Precipitation behavior and its effects on tensile properties of FeCoNiCr

high-entropy alloys

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Abstract

In this work, we present a systematic study on the precipitation behavior and mechanical properties of a FeCoNiCr-based high-entropy alloy alloyed with dilute amounts of Ti and Al, (FeCoNiCr)_{100-x-y}Ti_xAl_y (where x=1~3, y=4~9 at.%). It was found that, upon aging, nano-sized L1₂-Ni₃(Ti, Al) particles are formed within grains, whilst L2₁-(Ni, Co)₂TiAl Heusler particles are formed mainly along grain boundaries. The relative thermal stability of the two phases were studied at different aging temperatures (700-900 °C) with various durations of time (up to 48 h) and the results were directly compared with Thermo-calc calculations. Tensile tests were also conducted on alloys aged under different conditions. The measured properties, including strength and ductility, were correlated with the microstructure of aged (FeCoNiCr)_{100-x-y}Ti_xAl_y alloys, with particular attention on the distribution and morphology of the two kinds of precipitate. Whereas both phases could contribute to the strengthening of the alloys via either Orowan bowing or particle shearing mechanism, the brittle (Ni, Co)₂TiAl Heusler phase was found to mainly affect the tensile plasticity. A simple composite model was proposed to describe the plastic strain of alloys. Based on observed microstructure and its corresponding mechanical performance, the alloy with the composition of (FeCoNiCr)₉₄Ti₂Al₄, when aged between 700 and 800 °C, gives the best balanced strength/ductility properties.

Keywords: High-entropy alloys; precipitation hardening; strengthening mechanisms; tensile behavior; thermodynamic stability

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1. Introduction

Recently, a new class of alloys, known as high-entropy alloys (HEAs), emerged and attracted large attention due to their many interesting properties and associated scientific understanding [1-7]. HEA systems usually contain multiple constituents (>5) with a nearly equal ratio and, therefore, a high resultant configurational entropy which usually promotes formation of simple solid-solution structures [8, 9]. Studies indicated that concentrated HEA matrices exhibited high phase stability, especially at high temperatures, and sluggish atomic diffusion, enabling to be promising candidate materials for high-temperature applications [10-12]. Up to date, serious efforts have been devoted to developing HEAs with a single phase for uses at elevated temperatures, e.g., bcc-structured [13, 14] or fcc-structured [15-17]. For example, in the case of fcc HEAs, FeCoNiCrMn and FeCoNiCr have a slower atomic diffusion because their close-packing lattice and good ductility of more than 60%. However, due to the lack of appropriate strengthening mechanism, the strength of these alloys is insufficient for structural applications [16].

Precipitation hardening is one of the widely used mechanisms and has been employed to strengthen several fcc HEAs, such as $\text{Al}_x\text{FeCoNiCrMn}$ [18], $\text{Al}_x\text{FeCoNiCr}$ [19] and $\text{Nb}_x\text{FeCoNiCr}$ [20]. Unfortunately, most of the precipitates formed were brittle intermetallic compounds with a size of some tens or hundreds of microns, which only provides moderate strength increment but dramatically degrade the plasticity. On the other hand, it was reported that minor addition of either Al or Ti in the FeCoNiCr matrix, e.g., $\text{FeCoNiCrAl}_{0.3}$ [21] and $\text{FeCoNiCrTi}_{0.3}$ [22], could induce the formation of coherent nano-precipitates in the as-cast condition, but the distribution of these nano-phases was not uniform.

Most recently, we demonstrated that simultaneous addition of 2 at.% Ti and 4 at.% Al, into the fcc-FeCoNiCr HEA induced the formation of nano-sized L_{12} coherent precipitates [23]. In fact, when the alloy was aged at 800 °C for 18 h, a uniform dispersion of high-density

Ni₃(Ti,Al)-type phase was observed in the matrix. More importantly, significant precipitation strengthening effect was achieved (strength > 1GPa) without sacrificing ductility (~39%) and work hardening capability. In this work, we carry out a systematic study of the effects of alloying additions (i.e., the Ti and Al concentration) and thermal mechanical treatment on the precipitation behavior and tensile properties in an attempt to shed lights on the nature of precipitation hardening in HEAs and the understanding of the structure-properties relationship.

2. Experimental

Alloys with compositions of $(\text{FeCoNiCr})_{100-x-y}\text{Ti}_x\text{Al}_y$ ($x=1\sim3$ and $y=4\sim9$ at.%) were prepared by arc-melting a mixture of pure metals (purity higher than 99.9%). For simplicity, four alloys $(\text{FeCoNiCr})_{95}\text{Ti}_1\text{Al}_4$ (at.%), $(\text{FeCoNiCr})_{94}\text{Ti}_2\text{Al}_4$, $(\text{FeCoNiCr})_{91}\text{Ti}_3\text{Al}_6$ and $(\text{FeCoNiCr})_{88}\text{Ti}_3\text{Al}_9$ are, hereafter, denoted as TA14, TA24, TA36 and TA39, respectively. All the alloy ingots were re-melted at least six times to ensure chemical homogeneity. The master ingots were then drop-cast into a copper mold with a dimension of $10\times10\times60\text{ mm}^3$, and subsequently tube-sealed and homogenized at $1200\text{ }^\circ\text{C}$ for 4 h. Before aging processes, the sliced samples were cold-rolled to a reduction ratio of 30%, followed by a recrystallization process at $1000\text{ }^\circ\text{C}$ for 2 h to obtain a uniform and stable grain size structure.

