Superior strength-ductility combination of a Co-rich CoCrNiAlTi high-entropy alloy at room and cryogenic temperatures

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Abstract

In the present study, a Co-rich CoCrNi-AlTi high-entropy alloy was designed and fabricated by hot forging and 700 °C for 8 h annealing process. The microstructure of the resultant alloy was composed of three multicomponent-phases with the face-centered cubic (FCC) structure, hexagonal close-packed (HCP) structure and L12 structure, respectively. The alloy exhibited a remarkable combination of tensile yield strength (gigapascal scale) and plasticity (uniform strain over 30%) at both room and cryogenic temperatures. The cooperative operation of multiple mechanisms consisting of refined-grain strengthening, second-phase strengthening, precipitation strengthening, stacking faults and phase-transformation toughening was suggested to be responsible for the excellent mechanical response.

1. Introduction

Structural metallic materials with gigapascal yield strength and large ductility (uniform elongations, UE) are highly desired for improving engineering performance and energy efficiency. Recently, the development of multi-principal-element alloys (MPEAs) that breaks through the category of ‘traditional alloys’ has provided an innovative routine in designing high-performance alloys owing to their high-entropy effects [1]. However, the coarse-grained high-entropy alloys (HEAs) with a face-centered cubic (FCC) structured single phase usually display good ductility but relative low yield strength at ambient temperatures [2]. Refining the grains to ultra-fine scale (UFG) as well as the introduction of high-density nano-precipitates (such as coherent γ' phase with L12 structure) in the FCC-structured matrix phase have proved to be effective methods in enhancing yield strength to a gigapascal level [3–8]. However, in such cases, the ductility (UE) is generally sacrificed severely because phase transformation (transformation-induced plasticity (TRIP) and twinning (twinning-induced plasticity (TWIP)) all lose their potent in these ultra-fine-grained as well as high-density nano-particles strengthened alloys [3–8].

It is known that to achieve a superior mechanical combination, it is necessary to sustain adequate strain hardening after yield even at the gigapascal level. For this, the materials should be fabricated into micrometer-grained (MG) structures with low-density nano-precipitates. However, in such a case, the refined strengthening and precipitation strengthening effects are inadequate to strengthen the yield stress of these materials to the gigapascal level. It seems to be a dilemma to obtain a good balance of strength and ductility in precipitated alloys.

Fortunately, recent research has shown that fabricating HEAs with dual high-entropy phases can increase yield stress significantly. For example, Li et al reported that increasing the content of hexagonal closed-packing (HCP) phase in the FCC phase can increase yield strength of HEAs significantly [9, 10]. Furthermore, the eutectic HEAs composed of FCC-structured and bulk-centered cubic (BCC-structured) phases can also obtain high yield stress [11, 12]. In addition, both dual-phase HEAs exhibit considerable uniform elongations [9–12], suggesting that fabricating dual high-entropy phases is an effective method in enhancing the combination of strength and ductility simultaneously. Based on the above discussion, in the present study, a nano-precipitated...
Co-rich CoCrNi-AlTi HEA with a dual-phase (HCP and FCC) matrix was designed and its tensile response at room and cryogenic temperatures were evaluated with the aim of achieving superior mechanical performance. As expected, an outstanding strength-ductility combination with tensile yield strength (gigapascal scale) and plasticity (uniform strain over 30%) was achieved at both room and cryogenic temperatures.

2. Experimental procedures

Based on the CALPHAD (CALculation of PHAse Diagrams) technique, a MPEA with compositions of Co_{35}Cr_{32}Ni_{27}Al_{3}Ti_{3} (at%) was designed, corresponding to the marked point of the red star in the phase diagram (figure 1). As shown in the diagram, a three-phase microstructure consisting of FCC structure, HCP structure and \(L_1_2\) structure presents in the equilibrium state. Thus, this alloy was determined as the target alloy in the present study.

A 16 kg ingot with a diameter of 80 mm was cast by a vacuum induction melting method under a pure Ar atmosphere using pure metallic elements (purity > 99.9 wt%). After homogenizing annealing at 1200 °C for 2 h, the ingot was forged repeatedly at about 1150 °C to a final diameter of 36 mm along the longitudinal direction. This corresponds to area reduction of 80%. After that, the alloy was subsequently annealed at 700 °C for 8 h followed by water quenching.

