



Ductilizing brittle high-entropy alloys via tailoring valence electron concentrations of precipitates by controlled elemental partitioning

T. Yang, Y. L. Zhao, W. H. Liu, J. H. Zhu, J. J. Kai & C. T. Liu

To cite this article: T. Yang, Y. L. Zhao, W. H. Liu, J. H. Zhu, J. J. Kai & C. T. Liu (2018) Ductilizing brittle high-entropy alloys via tailoring valence electron concentrations of precipitates by controlled elemental partitioning, Materials Research Letters, 6:10, 600-606, DOI: [10.1080/21663831.2018.1518276](https://doi.org/10.1080/21663831.2018.1518276)

To link to this article: <https://doi.org/10.1080/21663831.2018.1518276>



© 2018 The Author(s). Published by Informa UK Limited, trading as Taylor & Francis Group



Published online: 07 Sep 2018.



[Submit your article to this journal](#)



Article views: 4271



[View related articles](#)



[View Crossmark data](#)



Citing articles: 45 [View citing articles](#)



ORIGINAL REPORT



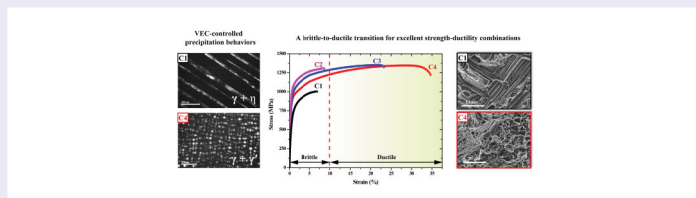
Ductilizing brittle high-entropy alloys via tailoring valence electron concentrations of precipitates by controlled elemental partitioning

T. Yang^a, Y. L. Zhao^b, W. H. Liu^a, J. H. Zhu^c, J. J. Kai^{a,b} and C. T. Liu^a

^aDepartment of Mechanical and Biomedical Engineering, City University of Hong Kong, Hong Kong, People's Republic of China; ^bCenter for Advanced Nuclear Safety and Sustainable Development, City University of Hong Kong, Hong Kong, People's Republic of China; ^cDepartment of Material Science and Engineering, Xiamen University, Xiamen, People's Republic of China

ABSTRACT

High-strength high-entropy alloys (HEAs) reinforced by hard intermetallics generally show a propensity for embrittlement, significantly undercutting their applications. Here we report a strategy to intrinsically toughen strong-yet-brittle HEAs via altering the valence electron concentration (VEC) of precipitates. It was found that a decrease of the VEC of precipitates by Co substitution for Ni atoms effectively destabilizes the brittle hexagonal-ordered precipitate and promotes the formation of ductile cubic-ordered nano-precipitates in Ni–Co–Fe–Cr–Ti system. Benefiting from such a transformation, a fivefold enhancement of tensile elongation (from 7% to 35%) was successfully achieved together with a simultaneously improved strength up to ~ 1.35 GPa.



IMPACT STATEMENT

An effective VEC strategy is proposed to optimize the precipitation behaviors in high-entropy alloys systems. High strength and large ductility are simultaneously achieved in the resultant alloys.

ARTICLE HISTORY

Received 1 June 2018

KEYWORDS

High-entropy alloys; valence electron concentration; phase transformation; precipitation strengthening

Introduction

Recently, the face-centered-cubic (FCC) high-entropy alloys (HEAs) developed based on 3d transition elements (Fe, Co, Ni, Cr, Mn) have attracted significant interest among the materials community due to their exceptional tensile ductility and fracture toughness at cryogenic temperatures [1–6]. Nevertheless, most single-phase FCC-type HEAs possess low yield strengths (only around 200 MPa) at ambient and elevated temperatures, rendering them insufficiently strong for practical engineering applications in many cases [5]. Therefore, a great deal of effort has been devoted to achieve superior strengths of HEAs through incorporating various strengthening methods. It is generally recognized that the precipitation of hard intermetallic compounds is one of the most powerful methods to strengthen the FCC HEA matrix due to their effective resistance to dislocation motion [7–13]. However, a considerably enhanced

strength obtained by increasing the concentration of hard precipitates generally makes alloys showing a propensity for embrittlement. One notable example has been reported in the Nb-modified FeCoNiCr-based HEA system. With the increase of the Nb content, the increased hard Laves phases lead to a substantial increase of strength, which in turn cause a sharp decrease of the tensile elongation to as low as 3% with a brittle failure [12]. Due to the long-standing strength-ductility trade-off, it still remains a daunting challenge to intrinsically toughen these strong-yet-brittle precipitation-hardened HEAs (PH-HEAs) without sacrificing their tensile strengths.

