not only sheds light on the fundamental understanding of the CP and DP mechanisms but also provides useful guidelines for the microstructure design of advanced $L1_2$-strengthened HEAs.

Keywords: high-entropy alloy; $L1_2$ precipitate; continuous precipitation; discontinuous precipitation; temperature effect.

1. Introduction

High-entropy alloys (HEAs) are emerging as a new class of metallic materials for structural and functional applications [1-7]. Particularly, face-centered cubic (fcc) HEAs have been receiving considerable attention due to their exceptional ductility and toughness over a wide temperature range [8-10]. These single-phase solid-solution alloys, however, generally exhibit low strength at ambient and elevated temperatures, which severely restricts their practical applications. Due to their superior combination of strength and ductility, $L1_2$-strengthened fcc-based HEAs have shown the promising potential as advanced structural materials for engineering applications [11-14]. The precipitation of $L1_2$ phases in fcc HEAs generally occurs in two competitive modes, namely continuous precipitation (CP) and discontinuous precipitation (DP). The CP refers to the uniform precipitation of $L1_2$ nanoparticles in grain interiors, which is associated with the continuous change of solute concentrations in the matrix [15, 16]. By contrast, the DP initiates at grain boundaries and proceeds inwards through the cellular growth of alternating plates of $L1_2$ precipitates and solute-depleted fcc matrix behind a moving grain boundary [17-19], leading to the non-uniform precipitation of coarse-sized $L1_2$-rods near grain boundaries. Previous studies indicated that CP and DP can occur simultaneously in $L1_2$-strengthened HEAs. For example, He *et al.* [20] reported that spherical CP nanoparticles form in the grain interior of a $(FeCoNiCr)_{94}Al_2Ti_4$ alloy, whereas coarse-sized DP rods intiate at grain boundaries. Kuo *et al.* [21] reported similar microstructures in a $Al_{0.2}Co_{1.5}CrFeNi_{1.5}Ti_{0.3}$ HEA, where they found that the DP microstructure is very sensitive to heat treatment. Zhao *et al.* [22] revealed that the volume fraction of DP colonies can be more than 50% in CoCrNi-based medium-entropy alloys (MEAs), occupying the majority of the microstructure. In terms of mechanical properties, the existence of DP rods not only decreases the precipitation strengthening efficiency but also deteriorates the strength of grain boundaries, resulting in a significant drop in both strength and ductility of HEAs [14, 21]. Thus, in order to facilitate alloy design and microstructural optimization for improved strength of alloys, it is crucial to systematically investigate the evolution of precipitate microstructures at different temperatures and mechanistically understand the CP and DP behaviors.

From the thermodynamic point of view, the driving force for the CP reaction is related to the degree of solute supersaturation in the matrix, whereas that of the DP reaction is the concentration difference of solutes across the boundary (reaction front) between the CP and DP regions. A strong DP reaction can lead to the invasion of DP colonies into CP regions, whereas a strong CP reaction can inhibit the DP process by reducing the concentration gradient across the boundaries. From the diffusion aspect, CP is controlled by bulk diffusion, whereas the DP is governed mainly by grain boundary diffusion. Therefore, the CP and DP are two competitive processes, and their competition determines the final microstructure of alloys. The competition of CP and DP is highly related to temperature, which can influence not only the driving force of CP and DP reactions but also the solute diffusion. In addition, since the DP initiates at grain boundaries and grows through grain boundary diffusion, the grain size can thus affect the DP behavior. It should be pointed out that due to the complexity of solute interactions, the elemental partitioning and solute diffusion in multicomponent HEAs are much more complicated than those in binary and ternary alloys [23-

25]. There is a lack of systematic investigations on the CP and DP behaviors of compositionally complex HEAs. To date, a clear scenario of the competition between the CP and DP reactions in $L1_2$-strengthened HEAs is not yet established, and a fundamental understanding of the key factors that control the CP and DP processes has not yet been fully evolved in these newly developed materials.

The purpose of this study is to systematically investigate the effects of aging temperature, aging time, and grain size on the CP and DP microstructures of $L1_2$-strengthened alloys and to elucidate the mechanism of the interplay of thermodynamics and kinetics in controlling precipitation processes. A $(FeCoCrNi)_{94}Al_3Ti_3$ alloy was chosen as a model system, because CP and DP can occur simultaneously in the alloy in a wide range of aging temperatures. Specifically, the volume fraction, morphology, and growth kinetics of CP and DP precipitates of the alloy at different aging temperatures and times and with different initial grain sizes were thoroughly investigated through a combination of X-ray diffraction (XRD), scanning electron microscopy (SEM), electron backscatter diffraction (EBSD), and atom probe tomography (APT). Particular attention was paid to the interplay of thermodynamic and kinetic factors in controlling precipitation and further the competition between CP and DP in $L1_2$-strengthened alloys.