To study the effects of thermal treatment, aging temperature was varied from 700 to $900\text{ }^\circ\text{C}$ while the aging duration was controlled from 0.5 to 48 h. To investigate the alloying effects, a standard process of aging at $800\text{ }^\circ\text{C}$ for 18 h was chosen [23], followed by water quenching.

For tensile tests, dog bone-shaped samples with a gauge length of 20 mm, a width of 5 mm and a thickness of 1.3 mm were prepared, and their surfaces were polished down to a 2000-grit SiC paper. A CMT4105 universal electronic tensile testing machine was employed for tests at room temperature with a nominal strain rate of $1\times10^{-3}\text{ s}^{-1}$.

For crystal structure characterization, X-ray diffraction (XRD) samples with a dimension of $6\times10\times1.5\text{ mm}^3$ were wire-electrode cut and polished, then examined using a MXP21VAHF machine with $\text{CuK}\alpha$ radiation. The scanning 2θ range is from 20 to 100° and the scanning step is 0.02° . For microstructure characterization, a Zeiss Supra55 scanning electron microscope (SEM) with an energy dispersive spectrometer (EDS) and a Tecnai F30 field emission transmission electron microscope (TEM) operated under a 300 KV acceleration voltage were employed. The SEM specimens were initially polished down to 2000-grit SiC paper and subsequently, electrochemically polished for the final surface finish using a $\text{HClO}_4\text{:C}_2\text{H}_6\text{O}=1\text{:}9$ solution with a direct voltage of 30 V at room temperature. The TEM sample discs with a diameter of 3 mm were

punched from the bulk and then ground to about 50 μm thick, followed by twin-jet electro-polishing using a mixed solution of $\text{HNO}_3\text{:CH}_4\text{O}=1\text{:}4$ at a temperature around $-40\text{ }^\circ\text{C}$.

3. Results

3.1 Effect of alloying addition of Ti and Al on microstructure

A standard recrystallization (1000 °C and 2 h) plus subsequent aging at 800 °C and 18 h was employed to investigate alloying effects of Ti and Al on the microstructural evolution in the current FeCoNiCr-based HEA. XRD patterns from the recrystallized (denoted as R) and aged (denoted as A) TA14, TA24, TA36, and TA39 samples are shown in Fig. 1. These samples all exhibit a main FCC (face-centered-cubic) structure. However, in TA36 and TA39 samples, the FCC peaks are noted to slightly shift toward a smaller angle, suggesting the lattice is dilated as a result of higher Ti and Al additions into the crystalline lattice. Furthermore, several extra peaks are detected in the two samples even in the recrystallized state, indicating the presence of second phases. X-ray analysis reveals that these additional peaks are from Ni_2AlTi and the peak intensities increase after aging.

Microstructures of these samples were initially characterized using SEM. Figures 2(a) and 2(c) are structures of recrystallized TA14 and TA24, respectively, both showing a simple structure with few impurities sporadically dispersed in the matrix, which is consistent with the XRD results presented in Fig. 1. It is particularly noted that, in these recrystallized samples, the formation of precipitated particles was absent. After aging at 800°C, however, numerous nano-precipitates (less than 50 nm) began to form, as shown in the red region of Figs. 2b and (d). These particles are not discernible in the XRD patterns, probably because of their small sizes. A few large white particles (as indicated by green arrows) located in the grain boundary region are also observed in Figs. 2b and (d). Again, they do not appear in the XRD patterns, probably due to its low volume fraction. In comparison with TA14 and TA24 samples, key microstructure features of TA36 and TA39 are drastically different, as shown in Figs. 2e and 2f, and Figs. 2g and 2h, respectively. In these two higher Ti and Al-containing alloys, the precipitation of micron-sized particles becomes dominant. Whilst the nano-sized phase still remains, but its distribution is inhomogeneous and the amount is small (red circled region), suggesting that these

fine precipitates become unstable and replaced by the more thermally stable coarse particles.