Controlling the valence electron concentration (VEC, the number of total electrons including the d-electrons accommodated in the valence band) has been demonstrated as an effective way for tuning the ordered crystal structures and mechanical properties of bulk

intermetallic compounds [14–17], which thereby opens up a promising way to toughen the constituent precipitates in PH-HEAs for improved ductility. Liu et al. [14] found that the ordered crystal structures of the bulk $\text{Ni}_3\text{V-Co}_3\text{V-Fe}_3\text{V}$ intermetallic system can be altered greatly by controlling the VEC values. With the decreased VEC via partial substitution of Co (VEC = 9) and Ni (VEC = 10) by Fe (VEC = 8), the hexagonal ordered $(\text{Ni,Co})_3\text{V}$ phase (VEC = 8.54) was gradually transformed into the cubic ordered L_{12} -type $(\text{Fe,Co,Ni})_3\text{V}$ phase (VEC < 7.89). Accordingly, the room-temperature tensile elongation was substantially improved from less than 2% to over 40%. Moreover, the VEC strategy has also been reported as one dominating factor in controlling the crystalline structures of brittle NbCr_2 -based Laves phases, which shows a great potential to tune their deformability [15]. Inspired by these attractive results, it is reasonable to expect that the VEC strategy would be applicable to the PH-HEA systems, in which the secondary hard/brittle precipitates can be ductilized by controllably adjusting their VEC values, eventually realizing a brittle-to-ductile transition of the corresponding bulk PH-HEAs. However, previous studies mentioned above were mainly focused on single-phase bulk intermetallic compounds, and very little attention has been paid to the dual-phase or multi-phase precipitation-hardened HEAs.

Along with this line of thinking, we attempted to extend the VEC strategy into the brittle PH-HEA for exploring the feasibility of an enhanced ductilization in the present study. As a proof of the concept, the high-strength, brittle $\text{Ni}_{56.4}\text{Fe}_{18.8}\text{Cr}_{18.8}\text{Ti}_6$ (at. %) alloy strengthened by Ni_3Ti -type precipitate (η phase) was selected as a prototype alloy. Subsequently, a series of modified $\text{Ni}_{56.4-x}\text{Co}_x\text{Fe}_{18.8}\text{Cr}_{18.8}\text{Ti}_6$ (at. %) PH-HEAs with various Co concentrations were fabricated. Co (VEC = 9) element is expected to partition into Ni_3Ti -type precipitates and substitute for Ni (VEC = 10) [18], the operation of which will lead to the decrease of the VEC value and help in triggering the formation of ductile ordered-FCC precipitates for strengthening. In the current study, the concentration of Ti was fixed at 6 at. % to guarantee a similar volume fraction level of precipitates for strengthening. Based on such a transformation, the tensile ductility of HEAs is expected to be greatly enhanced without sacrificing their strengths.

Materials and methods

To start with, alloy ingots with nominal compositions of $\text{Ni}_{56.4-x}\text{Co}_x\text{Fe}_{18.8}\text{Cr}_{18.8}\text{Ti}_6$ ($x = 0, 18.8, 28.2$ and 37.6 at. %, referred to as C1, C2, C3 and C4 hereafter, respectively) were prepared by arc-melting under a Ti-gettered

argon atmosphere and then casted into a cooper mold ($50 \times 12 \times 5$ mm). Purity of the raw materials is greater than 99.9 wt. %. All ingots were flipped and re-melted at least four times to promote a chemical homogeneity. Subsequently, the as-cast samples were thermo-mechanically processed under the same conditions: solution treated at 1175°C for 2 h, cold rolled to ~ 1.7 mm with a thickness reduction of $\sim 65\%$ and then treated at 1175°C for 2 min for recrystallization. After that, the recrystallized samples were further aged at 780°C for 24 h to introduce precipitates. The VEC was calculated according to the equation of $\text{VEC} = \sum_{i=1}^n c_i (\text{VEC})_i$, where c_i and $(\text{VEC})_i$ are the atomic percentage and VEC for the individual element, respectively [14]. The microstructures were characterized using a Quanta FEG450 scanning electron microscope (SEM) in a secondary electron (SE) mode and a JEM-2100F transmission electron microscope (TEM) coupled with an energy dispersive spectrometer (EDS). The samples for SEM observation were mechanically polished and then chemically etched using a dilute aqua regia solution. The TEM specimens were prepared by mechanically grinding and followed by ion-milling using a precision ion polishing system (PIPS, Model 695, Gatan). Phase identification was examined using a Rigaku X-ray diffraction (XRD) instrument by $\text{Cu-K}\alpha$ radiation with a monochromator. The volume fractions of different phases were estimated from their area fractions by employing a commercial software package (Image-J). Subsequently, dog-bone-shaped tensile samples with a cross-section of 3.2×1.5 mm and a gauge length of 12.5 mm were prepared by electro-discharge machining. Uniaxial tensile tests were carried out on a Material Testing System (MTS, Alliance RT30) tensile machine with a strain rate of $1 \times 10^{-3} \text{ s}^{-1}$ at ambient temperature. A 10 mm MTS extensometer was used to for measuring the tensile strain, and the yield strength was determined by the 0.2% offset plastic strain method. After tensile the test, fracture surfaces were examined by SEM.