2. Experimental

The alloy with a nominal composition of $(FeCoCrNi)_{94}Al_3Ti_3$ (at.%) was prepared by arc-melting a mixture of pure metals with purities higher than 99.9 wt.% under a protective argon atmosphere. Ingots were melted five times to ensure the chemical homogeneity and then drop-cast into a copper mold with a cavity of $50 \times 15 \times 3$ mm^3. The as-cast sheets were homogenized for 2 h at 1150 °C and then cold-rolled with a total reduction of approximately 70%. The cold-rolled plates were subjected to recrystallization for 3 min at 1150 °C, followed by water quenching and then aging at 500, 600, 700, 800, and 900 ºC for various periods of time. To fabricate samples with different initial grain sizes, the cold-rolled plates were subjected to recrystallization at 1150 ºC for various periods of time ranging from 70 s to 24 h, and the obtained samples were aged for 1 h at 800 ºC.

The resulting microstructures were examined by SEM, EBSD, and APT. SEM samples were mechanically polished using 0.3 μm alumina particles and then electrochemically etched with a solution of HNO_3 (25%) and C_2H_5OH (75%) for 2 min at 20 V and -40 ºC. EBSD samples were mechanically polished using 0.3 μm alumina particles, followed by electrochemically polishing with a solution of HNO_3 (15%) and C_2H_5OH (85%) for 1 min at 20 V and -40 ºC. APT needles were prepared by lift-outs and annular milled using an FEI Scios focused ion beam/scanning electron microscope (FIB/SEM). The APT characterization was performed in a local electrode atom probe (CAMECA Instruments LEAP 5000XR). The APT needles were analyzed in voltage mode, at a specimen 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. 3D reconstructions and data analysis were conducted by using Imago Visualization and Analysis Software version 3.8. Crystal structures were examined by XRD with Cu Kα radiation at a scanning rate of 5 °/min in the 2θ range from 20° to 100°. The DP volume fraction was estimated based on the SEM images by measuring the area fraction of DP regions. The DP regions were manually traced, and at least four SEM images with an area of 300 × 300 μm^2 were measured for each sample.

3. Results

3.1 Microstructural evolution with aging temperature and time

Representative SEM micrographs of the $(FeCoCrNi)_{94}Al_3Ti_3$ alloy aged at 500–900 °C for various periods of time are presented in Fig. 1. The DP regions containing coarse-sized rod-like precipitates exhibit a bright contrast as compared with the untransformed and CP regions. The volume fractions of DP regions at different temperatures are summarized in Fig. 2 as a function of aging time. It is noted that Fig. 2 contains more data points than Fig. 1, because more than 10 aging conditions at each temperature were measured in statistical analysis of volume fractions and Fig. 1 only presents the representative images at five conditions. At 500 °C, no DP regions were observed at the 3-min condition, and the DP structure starts to form at the 20-min condition. As the aging time increases, the DP structure can be observed at more grain boundaries, but the growth rate is very slow. The volume fraction of DP regions increases slowly to approximately 2% at the 4-h condition and to approximately 7% at the 48-h condition. At 600 °C, there is still no DP structure at the 3-min condition, but a considerable amount of DP regions can be clearly observed after further aging. The DP colonies are localized along grain boundaries within a narrow region (less than 5 μm in width) at the 20-min condition, and they gradually proceed from grain boundaries to grain interiors with increasing aging time and eventually occupy the entire sample. Statistical analyses reveal that the volume fraction of DP regions increases from 13% at 20 min to 20% at 1 h to 47% at 4 h and finally to 100% at 48 h, showing a higher growth rate at 600 °C than that at 500 °C. When the temperature increases to 700 °C, the DP grows even faster. The DP can be clearly observed at the 3-min condition and rapidly covers half of the microstructure after aging for 20 min, which is much shorter than that at 600 °C (4 h). The volume fraction of DP regions is approximately 71% at 1 h, 87% at 4 h, and almost 100% at 48 h. It is evident that the DP is the dominant mode of precipitation at 600 and 700 °C, and a full DP microstructure can be obtained within 48 h. When further increasing the temperature to 800 °C, a thin layer of DP regions can be observed at most grain boundaries under the 3-min condition, and it grows rapidly into grain interiors in the first 20 min. After that, the growth of DP slows down substantially and almost stops after aging for 4 h. The volume fraction of DP remains at around 50% with further aging, resulting in a mixed microstructure consisting of a half of CP and a half of DP regions. When the temperature further increases to 900 ºC, a small amount of DP regions (approximately 7%) can be observed under all the studied conditions, which are limited at the grain boundaries without invasion into the grain interiors.