A bright-field TEM image of the aged TA36 HEA is presented in Fig. 3(a). Ellipse-shape particles with a size ranging from 0.3 to 1 μm along the length direction are observed to disperse in a matrix (highlighted by green arrows), which consists of a small fraction of nano-sized particles shown in red circles. The selected area electron diffraction (SAED) result of the coarse particles is given in the up-right inset of Fig. 3(a). A $L2_1$ -type Heusler pattern is clearly seen, and its lattice parameter is determined to be ~ 0.592 nm. The corresponding EDS spectra reveal its average composition is Al: 20.3 at. %, Ti: 18.5 at. %, Cr: 4.5 at. %, Fe: 4.7 at. %, Co: 19.1 at. %, and Ni: 32.9 at. %, indicating that substantial amount of Ni is substituted by Co. Based on these results, we can eventually identify it as $(\text{Ni}, \text{Co})_2\text{TiAl}$ Heusler phase. Due to its brittle nature [24], the presence of this phase is expected to be detrimental to the macroscopic plasticity of the alloy, which will be discussed later. In addition, the SAED pattern of the nano particles is also inserted in the down-right of Fig. 3(a), showing a $L1_2$ -type $\text{Ni}_3(\text{Ti}, \text{Al})$ crystal lattice, similar to the γ' particles in Ni-based superalloys. It is particularly noted that for all object HEAs in this study, the coarse precipitates are all detected the same Heusler phase, whereas the fine nano-precipitates are the γ' phase. With additional Ti and Al, the microstructure of aged TA39 sample is shown in Fig. 3(b). The Heusler particles are apparently coarser than that in the TA36 sample (> 1 μm) and the amount of fine γ' is further reduced. These observations suggest that excessive amount of Ti and Al can promote the formation of $(\text{Ni}, \text{Co})_2\text{TiAl}$ ordered intermetallic phase and, meanwhile, the formation of coherent γ' phase is significantly suppressed.

3.2 Effect of aging temperature on microstructure

A systematic study was also carried out to investigate the effect of aging on the precipitation behavior in the current TAx systems. Scanning electron micrographs taken from TA24 alloy aged at different temperatures for 18h are shown in Fig. 4. At a lower aging temperature, for example, 700 $^{\circ}\text{C}$ (Fig. 4a) and 750 $^{\circ}\text{C}$ (Fig. 4c), numerous precipitates are found to spread in the vicinity of grain boundaries. Enlarged images (Figs. 4b and 4d) indicate that the distribution of

precipitated particles is not uniform; in fact, it consists of two regions. In Region I (highlighted by red circles), fine spherical particles with a diameter of less than 50 nm are dispersed inside the grain interior. In Region II (indicated by yellow circles), in contrast, plated-like particles larger than 100 nm are formed along grain boundaries, together also with some discrete Heusler particles marked by green arrows.

From the morphological variation of nanoparticles, we tentatively conclude that Region II is probably resulted from a discontinuous precipitation [25]. Upon aging, precipitates would preferentially form at microstructural heterogeneous sites such as grain boundaries. In addition, at a low aging temperature, for example 700 °C, diffusion along grain boundary is expected to be much faster than that within the lattice. This leads to the growth of plate-shaped precipitates at grain boundaries.

However, when the aging temperature is raised to 800 °C, Region II disappears and the agglomeration of nano-sized particles along grain boundaries is no longer observed. Instead, grain boundary is now decorated with a layer of semi-continuous micron-sized Heusler particles, whilst nano-sized $L1_2$ precipitates are still uniformly distributed within grain interior, as marked by red circles. At yet higher temperature, e.g., 850 °C, nano-precipitates within grains gradually diminish (Fig. 4g) and, eventually, vanish at 900 °C (Fig. 4h). On the other hand, the formation of coarse Heusler particles overwhelms and these particles evolve into rod shape, primarily along grain boundaries. Obviously, the nano-sized γ' particles are thermally less stable than those coarse Heusler particles at high temperatures (> 800 °C).

To investigate temporal evolution of these precipitates, we conduct systematic aging experiments on TA24 alloy at 800 °C with aging times from 0.5 to 48 h. Microstructures of samples aged at various periods of time are presented in Figs. 5a to 5d. The general morphology changes only slightly with the aging time except the fact that both the size and amount of the micron-sized Heusler particles increase slightly, and they develop initially along the grain boundaries to eventually within the grain interior. Meanwhile, the coherent nano-precipitates

distributed inside grain interior begin to coarsen, as revealed in the high-magnification TEM dark field images (Figs. 5e through 5g). In fact, the average diameter of spherical γ' phase grows from 8.1 nm (0.5h) to 26.8 nm (18h) and finally 36.5 nm (48h). However, the shape of these coherent nanoprecipitates remains spherical, indicating stable particle-matrix interfaces with a low interfacial energy. Specifically, the lattice mismatch between the precipitate and matrix is only about 0.26% measured from neutron scattering measurements [23]. Interestingly, the coarsening of these nano-particles closely follows the classical Oswald ripening; this is demonstrated in Appendix A.

In Fig. 6, we present schematic diagrams illustrating the effects of Ti and Al contents, and the aging conditions on microstructural evolution. Note that the effect of aging time is not included due to its relatively small influence. For convenient discussion of the correlation between the microstructure and mechanical property, the average size and volume fraction of the two main precipitates, $L1_2$ and Heusler particles, under different thermal aging conditions are listed in Tables 1 through 3.