Results and discussions

Microstructural evolutions of the aged $\text{Ni}_{56.4-x}\text{Co}_x\text{Fe}_{18.8}\text{Cr}_{18.8}\text{Ti}_6$ ($x = 0, 18.8, 28.2$ and 37.6 at. %) alloys were characterized by SEM (Figure 1(a–d)) and XRD analysis (Figure 1(e)), and the results demonstrate a dramatic change of the precipitated structures. Figure 1(a) shows the typical SEM image of the $\text{Ni}_{56.4}\text{Fe}_{18.8}\text{Cr}_{18.8}\text{Ti}_6$ (at. %) prototype alloy (i.e. C1 alloy). A large amount of plate-like phases with an average thickness of 64 ± 30 nm were clearly observed. And the volume fraction of these plate-like phases can be estimated as $\sim 33\%$. The corresponding crystalline structure was presented in Figure 1(e),

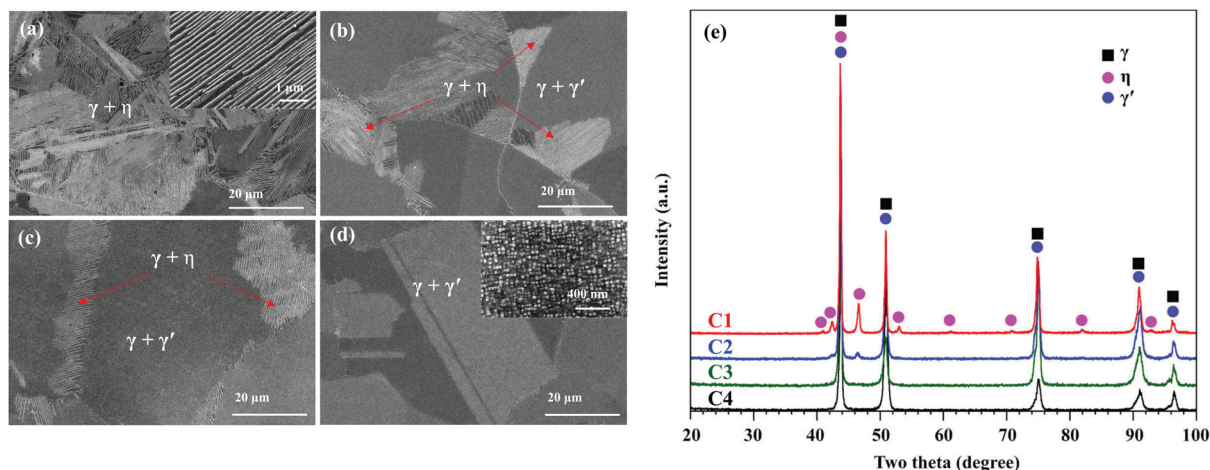


Figure 1. SEM images of (a) C1, (b) C2, (c) C3 and (d) C4 alloys, indicating the phase transformation of precipitates from hexagonal ordered η phase to $L1_2$ -type γ' phase. (e) X-ray diffraction patterns of the investigated alloys.