From the volume fraction profiles (Fig. 2), it is clear that the kinetics of DP reaction is significantly different at different temperatures in the range of 500–900 ºC. At 500 ºC, the volume fraction profile shows a slow growth of DP, and less than 10% of DP regions form even after aging for 120 h. When the temperature increases to 600 and 700 ºC, the volume fraction curves display a sigmoidal relationship with aging time, and the volume fraction of DP reaches 100% within 120 h. Furthermore, the volume fraction curve reaches the half saturation after 20 min at 700 ºC and after more than 200 min at 600 ºC, indicating a faster kinetics of DP at the higher temperature. In contrast, with further increasing the temperature to 800 ºC, the volume fraction of DP regions reaches a saturation value of approximately 50% after aging for 2 h, instead of 100% as observed at 600 and 700 ºC. At 900 ºC, the volume fraction of DP regions is steady and does not change with aging time. Therefore, the DP formation is sensitive to both aging temperature and time.

High-resolution SEM images of the CP and DP regions after aging for 48 h at 800 ºC are shown in Figs. 3a and b, respectively. Evenly distributed nanoparticles in the grain interior are formed via the CP mode, whereas the colonies of parallel precipitates with a lamellar structure perpendicular to grain boundaries are formed via the DP mode. It is revealed that the width of the DP rods is much larger than the diameter of the CP nanoparticles. The phase structures of the

$(FeCoCrNi)_{94}Al_3Ti_3$ alloy after aging for 120 h at 500-900 ºC were examined by XRD, and the corresponding patterns are shown in Fig. 3b. It is noted that although the samples aged at different temperatures contain considerably different amounts of CP and DP regions, they exhibit similar XRD peaks indexing to the FCC/$L1_2$ phases, confirming that the precipitates in the CP and DP regions have the same crystal structure.

3.2 APT characterization

For the samples aged at 800 and 900 ºC, the nanoparticles can clearly be observed in the dark-contrasted grain interior from SEM (Fig. 1), indicating the occurrence of CP reaction at these temperatures. In contrast, the microstructure of the dark-contrasted regions in the samples aged at 500–700 ºC can not be clearly revealed by SEM, because the size of CP nanoparticles, if any, may be beyond the resolution limit of SEM. In order to figure out whether the CP reaction occurs or not at these temperatures, the grain interiors of the samples aged for 1 h at 500, 600, and 700 ºC were investigated by APT, and the required samples were cut out from the dark-contrasted grain interiors by using the site-specific FIB lift-out technique.

The APT microstructures of the grain interiors at 500 and 600 ºC are shown on the left side of Figs. 4a and b, respectively. It is evident that all the elements were uniformly distributed without any signs of precipitation, indicating that these regions are untransformed regions, rather than CP regions. To statistically confirm the observed results, the frequency distributions of solute elements at 500 and 600 ºC are plotted on the right side of Figs. 4a and b, respectively. It is found that the distributions of all elements are in good agreement with the binomial distribution, which statistically confirms the random distribution of solute elements in the two samples. The degree of randomness, μ, is measured by the Pearson coefficient, which can be calculated by

$$\mu = \sqrt{\frac{\chi^2}{N + \chi^2}} \tag{1}$$

where χ^2 is the deviation of the experimentally measured distribution from the binomial. The μ value varies between 0 and 1, where 0 represents the complete randomness and 1 refers to the formation of clusters or precipitates [26]. The Pearson coefficient for Fe, Co, Cr, Ni, Al, and Ti at 500 and 600 °C are all very close to 0, further confirming that all the elements in the samples aged for 1 h at 500 and 600 °C are in random distribution and no clusters and precipitates form under these two conditions. Therefore, the CP reaction does not occur after aging for 1 h at 500 and 600 °C, and the dark-contrasted grain interiors are the untransformed regions in these two samples.