3.3 Tensile properties

To investigate effects of alloying addition, tensile tests were conducted on the current HEAs containing various amounts of Al and Ti in both recrystallized and aged conditions. The tensile stress-strain curves are displayed in Fig. 7(a) for the dilute Al/Ti alloys TA14 and TA24 and Fig. 7(b) for the heavily-alloyed TA36 and TA39, separately. A direct comparison of the variation of ultimate tensile strength (UTS) and ductility of these alloys is summarized in Figs. 7(c) and (d). It is evident that, in both the recrystallized and aged states, TA36 and TA39 exhibit a higher tensile strength but a much lower tensile ductility than the dilute A14 and A24 alloys. In fact, TA39 is so fragile it fractures almost immediately after yielding. The poor ductility of heavily alloyed TA36 and TA39 is attributable to the presence of large Heusler particles in the matrix. By contrast, TA14 and TA24 exhibit an outstanding tensile ductility but still keep respectable strength after aging. Specifically, the UTS enhancement after aging is about 126 and 281 MPa

for TA14 and TA24, respectively. From the viewpoint of having a balanced strength-ductility property, TA24 is obviously the alloy of choice for potential structural applications. Thus, in the following, we will focus on the study of the aging response of this particular alloy at different temperatures and times.

Tensile stress-strain curves of TA24 aged at different temperatures for different durations are shown in Fig. 8. Result from the recrystallized state is also included for comparison. For clarity, a summary of the tensile strength and ductility of this alloy as a function of aging time and temperature is presented in Fig. 9. The strength is noted to increase initially with the aging time at every aging temperature (Fig. 9a), reaches the maximum value at the aging time of about 8h, and remains almost unchanged afterwards. On the other hand, the tensile elongation gradually decreases with the aging time at all aging temperatures (Fig. 9b).

To examine the influence of aging temperature on the strength, tensile strength of TA24 is plotted as a function of temperature at various aging times (Fig. 9c). The strength of the alloy reached its maximum value of 983 MPa at 700 °C and decreases slightly at 800 °C. In fact, it remains essentially at a high level of 900-1000 MPa below 800 °C, but sharply decreases when temperature exceeds 800 °C. This rapid softening at $T > 800$ °C is apparently caused by the disappearance of the nano-precipitates in the same temperature range, as demonstrated in Figs. 4g and 4h. The corresponding ductility as a function of temperature (Fig. 9d) exhibits a minimum at around 800 °C, which is probably associated with the formation of brittle Heusler phase. From the above data, we conclude that the optimal property combination for TA24 is tensile strength > 900 MPa and ductility $> 40\%$, when the sample is aged at 700-800 °C for about 8 h.

4. Discussion

Based on the aged microstructures, there is a complex synergy of Ti and Al elements during the precipitation processes in the current TAx_y HEAs. However, only two different precipitates are formed: coarse Heusler phase and fine L1₂ phase. In the following, we focus on the evolution of these two phases and its microstructural correlation with the resultant mechanical properties of the TAx_y alloys, including strength and ductility.

4.1 Phase competition between precipitates

To understand the appearance of various phases, we carried out thermodynamic calculations on the current four TAx_y HEAs, using Thermo-Calc high entropy alloys database, TCHEA1. To make a comparison, calculations for alloys which contain only 2 at. % Ti (denoted as Ti2) or 4 at. % Al (denoted as Al4) were also conducted, and the results are presented in Fig. 10, which are plotted in equilibrium phase mole fraction as a function of temperature. The results (Figs. 10a and b) indicate that both Ti2 and Al4 alloys have only two equilibrium phases in the given temperature range (600-1000 °C), but neither L1₂ nor the Heusler phase is expected, suggesting that the addition of each elements alone can not lead to the expected L1₂ phase precipitation. By contrast, when both elements are added simultaneously in the TAx_y HEAs, more phases are predicted due to the synergistic alloying effect of the Ti and Al elements. To simplify the discussion, let us focus on the formation of the L1₂ and Heusler phases individually, and the results are shown in Figs. 10c and d.

For the L1₂ phase, its volume fraction increases drastically from TA14 to TA24, but the value remains around 0.2 even with further alloying additions of Ti and Al. It is also noted that the temperature range for the phase formation shifts continuously to a lower temperature, suggesting decreasing phase stability at increasing Ti and Al contents when the temperature is higher than 750 °C. For the Heusler phase, on the other hand, the formation temperature keeps expanding gradually, whilst the equilibrium mole fraction also increases with the TA36

composition setting the upper bound limit. This trend indicates an increasing driving force for the formation of the Heusler phase as well as the thermal stability when adding more Ti and Al. In addition, comparing the curves of the two phases, the temperature range for the formation of stable Heusler phase is obviously higher than that of γ' . For the TA24 alloy, in particular, the crossover of the two phases occurs at about 800 °C.