Dog-bone-shaped specimens with a gauge reduced parallel length of 12.5 mm and a cross-section area of \(3.2 \times 1.0\) mm\(^2\) were fabricated from the annealed alloy by electrical-discharge machining. All specimens were mechanically polished before the measurement of mechanical properties. According to the ASTM E8M standard, uniaxial tensile tests were carried out at both room temperature (293 K) and cryogenic temperature (77 K) using a universal testing machine (GOTECH AI-7000-LA20, Taiwan) at a constant strain rate of \(1 \times 10^{-3}\) s\(^{-1}\). Three samples were tested to confirm reproducibility of results, and the representative data were used to describe the typical mechanical properties of the alloy.

Transmission electron microscopy (TEM) characterizations were conducted on a JEOL JEM-2100 F instrument. Scanning transmission electron microscopy (STEM) images and energy-dispersive spectrometry (EDS) maps were acquired on Thermo Fisher Titan G260-300 S/TEM (fitted with a high-brightness field emission gun (X-FEG), probe Cs corrector and super X EDS with four windowless silicon drift detectors). TEM and STEM samples with dimensions of \(\Phi 3\) mm \(\times 0.5\) mm were sliced by a Struers cutting machine and then thinned to 50 \~ 60 mm using variant grit silicon carbides. After mechanical thinning, these samples were subject to a precise dimple grind for further thinning and polishing. Finally, ion milling was carried out on a cold stage (about -50 °C) at 5 keV, 5° until perforation and then at 2.5 keV, 3° for 10 min to reduce the thermal damage and surface amorphization. Synchrotron X-ray radiation (SXRD) was also applied to examine structural evolutions during the aging treatment and deformation process, which were performed on the 11-ID-C beam line of the Advanced Photon Source, Taiwan. A monochromatic X-ray beam with an energy of 115 keV (with wavelength 0.010801 nm) was used.
3. Results and discussion

3.1. Characterization of microstructure by OM, SXRD, TEM, STEM

Figure 2(a) shows the macrostructure of the CoCrNi-AlTi alloy after hot rolling and subsequent annealing at 700 °C for 8 h, observed by optical microscope. The integrated shape of the equiaxed grains indicates that a fully-recrystallized microstructure had been achieved after experiencing this thermomechanical process. Although the distribution of grains was non-uniform to some extent, it does not belong to a hierarchical microstructure owing to that all grains were fallen into the micrometer scale. Otherwise, it is a micrometer-grained structure (MG) with mean grain size of about 10 μm. The SXRD pattern indicated that a complex microstructure composed of a FCC-structured phase, a HCP-structured phase and a L12-structured phase had formed in the alloy (figure 2(b)). STEM-EDX mapping images (figure 2(c)) shows low-density L12 particles (with an average diameter of 15 ± 0.5 nm) precipitating in the matrix and the elemental distribution between the L12 nanoparticles and matrix. TEM observation (figure 2(d)) showed a dual-phase microstructure composed of a FCC-structured phase and a HCP-structured phase, as confirmed by the SAED map (figure 2(e)).

Furthermore, the HCP-structured phase has similar compositions to the FCC-structured phase, which is about Co39Cr35Ni22Al2Ti2 based on the STEM-EDX results (figure 3(a)). The compositions of L12 precipitates are estimated to be Ni10Co10Cr10Al10Ti15 based on the measuring data of STEM-EDX (figure 3(b)). It is interesting to observe that the nano-lamellar or tiny-block HCP-structured phase was distributed dispersedly in the FCC-structured phase although its volume fraction was small. For these results, it is important to highlight that all these three phases belong to the ‘high-entropy’ category owing to their multicomponent characteristics.

3.2. Mechanical response of the alloy at room and cryogenic temperatures

Figure 4(a) shows the excellent mechanical properties of the three-phase alloy at 293 K and 77 K. A gigapascal-scale yield stress (YS) of ~1.12 GPa and ultimate tensile stress (UTS) of ~1.4 GPa together with a large tensile elongation (UE) of ~36% can be achieved at room temperature. Moreover, at cryogenic temperature, a better strength-ductility combination can be obtained, i.e., the YS, UTS and UE were 1.3 GPa, 1.8 GPa and 53%, respectively. Figure 4(b) shows the corresponding strain-hardening rate curves. It shows that the strain hardening rate curves of ageing alloys at 293 K and 77 K all exhibit a non-monotonous evolution behaviour. In particular, at 77 K, the alloy exhibits a steady hardening rate of about 4800 MPa until arriving at a true strain of 0.2. After that the strain hardening rate gradually decreases to about 3000 MPa at the true strain of 0.40. Thus, the alloy sustains relatively steady strain hardening behaviour with a high hardening rate (over 3000 MPa) during the entire plastic straining stage. Recently, Yang et al and Tong et al reported that nano-precipitated HEAs exhibited abnormal increases of strain-hardening rate during the plastic straining process both at 293 K.
and 77 K \cite{6, 8}. It is clearly that our alloy displays a different plastic deformation behaviour compared to the research of Yang et al suggesting different underlying mechanisms operative in the two alloys.