The APT maps of the dark-contrasted grain interiors in the sample aged for 1 h at 700 °C are displayed on the left side of Fig. 5a. The partitioning of Ni, Al, and Ti to the precipitates and Fe, Co, and Cr to the matrix is clearly evident, indicating that the CP reaction occurs in this condition. The 12 at.% (Al + Ti) concentration isosurfaces were used to visualize the precipitates. It is revealed that the CP nanoparticles have a near-spheroidal shape and are uniformly distributed in the matrix. The corresponding proximity histogram based on the concentration isosurfaces is displayed on the right side of Fig. 5a, and the concentrations of the precipitate core and far-field matrix are summarized in Table 1. The precipitates contain 59.5 at.% Ni, 10.6 at.% Co, 8.7 at.% Al, and 17.8 at.% Ti. The atomic ratio of (Ni + Co + Fe + Cr) : (Al + Ti) in the precipitates is approximately 3:1, indicating a $L1_2$-type $(Ni,Co,Fe,Cr)_3(Al,Ti)$ phase. The matrix is depleted in Ni, Al, and Ti and enriched in Fe, Co, and Cr, and its composition can be regarded as 27.8Fe-24.6Co-26.2Cr-18.1Ni-2.1Al-1.2Ti (at.%).

Because of the concurrence of CP and DP in the sample aged for 1 h at 700 °C, we also examined the precipitate microstructure of the DP region through APT, the required specimens for which were obtained by using the site-specific FIB lift-out technique. The atom maps of Ni, Al, Ti, Fe, Co, and Cr in the DP region are illustrated on the left side of Fig. 5b, and the 12 at.% (Al + Ti) concentration isosurfaces and proximity histogram are displayed on the right side of Fig. 5b. The DP rods are enriched in Ni (58.6 at.%), Al (9.0 at.%), and Ti (15.9 at.%) and depleted in Fe (2.8 at.%), Co (11.8 at.%), and Cr (1.9 at.%). They are highly oriented and aligned parallel to each other; this observation is consistent with the SEM results (Fig. 3a). The concentrations of the DP rods and far-field matrix are also given in Table 1. The matrix composition was determined to be 28.9Fe-26.1Co-26.2Cr-16.2Ni-1.8Al-0.8Ti (at.%). It is revealed that the Ni, Al, and Ti concentrations in the DP matrix are much lower than that in the CP matrix, suggesting that the DP matrix is closer to equilibrium as compared with the CP matrix.

3.3 Grain size effect

Since the DP reaction initiates at grain boundaries, the effects of grain size on the DP microstructure were also investigated. The initial grain size was controlled by changing the recrystallization time in the range of 70 s – 30 min. The representative EBSD inverse pole figure (IPF) maps of the samples with different initial grain sizes are shown in Figs. 6a–d. All the samples exhibit a uniform distribution of equiaxed grains and random orientations, and their average grain sizes were determined to be 4 ± 2, 10 ± 6, 35 ± 6, and 60 ± 8 μm, respectively. The samples with different grain sizes were subjected to aging at 800 ºC for 1 h, and the corresponding SEM microstructures are displayed in Figs. 6e–h. For the sample with an average grain size of 4 μm, the DP region occupies the majority of the microstructure (86%). When the grain size increases to 10 μm, the volume fraction of DP regions decreases to 67%. Further increasing the grain size to 38 and 60 μm, the volume fraction of DP drops to 35% and 25%, respectively. For the statistical analysis of the relationship between the grain size and volume fraction of DP regions, 9 samples with average grain sizes in the range of 4–170 μm were examined, and the variation of volume fraction of DP regions is shown in Fig. 7 as a function of initial grain size. It is found that the volume fraction of DP regions decreases with the increase of grain size. The microstructure in Fig. 6e–h shows the competition between CP and DP with the variation of the initial grain size. The DP dominates in the fine-grained samples, whereas the CP dominates in the coarse-grained samples. Therefore, the grain size refinement promotes the DP in the $L1_2$-strengthened HEAs.

4. Discussion

The aforementioned results indicate that the CP and DP reactions are two competitive processes, and their combination determines the final microstructure of alloys. In the following sections, the effects of aging temperature, aging time, and grain size on the competition of CP and DP behaviors will be analyzed and discussed in detail.