In summary, thermodynamic equilibrium calculations agree with the experimental observations, specifically, the competing behavior of two main precipitates. The stability of the Heusler phase is enhanced with the addition of Ti and Al, with the TA36 composition appears to be as the upper bound limit. This Heusler phase is also stable when the temperature is above 800 °C. On the other hand, the amount of γ' in the TAxY alloys depends on the Ti and Al contents, and it generally increases with the Ti and Al contents, but accompanied by a sacrifice of useful temperature range. From the viewpoint of having a balanced strength-ductility, the TA24 composition seems to be the optimum.

4.2 Correlation between precipitate morphology and mechanical properties

In this subsection, we discuss the strength first and, then, ductility. In a precipitation-hardened alloy, the strength is determined by the morphological distribution of particles, including particle size, shape and inter-particle spacing. Traditional models used to describe the precipitation hardening mainly include Orowan bowing/looping and particles shearing [26]. Whereas Orowan bowing usually occurs when coherent particle's radius exceeds a critical value or the particle is incoherent with the matrix, the shearing mechanism takes place when the precipitates are small and coherent. For brevity, detailed calculations of both Orowan bowing and particle-shearing strengthening are summarized in Appendix B. In the following, we only use their values for mechanistic evaluation.

In Appendix B, we insert proper values of each microstructural parameter (e.g. particle fraction and size) into appropriate equations to calculate the Orowan (σ_{or}) and shearing stresses (σ_{sh}) for the four different TAxY HEAs (aged 18h at 800 °C) and the results are listed in Table 4.

It should be particularly noticed that those Heusler particles located at the grain boundaries actually do not contribute to the Orowan strengthening. In the two alloys TA14 and TA24, Heusler particles (all less than 5 % in volume fraction) mainly distributed along grain boundaries, thus the practical value of σ_{or} can be taken as zero. However, in alloys TA36 and TA39, the majority of the Heusler phase are distributed in the grain interior and they do contribute to Orowan strengthening. We can see from the results that the calculated Orowan stresses from the fine-dispersion of $L1_2$ particles within the grains far exceed their yield stresses, suggesting that Orowan looping is unlikely to be the operating mechanism; these fine $L1_2$ precipitates must be sheared by dislocation during deformation. Therefore, we may conclude that Heusler particles strengthen the alloy through Orowan mechanism, but $L1_2$ particles strengthen the alloy through a shearing mechanism.

In view of the volume fraction of the two different strengthening particles, shearing mechanism is anticipated to dominate in the dilute Ti and Al-containing alloys, TA14 and TA24, but Orowan mechanism should prevail in the heavily alloyed TA36 and TA39. The resultant contribution of precipitation hardening is expected to be the larger one between the two. To evaluate the strength of each alloy, we use the yield strength of the homogenized FeCoNiCr sample (165MPa [23]) as the baseline value, i.e., the lattice intrinsic strength. The calculated contributions from each mechanism as well as the experimental values measured from aged samples are plotted in Fig. 11. It is apparent that in all HEAs, no matter it is Orowan or shearing mechanism, precipitation hardening mechanism plays a major role in the final strength. Other mechanisms (in grey), including solid-solution hardening, grain-boundary hardening, and dislocation hardening appear to be insignificant as compared to precipitate hardening. The relatively larger contribution from “other” mechanisms in the heavily alloyed TA36 and TA39 is also expected, since excessive Ti and Al would cause additional solid-solution hardening and produce smaller grains in these alloys, which can lead to extra grain-boundary strengthening.

In comparison with the strength, which is relatively easy to evaluate using existing models,

a quantitative estimation of the tensile ductility is quite challenging. Tensile ductility of the current TAxY alloys also varies with the alloy composition and aged conditions. It can be as high as 50% (TA24, 900 °C, 2h), but drops to less than 5% (TA39, 800 °C, 18h). In view of the fact that $L1_2$ particles are extremely small (~ 10 nm in radius), they can hardly contribute to stress concentration, thus cause a reduction in ductility. By contrast, the Heusler particles are brittle and about one order of magnitude larger (> 100 nm) than the $L1_2$ phase, thus expected to contribute to the ductility loss. The volume fraction and mean diameter of the Heusler particles in each of the HEAs are listed in Tables 1 to 3 for easy discussion.

From fracture point of view, the present Heusler particles-containing HEAs can be envisioned as ceramic particles-reinforced metal-matrix composites (MMCs) [27, 28]. In the case of discontinuously reinforced metal-matrix composites, when the reinforced phase has a size larger than about 5 μm and the volume fraction is about 20%, the composite is expected to exhibit the most balanced strength-ductility properties. Typically, the ductility value is limited to about 5% [29]. In an analogy to metal-matrix composites alloys, the current alloys exhibit a tensile elongation of about 8% in TA36 containing about 30% Heusler phase with an average particle diameter smaller than 0.5 μm , which appears to be quite consistent. Thus, to estimate the tensile elongation of the current HEAs, let us borrow an equation from MMCs [30]:

$$\varepsilon_c / \varepsilon_m = (1 - f)(1 + \varepsilon_{cav})(1 - f_{con}) \quad (1)$$