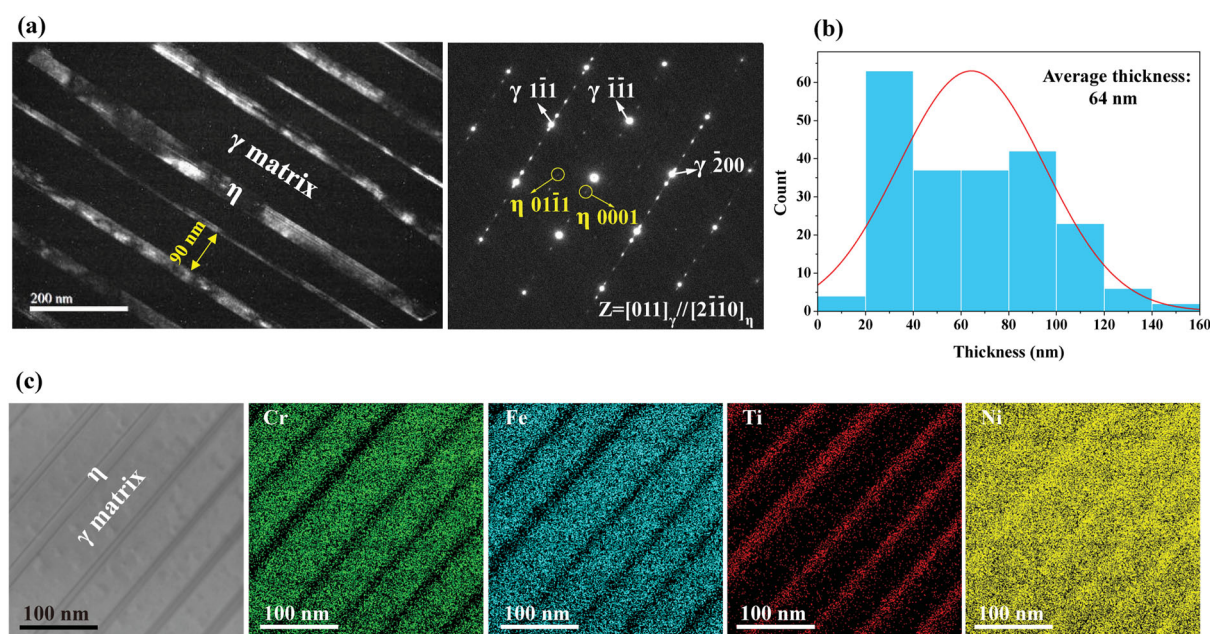


Figure 2. (a) High-magnification DF-TEM image and the corresponding SAD pattern of C1 alloy, showing the plate-like η phase embedded in the γ matrix. (b) Thickness distribution of plate-like η phase (average thickness = 64 nm). (c) Representative STEM-EDX maps of C1 alloy, indicating that the plate-like η phase is rich in Ni and Ti elements.

clearly showing the 'FCC + η ' phase structure. Figure 2(a) further shows a representative dark-field TEM (DF-TEM) image and the corresponding selected area diffraction (SAD) pattern taken from the C1 alloy. Together with the XRD and TEM-EDS results (Figure 2(b)), we can eventually identify the plate-like phases as the Ni_3Ti -type η phase with a hexagonally ordered structure, whilst the matrix has the FCC structure (γ phase). Surprisingly, as shown in Figure 1(b–d), as the Co content is increased to 18.8% (i.e. C2), 28.2% (i.e. C3), and 37.6% (i.e. C4), it is found that the volume fraction of plate-like η phase gradually decreases, suggesting that formation of the η phase is suppressed, while that of the γ' phase with an

ordered-FCC structure ($L1_2$ -type) is greatly promoted. Particularly, for the C4 alloy, as shown in Figure 1(d), the plate-like η precipitate is almost completely eliminated, and the microstructure is dominated by a γ/γ' dual-phase structure. Figure 3(a) clearly presents a typical DF-TEM image of the C4 alloy. Near-spherical $L1_2$ -type γ' nano-precipitates with an average diameter of about 39 ± 6 nm (as shown in Figure 3(b)) can be observed in a highly dispersed distribution with a volume fraction of about 38%. High-resolution TEM (HRTEM) images presented in Figure 3(c) indicate that these $L1_2$ -type γ' nano-precipitates are interfacially coherent with the surrounding γ matrix. Moreover, TEM-EDS mapping (as