4.1 Growth kinetics of DP

The growth kinetic of DP can be described by the Johnson–Mehl–Avrami–Kolmogorov (JMAK) equation [34], in which the volume fraction (X) of DP regions can be expressed by

$$X = 1 - \exp\left[-(kt)^n\right] \tag{2}$$

where k is a temperature-dependent parameter, which is related to the nucleation and growth rates, t is the aging time (s), and n is the Avrami exponent associated with the nucleation sites of DP. n = 1, 2, and 3 represent the DP nucleation at grain boundaries, interface edges, and crystal corners, respectively [27]. The growth rate of DP was evaluated using Eq. 2 by plotting $\ln[-\ln(1\text{-}X)]$ versus $\ln t$ at 600, 700, and 800 °C, and the results are illustrated in Fig. 8a. At 600 and 700 °C, there is an approximately linear relationship between $\ln[-\ln(1\text{-}X)]$ and $\ln t$. In contrast, the plot at 800 °C gives a linear relationship at $\ln t < 7$ and beyond that the plot deviates from the linear relationship. The decrease of the slope at the later stage of aging can be attributed to the decrease of the DP growth rate. The change of DP growth rate is probably affected by the strong CP reaction, and the reasons can be twofold. First, the CP reaction for a period of 10 min leads to a substantial decrease of the supersaturation of the CP matrix, which decreases the concentration difference between the CP and DP matrices and hence the driving force for the DP growth. Second, the CP nanoparticles can pin the moving grain boundaries, which kinetically retards the DP growth. Therefore, for the plot at 800 ºC the data of the first 10 min of aging was used to calculate the DP kinetic parameters. The n and k values at different temperatures were calculated by linear fitting and are listed in Table 2. It is noted that the n values at different temperatures are close to 1, indicating that the DP colonies nucleate mainly at grain boundaries. The k value increases from 3.56×10^{-5} s^{-1} at 600 ºC to 1.03×10^{-4} s^{-1} at 700 ºC and to 5.48×10^{-4} s^{-1} at 800 ºC, implying that the growth rate of DP increases substantially with the aging temperature.

The activation energy of DP growth can be denoted by the Arrhenius equation

$$k = k_0 \exp\left(-\frac{Q}{RT}\right) \tag{3}$$

where k_0 is a constant, Q is the activation energy of the DP reaction which is related to the energy barrier for the DP growth, R = 8.314 J/mol is the gas constant, and T is the aging temperature (K). The activation energy of DP can be determined from the slope of the plot of ln$k$ versus 1/T, as illustrated in Fig. 8b. Based on the slope, the activation energy of DP was determined to be 105.3 kJ/mol. We compared this value with the activation energy of CP reactions in multicomponent alloys. From literature, the activation energy of CP reactions in $L1_2$-strengthened superalloys is around 245-298 kJ/mol [28-30]. Notably, the activation energy for the coarsening of CP nanoparticles in $(FeCoCrNi)_{94}Al_4Ti_2$ HEAs, which have very similar compositions to this research, is estimated to be 276 kJ/mol [31]. The activation energy of DP is distinctly smaller than that of the CP in multicomponent alloys, which is related to the growth mechanisms of the two precipitation modes. The CP precipitates grow through bulk diffusion, whereas the DP precipitates grow through grain boundary diffusion; the rate of the latter is known to be exceptionally higher than that of the former. Thus, the DP reaction can be activated more easily than the CP reaction. As a result, the DP-dominant microstructures exist in the samples aged at 600–800 °C.

It is worthy to mention that the DP is a very common phenomenon in $L1_2$-strengthened HEAs. The prevalence of the DP behavior in this kind of alloys is likely to be related to the grain boundary segregation of Ni, Al and Ti in these materials, as revealed by Yang *et al*. [32] by using scanning transmission electron microscopy-energy dispersive X-ray spectrum (STEM-EDS). These three elements are the major components of $L1_2$ precipitates in HEAs. Thus, the grain boundary segregation of Ni, Al, and Ti provides the chemical condition for the precipitation of $L1_2$ precipitates in the DP mode. Therefore, the DP microstructures are often observed in $L1_2$-strengthened HEAs.