where ε_c is the failure strain of the composites, ε_m the failure strain of the unreinforced matrix, f the volume fraction of particles (i.e., the brittle Heusler phase). In the above equation, $\varepsilon_{cav} = f^{4/3}/s$ [30] is the contribution to the failure strain from cavity formation, and s is the aspect ratio of the particles. In the four aged TAxY alloys, s values are estimated as: $s_{14} = 1.46 \pm 0.12$, $s_{24} = 1.37 \pm 0.20$, $s_{36} = 1.76 \pm 0.17$ and $s_{39} = 1.89 \pm 0.29$, showing a gradual change from spherical to rod-shaped. The parameter f_{con} in Eq. 1 represents the ratio of the constrained to the matrix volume, and can be approximately written as [30]:

$$f_{con} = 2s/(5(f^{-1} - 1)) \quad (2)$$

Combine Eqs. (1) and (2), we readily obtain

$$\varepsilon_c/\varepsilon_m = (1 - f)(1 + f^{4/3}/s)(1 - 2s/(5(f^{-1} - 1))) = F \quad (3)$$

Now, we can plot ε_c as a function of F , and the result is shown in Fig. 12. The graph shows a good linear correlation with the slope of the curve to be about 0.62. This slope is expected to be the fracture strain of the unreinforced alloy matrix, ε_m , according to Eq. 3. A value of 0.62 compares favorably to the elongation value of the homogenized TA24 (~ 0.6), whose structure is nearly free of Heusler precipitates. The slight offset from the origin in Fig. 12 may be attributable to the additional effect from the $L1_2$ phase and inhomogeneous distribution of non-randomly oriented Heusler particles. Nevertheless, it is known from Fig. 12 that the tensile ductility in the current HEAs is decisively determined by the volume fraction and morphology of the brittle Heusler phase.

5. Conclusion

In this work, we have conducted a systematic study of the aging behavior of FeCoNiCr-based high-entropy alloys, $(\text{FeCoNiCr})_{100-x-y}\text{Ti}_x\text{Al}_y$ (denoted as TAx_y), which are precipitation-hardened by minor alloying additions of Ti and Al. Several conclusions can be drawn from this study and they are described in the following.

(1) Two types of precipitates are formed during aging: nanosized, coherent $\text{L1}_2\text{-Ni}_3(\text{Ti, Al})$ precipitates and $\text{L2}_1\text{-(Ni, Co)}_2\text{TiAl}$ Heusler phase. The amount of $\text{Ni}_3(\text{Ti, Al})$ -type precipitates increases with the Ti and Al contents. However, excessive addition of the two elements also promotes the formation of brittle micron-sized $(\text{Ni, Co)}_2\text{TiAl}$ Heusler phase, which greatly deteriorates the tensile ductility.

(2) The optimum aging temperature is between 700 and 800 °C. In this temperature range, the nano-scaled $\text{L1}_2\text{-Ni}_3(\text{Ti, Al})$ is preferentially formed. At a temperature higher than 800 °C, the L1_2 phase is greatly suppressed and the brittle $(\text{Ni, Co)}_2\text{TiAl}$ phase begins to take over.

(3) Thermo-calc has been carried out to evaluate the competition between L1_2 and L2_1 Heusler phases. The stability of the Heusler phase is enhanced with higher Ti and Al contents and at higher temperatures. On the other hand, the formation of L1_2 improves with more Ti and Al additions, but is limited by the TA24 composition, beyond which the stability of L1_2 drops. Also, the upper temperature range for stable L1_2 appears to be 800 °C. The calculations compare favorably with experimental observations. Based on both calculations and experiments, we conclude that $(\text{FeCoNiCr})_{94}\text{Ti}_2\text{Al}_4$ exhibits the optimal aged microstructure and has the most balanced tensile properties.

(4) Tensile properties of TAx_y HEAs are well correlated with their microstructures, in particular, the morphological distribution of precipitated particles. Both $\text{L1}_2\text{-Ni}_3(\text{Ti, Al})$ and $\text{L2}_1\text{-(Ni, Co)}_2\text{TiAl}$ Heusler precipitates can contribute to strengthening, whereas brittle Heusler particles are primarily responsible for the ductility loss in the current HEAs. The ductility of the current HEAs is rationalized using theory developed for metal-matrix composites.

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Appendix A

A classical equation used to describe the ripening of dispersed particles is [31, 32]:

$$D^n - D_0^n = Ct \quad (\text{A.1})$$

where D and D_0 are the average diameter of the particles at time t and the initial size ($t = 0$), respectively, and C the coarsening rate coefficient, and n the ripening exponent. Assuming the initial particle size is small, i.e., $D_0 \ll D$, and using data measured from various aging times (i.e. 0.5h, 18h and 48h at 800 °C), we obtain a log-log plot shown in Fig. A.1, from which we readily determine n to be about 3. This n value demonstrates that these $L1_2$ precipitates grow following the LSW coarsening theory for Ostwald ripening. Also, from the fact that these particles remain spherical after prolong annealing suggests that they are thermally stable. It may be attributable to the small lattice mismatch between the coherent $L1_2$ particle and the HEA matrix, which is expected to result in a low interfacial strain energy [32].