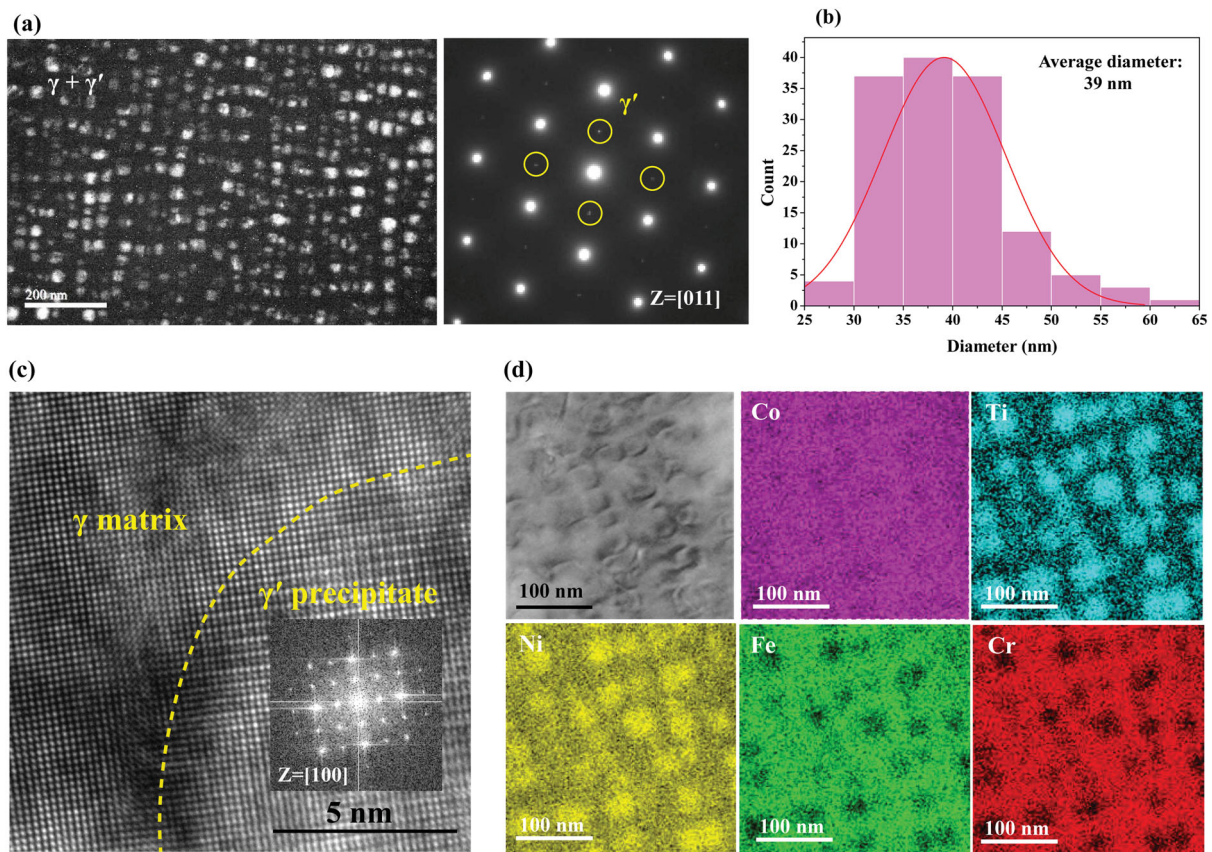


Figure 3. (a) High-magnification DF-TEM image and the corresponding SAD pattern of C4 alloy, revealing the uniform precipitation of L_{12} -type γ' nano-precipitates embedded in the γ matrix. (b) Size distribution of γ' nano-precipitates (average diameter = 39 nm). (c) High-resolution TEM (HRTEM) image showing the coherent feature of the γ/γ' interface. Inset shows the Fast-Fourier-Transformation (FFT) image taken from the HRTEM image of the L_{12} -type γ' nano-precipitate. (d) Representative STEM-EDX maps of C4 alloy, indicating that the γ' nano-precipitate is rich in Co, Ti and Ni elements.

shown in in Figure 3(d)) further reveals that these γ' nano-precipitates are rich in (Co, Ni and Ti) but largely depleted in (Cr and Fe), which thereby can be identified as the $(\text{Co,Ni})_3\text{Ti}$ -type γ' phase.

As described above, Co plays a significant role in controlling the phase structure, transformation potency and also morphology of precipitates. For the close-packed ordered A_3B -type intermetallic phase, its stacking character and the associated crystalline structure are intrinsically determined by two alloying parameters—the atomic-radius ratio (R_A/R_B) and number of VEC [14,19,20]. Note that the elements Ni, Co, Fe and Cr have almost the same atomic size (ranging from 1.24 ~ 1.28 Å) [15], the resulting difference in atomic-radius ratio caused by Co substitution can be essentially ignored. As such, the beneficial effect of Co element could lie in its contribution to the change of the VEC. More specifically, as shown in Figure 3(c), Co element shows a strong tendency to partition into the Ni_3Ti -type precipitates and prefers to occupy the Ni sublattice sites, consequently lowering the VEC and triggers the hexagonal-to-cubic transformation. Table 1 further summarized the

Table 1. Chemical compositions and VEC values of the C1 and C4 alloys based on TEM-EDX analysis^a.

Alloy	Phases	Compositions (at. %)					VEC
		Ni	Co	Fe	Cr	Ti	
C1	Overall	56.4	0	18.8	18.8	6	8.63
	Precipitate	74.61	0	1.42	1.78	22.19	8.57
C4	Overall	18.8	37.6	18.8	18.8	6	8.14
	Precipitate	42.68	31.79	1.42	1.25	22.86	8.23

^a(VEC values of some pure elements: VEC(Ni) = 10; VEC(Co) = 9; VEC(Fe) = 8; VEC(Cr) = 7; VEC(Ti) = 4).

chemical compositions and VEC values of the C1 and C4 alloys, which shows that the VEC decreases from 8.57 to 8.23 with the increase of Co content. Similar results were demonstrated in the $(\text{Ni,Co})_3\text{V}$ -type bulk intermetallic compounds, in which the lowered value of VEC due to the Fe substitution could gradually promote the formation of $(\text{Fe, Ni, Co})_3\text{V}$ -type compounds with cubic ordered L_{12} -phase [14].