In the present study, it should be highlighted that high yield stress (gigapascal level) and large UE (more than 30\%) have been achieved simultaneously at both room and cryogenic temperatures. In comparison with other potential structural high-performance high-entropy alloys, it is clear that the present alloy shows a superior yield stress-ductility combination at both room and cryogenic temperatures, making it a more promising candidate for many engineering applications, as shown in figures 4(c) and (d).

### 3.3. Discussion

Obviously, in the present study, the multicomponent CoCrNi-AlTi alloy exhibits superior combination of yield stress and tensile elongation at both 293 K and 77 K. According to the microstructural features of the alloy, the additional yield stress should be the result of the following factors: solid solution strengthening, refined-grain strengthening, precipitation strengthening and second-phase strengthening. Firstly, owing to the addition of 3 at\% Al, 3 at\% Ti elements, the solid-solution hardening can be estimated to be around 175 MPa \cite{13, 14}.

Secondly, by accounting for the refined-grain hardening effect, the yield stress of the alloy with mean grain size of 10 \( \mu \text{m} \) can be estimated by \( \sigma_{YS} = \sigma_0 + kd^{-1/2} \) \cite{15, 16}, in which \( \sigma_0 \) is the lattice friction (218 MPa for the CoCrNi alloy \cite{17}); and \( K \) is the Hall-Petch constant (568 MPa/\( \mu \text{m}^{-1/2} \) for CoCrNi-AlTi alloy \cite{18}) and \( d \) is the mean grain size. Based on the above calculation, the contribution to the yield stress from the refined-grain
strengthening is determined to be about 390 MPa. Thirdly, the precipitation strengthening effect is ascribed mainly to the pronounced ordering strengthening of the γ′ particles, which can be calculated by

\[ \Delta \sigma_{\text{order}} = 0.81 \frac{M \gamma_{\text{APB}}}{2b} (3\pi f/8)^{1/2} \]

where \( M \) is the Taylor factor (3.06 for the FCC polycrystalline matrix), \( \gamma_{\text{APB}} \) is the antiphase boundaries energy of the nanoparticles (estimated to be 200 mJ m\(^{-2}\)), \( b \) is the Burgers vector of the dislocation (~0.254 nm), \( f \) is the volume fraction of precipitates (~12 ± 5%)\(^{[5, 6, 18]}\). Based on the above calculation, the contribution to the yield stress from the ordering strengthening of γ′ particles is determined to be 310 MPa. Thus, based on the above results, the sum contribution to yield stress from solid solution strengthening, refined-grain strengthening, precipitation strengthening is 875 MPa, which is remarkably lower than the experimental yield stress of 1210 MPa at room temperature.

As shown in the above observations, the matrix of the alloy consists of two multi-component phases with FCC and HCP structures. Compared with the FCC phase, the high-entropy HCP phase is a strengthening phase owing to a decrease in the number of slip systems with respect to the FCC structure, as shown by the work of Li et al\(^{[10]}\). Furthermore, the HCP phase is distributed disperely in the FCC-structured phase although its volume fraction is small (~5% according to the SXRD results). This distribution of the second phase is also beneficial for the enhancement of yield stress, similar to the function of precipitation strengthening. As a result, the HCP phase with disperse distribution in the FCC matrix provides the additional strengthening effect, making the alloy exhibit gigapascal-scale yield stress. It is noted that the yield stress at 77 K is slightly higher than that of at 293 K, which might be originated from the increase of friction stress of lattice at 77 K.