Appendix B

Calculations of Orowan strengthening

In the case when precipitates are bypassed by dislocations via Orowan looping, the critical stress, σ_{or} , can be expressed according to the classical equation [33, 34]:

$$\sigma_{or} = M \cdot 0.4Gb/(\pi\sqrt{1-\nu}) \cdot \ln(2\bar{r}/b)/L_p \quad (\text{B.1})$$

where $M = 3.06$ is the Taylor factor, $G = 78.5$ GPa is the shear modulus, $\nu = 0.31$ is the Poisson ratio (referring to the former study [23]), b is the burger vector which for a fcc structure is $b = \sqrt{2}/2 \times a_{Ti2Al4} = 0.255$ nm. $\bar{r} = \sqrt{2/3} \cdot r$ is the mean particle radius on the slip planes, where r is the average radius of particles. $L_p = 2\bar{r}(\sqrt{\pi/(4f)} - 1)$ is the mean interparticle spacing and f is the volume fraction of the precipitates. Orowan stresses for each precipitates in the four aged HEAs with different volume fractions and sizes are calculated and results are tabulated in Table 4.

Calculations of particle-shearing strengthening

When particle shearing takes place, three factors are considered: coherency strengthening (σ_{CS}), moduli mismatch strengthening (σ_{MS}) and order strengthening (σ_{OS}) [35, 36]. The former two occur before the shearing, while the later one occurs during shearing. For such sequential processes, the larger value between $\Delta\sigma_{CS} + \Delta\sigma_{MS}$ and $\Delta\sigma_{OS}$ represents the critical stress of the shearing. The relevant equations are [37];

$$\sigma_{CS} = M \cdot \alpha_\varepsilon (G \cdot \varepsilon)^{3/2} (rf / (0.5Gb))^{1/2} \quad (B.2)$$

$$\sigma_{MS} = M \cdot 0.0055 (\Delta G)^{3/2} (2f/G)^{1/2} (r/b)^{3m/2-1} \quad (B.3)$$

$$\sigma_{OS} = M \cdot 0.81 \gamma_{APB} / (2b) \cdot (3\pi f/8)^{1/2} \quad (B.4)$$

where $\alpha_\varepsilon = 2.6$ for a fcc structure, $m = 0.85$, $\varepsilon \approx 2/3 \cdot \Delta a/a$ is the constrained lattice parameter mismatch and Δa is the lattice constant difference between $L1_2$ particles and the fcc matrix, ΔG is the shear modulus mismatch between the precipitate and matrix, and γ_{APB} is the anti-phase boundary energy of the precipitates. In the current calculation, we use $\Delta a/a = 0.0026$ from our previous work, $\Delta G = 4 \text{ GPa}$, and $\gamma_{APB} = 0.12 \text{ J/m}^2$ taken from the conventional Ni-based superalloys [38]. The calculated results are listed in Table 4 for comparison.

Captions

Table 1 Volume fraction and particle radii of precipitates in the aged TAx HEAs. The data were obtained statistically from SEM/TEM images, and Heusler particles are approximately treated as spherical in shape.

Table 2 Volume fraction and particle radii of precipitates in TA24 HEAs aged for 18 h at different aging temperatures. Note that data after 700 °C and 750 °C aging are not calculated due to different sizes and morphologies of the L1₂ phase in Regions I & II.

Table 3 Volume fraction and particle radii of precipitates in TA24 HEAs aged at 800 °C with different aging times.

Table 4 The calculated Orowan and Shearing stress in the four aged TAx HEAs for different precipitates. The final precipitation strengthening contribution is the larger one between the two mechanisms.

Figure 1 X-ray diffraction patterns of the four HEA samples in the as-recrystallized (denoted as R) and the as-aged state (denoted as A). A face-centered cubic structure is detected.

Figure 2 SEM images of the four TAx HEAs: (a) and (b) are from alloy TA14, (c) and (d) are from alloy TA24, (e) and (f) are from alloy A36 and (g) and (h) are from alloy TA39. Specifically, (a), (c), (e), (g) show the structures in the recrystallized state, while (b), (d), (f), (h) are in the aged condition.

Figure 3 Bright Field (BF) TEM images for aged TA36 alloy (a) and TA39 alloy (b). Corresponding SAED patterns are also shown to identify the crystal structure of the precipitates.

Figure 4 SEM images of the TA24 alloy at different aging temperatures: 700 °C (a), 750 °C (c), 800 °C (e), 850 °C (g), 900 °C (h); corresponding enlarged views are shown in (b), (d), (f) for 700 °C, 750 °C and 800 °C, respectively.