It is also worth mentioning that the VEC rule has been recently proposed as one important strategy for predicting the phase formation and mechanical properties of as-cast HEAs [21–23]. For example, by calculating the

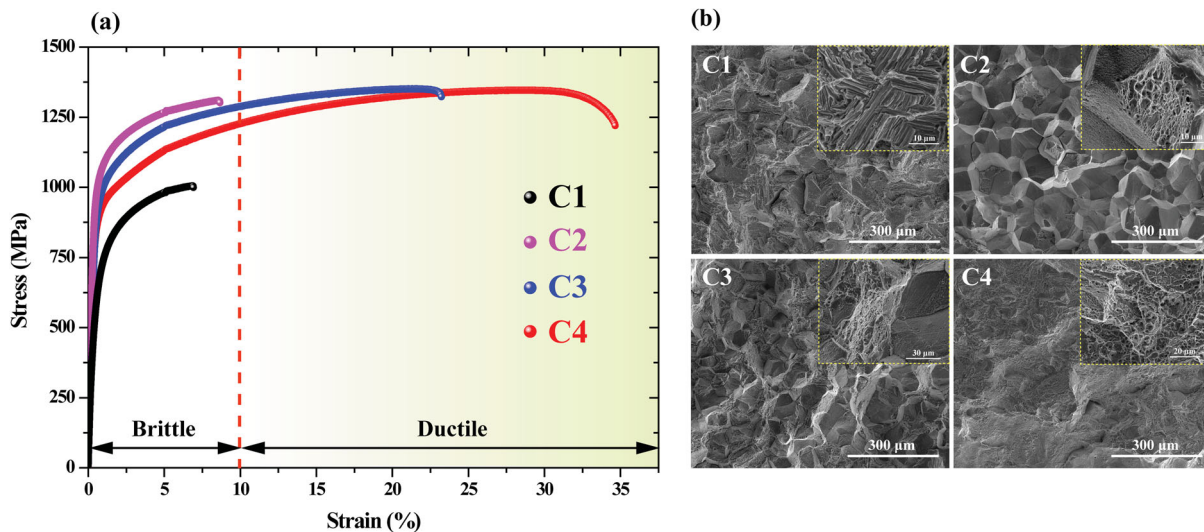


Figure 4. (a) Room-temperature tensile engineering stress–strain curves of the investigated alloys, exhibiting a clear brittle-to-ductile transition with a combined increase of tensile strength. (b) The corresponding fracture surfaces of the investigated alloys after tensile tests, respectively.

VEC based on the initial chemical compositions of alloys, it was revealed that a large VEC (> 8.0) favors the FCC solid solution, while a smaller VEC (< 6.87) stabilizes the BCC solid solution [21]. Nevertheless, such a criterion arising from metastable as-cast HEAs is not well applicable to our present work on PH-HEAs. As indicated in Table 1, although both the C1 and C4 alloys have a larger VEC than 8.0 (8.63 and 8.14, respectively); however, they possess the distinctive structures with different types of precipitates, rather than the FCC solid solution. In other words, for the PH-HEAs containing multiple phases, in order to obtain desired structures and properties, the VEC of individual phases should be carefully tailored by controlled alloying. As described above, by decreasing the VEC of precipitates via Co substitution, the resulting C4 alloy hardened by coherent $(\text{Co,Ni})_3\text{Ti}$ -type nano-precipitates is expected to achieve a greatly enhanced strength-ductility combination.

Figure 4(a) shows the representative tensile engineering stress–strain curves of the $\text{Ni}_{56.4-x}\text{Co}_x\text{Fe}_{18.8}\text{Cr}_{18.8}\text{Ti}_6$ alloys at ambient temperature. Interestingly, a brittle-to-ductile transition can be clearly observed from these high-strength alloys with different Co concentrations, demonstrating the feasibility of our VEC toughening strategy. The C1 alloy shows a high tensile strength of ~ 1 GPa but with a limited tensile ductility of $\sim 7\%$. The high tensile strength of C1 alloy is ascribed to the precipitation hardening of the η phase. And its poor tensile ductility can be explained from two aspects. On one hand, the hexagonally ordered η phase as a low-symmetry crystal structure is intrinsically brittle due to its insufficient number of independent slip systems, which inevitably poses a damaging impact on tensile ductility [14,24].

Moreover, the large lattice difference between the η phase and γ matrix causes serious dislocations pile-up and stress localization on the η/γ interfaces, which in turn promotes crack initiation and propagation under load [25]. The brittle failure of the C1 alloy can be also evidenced from its fractured surfaces (as shown in Figure 4(b)), which exhibits a large amount of strip-like cleavage facets. For the C2–C4 alloys, increased ductile dimpled structures can be gradually observed. For the C2 and C3 alloys, certain amounts of brittle intergranular fracture can be observed, which were ascribed to the formation of brittle η phase along grain boundaries in these two alloys. Finally, due to the complete transformation towards L_{12} -type nano-precipitates, a fully ductile fracture dominated by dimples can be clearly identified in the C4 alloy.