In this study, the alloy displayed remarkable ductility apart from the source yield stress. The ductility at 77 K was obviously better than that at 293 K. In order to identify the underlying mechanism responsible for the superior mechanical properties for the alloy, in particular at 77 K, microstructural evolution of the deformed samples was characterized in this study. The TEM observations of the deformed sample at 293 K (with strain of 0.20) were shown in figure 5(a), in which only low-density stacking faults has been found according to the selected area electron diffraction (SAED) (figure 5(b)). Furthermore, the SXRD of the deformed alloy at 77 K (with strain of 0.20, corresponding to the steady stage of strain hardening rate) showed that the amount of HCP phase had increased compared with that of ageing samples, suggesting that the TRIP effect was operative during the deformation process (figure 6(a)). Moreover, TEM observations showed that dense HCP lamella had been formed in the deformed samples (figures 6(b) and (c)). These findings provide evidence in support of phase transformation (From FCC to HCP) during the plastic straining process. In addition, TEM observations (figures 6(b) and (c)) on the deformed alloy did not detect nanotwins which coincides with the observations of Yang et al and Tong et al\(^{[6, 8]}\). Instead, dense stacking faults were formed during the tension process at 77 K. According to the results of Tong et al\(^{[8]}\), the contribution of stacking faults to the strain hardening is weak owing to the space of stacking faults is broad. Hence, the TRIP effect provides an additional strengthening mechanism contributing to the pronounced strain hardening rate. This is different from the deformation mechanism of equimolar CoCrNi alloy at 77 K, in which continuous formation of mechanical nano-twins was regarded to be responsible for the pronounced ductility\(^{[20]}\). Moreover, the TRIP effect should be originated from the FCC/HCP phase interface hardening, as showed in the literatures\(^{[21]}\). During the initial strain stage, the soft FCC phase undergoes the plastic straining and the hard HCP phase undergoes the elastic straining. The HCP phase begins to deform plastically until the FCC phase achieves a certain degree of strain hardening owing to the accumulation of dislocations at the FCC/HCP phase interface\(^{[22]}\).

Research on Co base alloys shows that a transformation from FCC structure to HCP structure happens when the alloys are meta-stabilized in thermodynamics\(^{[20–22]}\). In this study, the Co-rich CoCrNi-AlTi alloy is also a meta-stabilized alloy based on the results from CALculation of PHAse Diagrams (figure 1). The FCC to HCP phase transformations can be induced athermally\(^{[20]}\), isothermally\(^{[21]}\), or through plastic straining\(^{[22]}\). According to the report of\(^{[23]}\) et al the HCP phase can be formed by the overlap of stacking faults, and in such a
case, the critical stress formed by HCP is relatively small. In this study, because high-density stacking faults were formed during the \(77 \text{ K}\) deformation process, the microstructure could accelerate the phase transformation. Here, the beneficial strengthening effect of transformation from FCC to HCP in this alloy should be emphasized by using the ‘high-entropy’ concept. It is known that the strain induced transformation (SIT) can cause appreciable work hardening [24]. For the conventional Co alloys, the transformed HCP phase (\(\varepsilon\)-martensite) was usually detrimental to the ductility due to shear band formation (microcrack) [25]. This kind of HCP phase (\(\varepsilon\)-martensite) were compositional sample and contain low levels of secondary elements. However, in this study, the transformed HCP phase was multicomponent owing to the ‘high-entropy’ effect, making it possible to deform in a ductile style by activating more slip systems (basal \(\langle a \rangle\) dislocations and prismatic \(\langle a \rangle\)-type dislocations), as shown in the literature [26]. Furthermore, it is known that multiple-principal-element CoCrNi-base alloys have stacking fault energy of 20 \(\sim\) 30 mJ m\(^{-2}\), which are significantly higher than that of pure Co (0 mJ m\(^{-2}\)) at room temperature and cryogenic temperature [27, 28]. The higher SFE promotes the activation of prismatic \(\langle a \rangle\)-type dislocations and restrains the occurrence of deformation twinning, as shown by previous research [26].

Thus, for the Co-rich CoCrNi-AlTi alloy, the SIT can provide substantial strain hardening without causing severe detrimental effects to the global plasticity. Further research should continue to examine the crystallographic characteristics during plastic deformation of this multicomponent HCP phase. Based on the analysis on the strain-hardening rate curve, the formation of SF and transformations continuously occur throughout the entire plastic straining range, counteracting the softening effect of dislocation slips, resulting in a good balance of strength and ductility.

### 4. Conclusion

In summary, we used CALPHAD method to develop a high-performance multiple-phase Co\(_{35}\)Cr\(_{32}\)Ni\(_{27}\)-Al\(_{3}\)Ti\(_{3}\) (at\%) HEA in this study. The microstructure, mechanical properties and the associated underlying mechanisms at room and cryogenic temperatures have been carefully investigated in our analyses. A beneficial microstructure composed of three multicomponent phases with FCC, HCP and multicomponent L\(_{12}\) structures was clearly identified in this alloy. As expected, the alloy exhibits exceptional yield strength-ductility synergy (yield stress (gigapascal level) and large UE (more than 30\%) both at room and cryogenic temperatures. The alloy sustained relatively steady strain hardening behaviour with a high hardening rate (over 3000 MPa) over the entire plastic straining stage at 77 K. The combined effect of stacking fault formation and phase transformation during the plastic straining process was determined to be the new toughening mechanism in the nano-precipitated HEAs. Our results present a novel method for fabricating high-performance structural materials by tailoring compositions to obtain multiple multicomponent-phase microstructure.
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