4.2 Temperature effect

The microstructural observations reveal that the precipitate mode changes from DP-dominant to CP-dominant when the temperature increases from 500 to 900 °C. Fundamentally, the combination of thermodynamic and kinetic factors determines the overall microstructure of alloys. The temperature effect on the precipitation behavior of $L1_2$-strengthened HEAs can be explained by the interplay of thermodynamic and kinetic factors. At 500 °C, the bulk diffusion is severely restricted, which kinetically inhibits the CP formation. As a result, no CP particles were observed in the 1-h aged sample (Fig. 4a). At this temperature, the grain-boundary diffusion takes place but at a very slow rate, through which the DP reaction proceeds slowly. Thus, the DP structure is limited in a narrow region along grain boundaries, and the grain interior is the untransformed region. At 600 °C, the bulk diffusion is still insufficient for the CP reaction, and thus, no CP nanoparticles were detected in the 1-h aged sample (Fig. 4b). However, the grain-boundary diffusion is substantially enhanced at this temperature, making the DP reaction kinetically favorable. As the DP reaction proceeds, the DP region gradually expands and eventually occupies the whole microstructure (Fig. 1). When the temperature increases to 700 °C, the CP and DP co-occur and compete with each other (Fig. 5). At this temperature, the bulk diffusion is pronouncedly enhanced, and the CP reaction is thus activated, as manifested by the observation of nanoscale particles in the grain interior of the 1-h aged sample. Meanwhile, the grain-boundary diffusion is also remarkably accelerated at 700 °C, leading to the higher growth rate of DP as compared with that at 600 °C. From the nucleation and growth points of view, the CP particles nucleate in grain interiors and grow through bulk diffusion, whereas the DP rods initial at grain boundaries and grow through grain-boundary diffusion. Thus, the DP reaction can be energetically more favorable than the CP reaction. In the $(FeCoNiCr)_{94}Al_3Ti_3$ alloy, the DP reaction is dominant at 700 °C, leading to the prevailing of rod-like DP precipitates in the microstructure. At 800 °C, both CP and DP reactions can proceed in the early stages of aging. The CP reaction is drastically enhanced due to the acceleration of the bulk diffusion, resulting in a rapid decrease of the supersaturation in the matrix ahead of the migrating reaction front of DP and hence decreasing the driving force for the DP growth. As a result, the DP reaction stops at later stages of aging, and a mixed microstructure containing CP in grain interiors and DP at grain boundaries was observed. As the temperature increases to 900 °C, the CP reaction is further enhanced, which has two effects on the DP reaction. First, the CP reaction is sufficient to establish a near-equilibrium state in a short period of time, which significantly reduces the composition gradient across the reaction front of DP cells, thereby thermodynamically decreasing the chemical driving force for the DP reaction. Second, the precipitates formed through the CP reaction tend to have a coarse size at high temperatures, which can generate a strong pinning effect on the migrating grain boundaries, thereby kinetically inhibiting the DP reaction. As a result of the two effects, the DP occurs at grain boundaries in the very initial stage of aging but stops to procced into the grain interior with further aging. Therefore, the CP reaction prevails at 900 ºC, leading to the CP-dominated microstructure.

4.3 Competition between CP and DP

Both the CP and DP occur simultaneously at 700–900 ºC, and the fraction of CP and DP changes with the aging time. Especially, at 700 ºC the DP region gradually sweeps all the CP region, leading to a full DP structure at the 48-h-aged condition. The sweeping of CP regions by the DP reaction in the $L1_2$-strengthened HEA can be schematically illustrated in Fig. 9 and described by

$$\gamma_{CP} + L1_2(CP) \rightarrow \gamma_{DP} + L1_2(DP) \tag{4}$$

where γ_{CP} is the supersaturated matrix in the CP region, γ_{DP} is a more thermodynamically stable matrix in the DP region, and $L1_2$(CP) and $L1_2$(DP) are the $L1_2$ precipitates in the CP and DP regions, respectively. The supersaturation of the CP matrix changes with the aging time, because the CP reaction continuously consumes the supersaturated matrix. In contrast, the DP reaction results in an abrupt change of the solute concertation in the DP matrix, the composition of which is considered to be close to that of the equilibrium state. The concentration difference of components across the migrating grain boundary between the CP and DP regions functions as a chemical driving force for the sweeping of CP regions by the DP reaction. As Ni, Al, and Ti are the major elements for the $L1_2$ precipitation, the Ni, Al, and Ti concentrations in the CP and DP matrix were compared, as illustrated in Fig. 10. The concentrations of Ni, Al, and Ti in the CP matrix are much higher than those in the DP matrix, providing a large driving force for the DP growth. The chemical driving force for the DP sweeping can be calculated by [33]:

$$\Delta G_{DP} = -RT\left(x_{Fe}^{CP} \ln\frac{x_{Fe}^{CP}}{x_{Fe}^{DP}} + x_{Co}^{CP} \ln\frac{x_{Co}^{CP}}{x_{Co}^{DP}} + x_{Cr}^{CP} \ln\frac{x_{Cr}^{CP}}{x_{Cr}^{DP}} + x_{Ni}^{CP} \ln\frac{x_{Ni}^{CP}}{x_{Ni}^{DP}} + x_{Al}^{CP} \ln\frac{x_{Al}^{CP}}{x_{Al}^{DP}} + x_{Ti}^{CP} \ln\frac{x_{Ti}^{CP}}{x_{Ti}^{DP}} \right) \quad (5)$$

where R is the gas constant, T is the temperature, x_{Fe}^{CP}, x_{Co}^{CP}, x_{Cr}^{CP}, x_{Ni}^{CP}, x_{Al}^{CP} and x_{Ti}^{CP} are the Fe, Co, Cr, Ni, Al, and Ti concentrations in the CP matrix, respectively, and x_{Fe}^{DP}, x_{Co}^{DP}, x_{Cr}^{DP}, x_{Ni}^{DP}, x_{Al}^{DP} and x_{Ti}^{DP} are the Fe, Co, Cr, Ni, Al, and Ti concentrations in the DP matrix, respectively. With the input of APT concentrations of the CP and DP matrix in the 1-h-aged condition, the chemical driving force for the DP reaction was estimated to be around -23 J/mol in this condition; this negative value means that the DP reaction still has a considerable chemical driving force to proceed. As a result, it is observed that prolonged aging results in an increase in the volume fraction of DP regions and eventually a full DP microstructure is formed at 48 h.

On the basis of the aforementioned discussion, the microstructural evolution of the L1$_2$-strengthened HEA as a function of temperature and time is schematically illustrated in Fig.11 and summarized in the following text. At low temperatures (such as 500–600 °C), the CP reaction does not occur due to the kinetic restriction, whereas the DP reaction occurs at grain boundaries, resulting in a DP-dominant structure. As the temperature increases, both the CP and DP reactions are activated and kinetically enhanced. The difference of solute concertation between the CP and DP matrices provides the chemical driving force for the sweeping of CP regions by the DP front. As a result, a part or the whole CP region is invaded by the DP region, and the microstructure can be of DP-dominant or a CP/DP mixture. Further increasing the temperature results in a substantial increase in the bulk diffusion, which makes the CP reaction sufficient to establish a near-equilibrium state within a short period of time, thereby thermodynamically decreasing the chemical driving force for the DP reaction and forming a CP-dominant microstructure.

4.4 Grain size effect

As mentioned in Section 3.3, the precipitate microstructure changes from CP-dominant to DP-dominant structure with decreased grain size, which reveals that the grain size can significantly influence the precipitation mode and microstructure. The grain size effect on the CP and DP competition can be explained based on the following considerations. First, grain boundaries are known to serve as the nucleation sites for the DP reaction. The grain size refinement results in an increased number of nucleation sites for DP. Therefore, the grain size refinement can promote the DP nucleation. Second, grain boundaries act as fast diffusion paths, and the solute diffusion along grain boundaries is much faster than the bulk diffusion in the grain interior. The DP reaction proceeds through grain boundary diffusion, and thus, fine structures with high numbers of grain boundaries facilitate the growth of DP. Third, the structures with fine grains have higher grain-boundary energy as compared with their counterparts with coarse grains. Upon annealing, fine grains tend to grow in order to reduce grain-boundary energy. As discussed previously, the DP colonies grow behind the moving grain boundaries. Therefore, fine grain structures result in a high grain-boundary mobility, which is also beneficial to the growth of DP. Consequently, the grain size refinement promotes the DP reaction by accelerating its nucleation and growth, leading to the change of precipitation mode from CP-dominated to DP-dominated (cf. Fig. 6).

It is worth pointing out that grain size refinement and precipitation strengthening are two of the most useful and commonly used methods to improve the strength of structural alloys, and these two methods are often used simultaneously in order to achieve superior mechanical properties. It needs to highlight that careful attention should be paid to the precipitation mode when the grain size refinement is employed in precipitation-strengthened alloys that have DP reactions, because the grain size refinement would promote the DP reaction, which leads to the formation of coarse precipitates, thereby weakening the precipitation strengthening effect. In these materials, it is important to develop efficient strategies to inhibit the DP reaction. For example, it was found that Nb alloying is effective to suppress the DP reaction and promote the CP reaction of $L1_2$-strengthened HEAs [34]. Therefore, for the design of high-performance HEAs, it is crucial to control the overall microstructure and optimize the contribution of various strengthening methods.