Enviably, increasing the Co content significantly destabilizes the brittle η phase and promotes forming the ductile γ' phase for precipitation strengthening, by which the serious embrittlement can be effectively reduced in the C2 and C3 alloys, and a completely ductile fracture is successfully achieved in the C4 alloy. The tensile elongation gradually increase to 9%, 23% to 35%, respectively. Furthermore, the necking is clearly visible for the C4 alloy. Such an excellent ductility achieved in the C4 alloy arises not only from the intrinsically ductile nature of γ' phase but also from the small lattice misfit of the coherent particle/matrix interface, which reduces local stress concentrations and thus helps improve the plastic stability for sustainable deformation [26]. Also, a combined increase rather than a decrease of tensile strengths can be achieved during such a ductilization process. For the C4 alloy, an excellent tensile strength as high as 1.35 GPa can be achieved simultaneously, successfully

defeating the long-standing strength-ductility trade-off existed in most conventional structural alloys. Such a pronounced strengthening obtained in the C4 alloy should be attributed to the highly dispersed distribution of the γ' nano-precipitates, leading to an enhanced precipitation-hardening effect. First, in comparison with the C1 alloy showing a plate spacing of around 87 nm, the highly dispersed precipitation of nano-precipitates in C4 alloy greatly decreases the inter-precipitate spacing to be of ~ 15 nm (as shown in Figure 3(a)). As a result, the movement of dislocations in the C4 alloy has to overcome a larger number of obstacles per unit length, contributing to an enhanced hardening efficiency [27,28]. Moreover, the passage of a dislocation through the γ' nano-precipitates produces an antiphase boundary with specific energy, giving rise to a considerable ordering strengthening response [29,30]. The contribution from ordering strengthening can be estimated by $\Delta\sigma_p^o = 0.81M(\gamma_{APB}/2b)(3\pi f/8)^{1/2}$ [29], where M is the Taylor factor (3.06 for the FCC polycrystalline alloys), f is the volume fraction (~ 0.38) of the nanoparticles and b is the magnitude of the Burgers vector of the matrix (~ 0.255 nm). γ_{APB} is the antiphase boundary energy (APB) of the nanoparticles, which was roughly estimated to be about 260 mJ/m² by averaging the APB values of L1₂-type Co₃Ti phase (200 mJ/m²) [31] and Ni₃Ti (320 mJ/m²) phase [32]. As a result, the contribution from ordering strengthening was determined to be about ~ 830 MPa, which contributes the majority to the total yield strength. It can be expected that the mechanical properties of the present alloys might be further improved by optimizing processing conditions, and the research on this topic certainly merits a systematical investigation in the future. Overall, considering the high compositional flexibility in multicomponent HEAs, it is reasonable to anticipate that this VEC strategy would be widely applicable to many other precipitation-hardened alloy systems for targeted structure control, thereby accelerating the development advanced structural materials with superior mechanical properties.

Summary

In summary, we have demonstrated the feasibility to toughen strong-yet-brittle precipitation-hardened HEAs (PH-HEAs) by tailoring the electron concentrations of precipitates for desirable phase transformation in the Ni-Co-Fe-Cr-Ti alloy system. The microstructures, tensile properties and fracture mechanisms with respect to different Co concentrations have been systematically investigated. It is clearly revealed that Co can strongly partition into the precipitates and substitute for Ni, and this substitution has effectively destabilized the

brittle plate-like η phase (Ni₃Ti-type) due to its decreasing electron concentration, leading to the formation of ductile γ' phase ((Co, Ni)₃Ti-type) with the ordered-FCC structure. Homogenous precipitation of these newly formed coherent γ' nano-precipitates results in remarkable enhancements in both strength (up to 1.35 GPa) and ductility (above 35%), successfully overcoming the long-standing strength-ductility trade-off for structural materials. Our present findings provide a useful route to design high-performance PH-HEAs for advanced structural applications.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This research was financially supported by the through the General Research Funds (GRFs) with the grant number of [CityU 11209314] and [11205515].

References

- [1] Gludovatz B, Hohenwarther A, Catoor D, et al. A fracture-resistant high-entropy alloy for cryogenic applications. *Science*. 2014;345:1153–1158.
- [2] Yao MJ, Pradeep KG, Tasan CC, et al. A novel, single phase, non-equiatomic FeMnNiCoCr high-entropy alloy with exceptional phase stability and tensile ductility. *Scr Mater*. 2014;72-73:5–8.
- [3] Zhang Y, Zhou YJ, Lin JP, et al. Solid-Solution phase formation rules for multi-component alloys. *Adv Eng Mater*. 2008;10:534–538.
- [4] Senkov ON, Miller JD, Miracle DB, et al. Accelerated exploration of multi-principal element alloys with solid solution phases. *Nat Commun*. 2015;6:6529.
- [5] Wu Z, Bei H, Pharr GM, et al. Temperature dependence of the mechanical properties of equiatomic solid solution alloys with face-centered cubic crystal structures. *Acta Mater*. 2014;81:428–441.
- [6] Yeh JW, Chen SK, Lin SJ, et al. Nanostructured high-entropy alloys with multiple principal elements: novel alloy design concepts and outcomes. *Adv Eng Mater*. 2004;6:299–303.
- [7] Shun T-T, Chang L-Y, Shiu M-H. Microstructure and mechanical properties of multiprincipal component CoCrFeNiMox alloys. *Mater Charact*. 2012;70:63–67.
- [8] Stepanov ND, Shaysultanov DG, Salishchev GA, et al. Effect of V content on microstructure and mechanical properties of the CoCrFeMnNiVx high entropy alloys. *J Alloys Compd*. 2015;628:170–185.
- [9] Yang T, Xia S, Liu S, et al. Effects of Al addition on microstructure and mechanical properties of AlxCoCrFeNi high-entropy alloy. *Mater Sci Eng, A*. 2015;648:15–22.
- [10] Liu WH, Lu ZP, He JY, et al. Ductile CoCrFeNiMox high entropy alloys strengthened by hard intermetallic phases. *Acta Mater*. 2016;116:332–342.
- [11] He JY, Liu WH, Wang H, et al. Effects of Al addition on structural evolution and tensile properties of