Figure 5 Microstructural evolution as a function of the aging time: 0.5h (a), 8h (b), 18h (c) and 48h (d) under a fixed temperature of 800 °C. A series of Dark Field (DF) images is also presented to show the development of γ' particle morphology: 0.5h (e), 18h (f) and 48h (g).

Figure 6 Schematic illustrations showing the effect of Ti and Al addition, and the aging conditions on the precipitate distribution and evolution.

Figure 7 Tensile stress-strain curves of the four TAx HEAs in their recrystallized as well as various aged states: TA14 and TA24 (a), and TA36 and TA39 (b). Detailed tensile strength and the elongation value are plotted in (c) and (d), respectively.

Figure 8 Tensile stress-strain curves of the TA24 HEAs with different aging temperatures and times: 700 °C (a), 750 °C (c), 800 °C (c), 850 °C (d), 900 °C (e). The black dotted curve for the recrystallized A24 is also shown in (a) and (d) for a direct comparison.

Figure 9 Variations of UTS and elongation as a function of the aging time (a) and (b) and

temperature (c) and (d), respectively.

Figure 10 The equilibrium phase mole fraction as a function of temperature calculated using the thermal-calc method for Ti2 (a) and Al4 (b). The curves of γ' and Heusler phase for the four TAxy HEAs are separated in (c) and (d) in order to show the alloying effect of Ti and Al.

Figure 11 Strengthening contributions from various hardening mechanisms, showing precipitation hardening is the dominant one in the current four aged TAxy HEAs.

Figure 12 The elongation displayed as a function of the volume fraction and mean particle diameter of Heusler phase in the current TAxy HEA system.

Figure A.1 Correlation between the average size of L1₂ particles and aging time at 800 °C. The slope of 3 shows the typical Ostwald ripening.

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Table 1

Alloys	Precipitates	Fraction[*] f (%)	Radius r (nm)
TA14	γ'	14.9 $\pm$ 1.2	12.1 $\pm$ 1.0
	Heusler	1.9 $\pm$ 1.0	188.2 $\pm$ 5.5
TA24	γ'	22.0 $\pm$ 0.8	13.4 $\pm$ 0.7
	Heusler	3.6 $\pm$ 1.2	173.0 $\pm$ 10.2
TA36	γ'	10.2 $\pm$ 2.0	11.6 $\pm$ 1.0
	Heusler	32.7 $\pm$ 0.7	230.8 $\pm$ 6.8
TA39	γ'	4.5 $\pm$ 1.1	10.5 $\pm$ 1.4
	Heusler	38.8 $\pm$ 0.9	350.3 $\pm$ 9.0

*: the volume fraction of the γ' phase is relative to the random solid solution matrix, not including the volume of Heusler phase; while the fraction of the Heusler phase is relative to the whole volume. So are the following Tables.

Table 2

Aging temperature T (°C)	Precipitates	Fraction f (%)	Radius r (nm)
700	γ'	-*	-*
	Heusler	0.6±0.5	151.8±6.4
750	γ'	-*	-*
	Heusler	0.9±0.5	179.9±7.0
800	γ'	22.0±0.8	13.4±0.9
	Heusler	3.6±1.2	173.0±10.2
850	γ'	11.2±1.1	19.8±2.8
	Heusler	10.7±1.8	300.0±16.8
900	γ'	0	-
	Heusler	9.3±1.2	228.3±13.3

*: the value is not calculated here due to the different size and morphology of the γ' phase in the two distinguished Region I & II.

Table 3

Aging time t(h)	Precipitates	Fraction f (%)	Radius r (nm)
0.5	γ'	13.1 $\pm$ 1.2	4.1 $\pm$ 0.8
	Heusler	1.0 $\pm$ 0.6	168.8 $\pm$ 5.1
8	γ'	20.6 $\pm$ 1.5	12.0 $\pm$ 0.8
	Heusler	2.8 $\pm$ 1.0	186.5 $\pm$ 7.7
18	γ'	22.0 $\pm$ 0.8	13.4 $\pm$ 0.9
	Heusler	3.6 $\pm$ 1.2	173.0 $\pm$ 10.2
48	γ'	19.0 $\pm$ 2.1	18.3 $\pm$ 1.4
	Heusler	3.8 $\pm$ 1.0	220.9 $\pm$ 7.6

Table 4

Alloys	Precipitates	Orowan stress σ_{or} (MPa)	Shearing stress σ_{sh} (MPa)	Precipitation hardening contribution (Mpa)
TA14	γ'	1595	244.3	244.3
	Heusler	39.9	-	
TA24	γ'	2148	296.9	296.9
	Heusler	63.5	-	
TA36	γ'	1203	202.2	330.7
	Heusler	330.7	-	
TA39	γ'	725.2	134.3	299.6
	Heusler	299.6	-	

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure A.1

- Precipitation behavior and tensile property of a HEA doped with Ti & Al was studied
- Effects of alloying and aging on phase competition was investigated
- Effects of alloying and aging on the structure-property relation were revealed
- Contribution of different strengthening mechanisms was examined
- The underlying reason for ductility loss was discussed