5. Conclusions

In this study, the effects of aging temperature, aging time, and grain size on the CP and DP behaviors in the $L1_2$-strengthened $(FeCoCrNi)_{94}Al_3Ti_3$ alloy were systematically investigated and the following conclusions are drawn:

1. Aging temperature has a significant impact on the CP and DP behaviors in the $L1_2$-strengthened HEA, which is due to the interplay of thermodynamic and kinetic factors. The CP nanoparticles nucleate in grain interiors and grow through the bulk diffusion, whereas the DP rods initiate at grain boundaries and grow through the grain-boundary diffusion. At 500 and 600 °C, the CP reaction is kinetically inhibited by the slow bulk diffusion, whereas the DP reaction occurs along grain boundaries, leading to a DP-dominant microstructure. As the temperature increases to 700–800 °C, both the CP and DP reactions occur simultaneously. The DP matrix, however, is closer to equilibrium than the CP matrix, leading to the sweeping of a part or the whole of CP regions by the DP front. At 900 °C, the CP reaction is sufficient to establish a near-equilibrium state in a short period of time, which thermodynamically decreases the chemical driving force for the DP reaction, thereby forming the CP-dominated microstructure.

2. The competition between CP and DP involves with the aging time. The supersaturation of the CP matrix changes continuously with the aging time, whereas that of the DP matrix varies abruptly to a near-equilibrium state. The APT results reveal that there is an obvious compositional difference between the CP and DP matrices at 700 °C, which provides the chemical driving force for the sweeping of the CP regions by the DP reaction. As the aging time increases, the volume fraction of CP regions decreases, while that of DP regions increases, leading to a full DP microstructure after aging for 48 h at 700 °C.
3. The competition between the CP and DP reactions is also influenced by grain sizes. Our results indicate that grain size refinement promotes the DP behavior, and the reasons could be threefold. First, the grain size refinement results in the increased number of grain boundaries, which provides more nucleation sites for DP. Second, the DP reaction proceeds through the grain-boundary diffusion, and therefore, fine structures facilitate the growth of DP. Third, fine-grain structures have the high grain-boundary mobility, which is also beneficial to the growth of DP.

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Figure captions

Fig. 1. Representative SEM micrographs of the $(FeCoCrNi)_{94}Al_3Ti_3$ alloy aged at 500–900 °C.

Fig. 2. The variation of volume fraction of DP regions versus aging time at 500–900 °C.

Fig. 3. (a) High-resolution SEM images of CP and DP structures of the $(FeCoCrNi)_{94}Al_3Ti_3$ alloy aged at 800 °C for 1 h and (b) XRD profiles of the Al_3Ti_3 alloy aged at 500–900 °C for 120 h.

Fig. 4. Atom maps and frequency distributions of the grain-interior region after aging for 1 h at (a) 500 and (b) 600 °C.

Fig. 5. Atom maps, 12 at.% (Al+Ti) isoconcentration surfaces, and proximity histograms of the (a) CP and (b) DP regions after aging at 700 °C for 1 h.

Fig. 6. (a–d) EBSD inverse pole figure maps of the $(FeCoCrNi)_{94}Al_3Ti_3$ alloy with different initial grain sizes and (e–h) the corresponding DP microstructures after aging at 800 °C for 1 h.

Fig. 7. The variation of volume fraction of DP regions after aging at 800 °C for 1 h versus initial grain sizes of the $(FeCoCrNi)_{94}Al_3Ti_3$ alloy.

Fig. 8. (a) The relationship between $\ln[-\ln(1-X)]$ and $\ln t$ and (b) Arrhenius plot of $\ln k$ versus $1/T$ of the $(FeCoCrNi)_{94}Al_3Ti_3$ alloy.

Fig. 9. Schematic diagram of the sweeping of CP regions by the DP reaction.

Fig. 10. The Ni, Al, and Ti concentrations in the CP and DP matrix after aging for 1 h at 700 °C.

Fig. 11. Schematic showing the microstructural evolution of the $L1_2$-strengthened HEAs as a function of aging temperature and time.