- the FeCoNiCrMn high-entropy alloy system. *Acta Mater.* **2014**;62:105–113.
- [12] Liu WH, He JY, Huang HL, et al. Effects of Nb additions on the microstructure and mechanical property of CoCr-FeNi high-entropy alloys. *Intermetallics.* **2015**;60:1–8.
- [13] Ming K, Bi X, Wang J. Precipitation strengthening of ductile Cr 15 Fe 20 Co 35 Ni 20 Mo 10 alloys. *Scr Mater.* **2017**;137:88–93.
- [14] Liu CT. Physical metallurgy and mechanical properties of ductile ordered alloys (Fe, Co, Ni) 3 V. *Int Met Rev.* **1984**;29:168–194.
- [15] Zhu J, Liaw P, Liu C. Effect of electron concentration on the phase stability of NbCr₂-based laves phase alloys. *Mater Sci Eng, A.* **1997**;239:260–264.
- [16] Davies T, Ogbu A. A possible route to improving the ductility of brittle intermetallic compounds. *J Alloys Compd.* **1995**;228:105–111.
- [17] Jiao Z, Luan J, Liu C. Strategies for improving ductility of ordered intermetallics. *Prog Nat Sci.* **2016**;26:1–12.
- [18] Han B, Wei J, Tong Y, et al. Composition evolution of gamma prime nanoparticles in the Ti-doped CoFeCrNi high entropy alloy. *Scr Mater.* **2018**;148:42–46.
- [19] Van Vucht J. Influence of radius ratio on the structure of intermetallic compounds of the AB₃ type. *J Less Common Metal.* **1966**;11:308–322.
- [20] Prakash U, Buckley R, Jones H, et al. DO₂₂ to L1₂ transition in intermetallic systems. *J Mater Sci.* **1992**;27:2001–2004.
- [21] Guo S, Ng C, Lu J, et al. Effect of valence electron concentration on stability of fcc or bcc phase in high entropy alloys. *J Appl Phys.* **2011**;109:103505.
- [22] Guo S, Liu CT. Phase stability in high entropy alloys: formation of solid-solution phase or amorphous phase. *Prog Nat Sci.* **2011**;21:433–446.
- [23] Sheikh S, Shafeie S, Hu Q, et al. Alloy design for intrinsically ductile refractory high-entropy alloys. *J Appl Phys.* **2016**;120:164902.
- [24] Jiao ZB, Luan JH, Liu CT. Strategies for improving ductility of ordered intermetallics. *Prog Nat Sci.* **2016**;26:1–12.
- [25] Zhao YL, Yang T, Zhu JH, et al. Development of high-strength Co-free high-entropy alloys hardened by nano-sized precipitates. *Scr Mater.* **2018**;148:51–55.
- [26] Jiang S, Wang H, Wu Y, et al. Ultrastrong steel via minimal lattice misfit and high-density nanoprecipitation. *Nature.* **2017**;544:460–464.
- [27] Gladman T. Precipitation hardening in metals. *Mater Sci Technol.* **1999**;15:30–36.
- [28] Ardell A. Precipitation hardening. *Metall Trans A.* **1985**;16:2131–2165.
- [29] He JY, Wang H, Huang HL, et al. A precipitation-hardened high-entropy alloy with outstanding tensile properties. *Acta Mater.* **2016**;102:187–196.
- [30] Zhao YL, Yang T, Tong Y, et al. Heterogeneous precipitation behavior and stacking-fault-mediated deformation in a CoCrNi-based medium-entropy alloy. *Acta Mater.* **2017**;138:72–82.
- [31] Masuda-Jindo K, Sluiter M. Application of tight-binding electronic theory to phase stability and mechanical properties of intermetallic compounds. *J Phase Equilibria.* **1997**;18:628.
- [32] Vittori M, Mignone A. On the antiphase boundary energy of Ni₃ (Al, Ti) particles. *Mater Sci Eng.* **1985**;74:29–37.