Effects of heat treatment on the microstructure and properties of cold-forged CoNiFe medium entropy alloy


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ABSTRACT

The effects of heat treatment on the microstructure and properties of cold-forged two-dimensional (2D) CoNiFe medium entropy alloy (MEA) are determined. Compared to the as-cast specimen with a columnar crystal structure, the cold-forged CoNiFe MEA has a heavily fragmented microstructure with deformation twins. As the annealing temperature is increased, the grain size becomes larger markedly. Annealing at 900 °C yields a fully recrystallized microstructure with a large population of annealing twins and the new orientation exhibits a first-order twin relationship (60° < 111 > rotation) during recrystallization. Moreover, the CoNiFe HEA annealed at 900 °C possesses excellent ductility (ε = 50%) and work-hardening ability (σUTS-σY = 246 MPa, σUTS/σY = 0.5), which depend on the annealing twins, dislocations, as well as micro-shear bands in the grains. Analysis of the fracture surface indicates that the main failure mechanism is ductile. Meanwhile, no phase separation occurs as the temperature is raised from 0 °C to 1000 °C as shown by the expansion rate versus temperature relationship, indicating that the materials have good stability at high temperature. The thermal expansion coefficient (CTE) of the sample annealed at 1100 °C for 1 h is 12.1 × 10⁻⁶ K⁻¹ which is less than that of traditional metals (14.4–16 × 10⁻⁶ K⁻¹).

1. Introduction

Development of new structural materials is spurred by technological advancement and high entropy alloys (HEAs) which consist of multiple elements have aroused much interest [1]. HEAs generally have five or more principal elements in equal or near-equal atomic concentrations and the concentration of each element is between 3% and 35%. The four effects of high entropy, sluggish diffusion, severe lattice distortion, and cocktail effects have been shown to play important roles in the properties of HEAs [2–7]. HEAs have many attractive properties such as the excellent oxidation resistance [8,9], thermal stability [10], elevated-temperature strength [11,12], fracture toughness [13–16], corrosion resistance [17], and surconductivity [5]. However, most HEAs have drawbacks in practice because of the low ductility and high brittleness especially at room temperature but medium entropy alloys (MEAs) composed of two to four principal elements with mixing entropy between 1R and 1.5R may deliver better performance [18–20].

The properties of CoNiFe MEAs have been studied [21]. Rathi et al. [22] prepared nano-crystalline equiatomic NiCoFe alloy powder by mechanical alloying and the materials possessed superior magnetic properties at ambient temperature. Tsau et al. [23] studied the microstructure and polarization behavior of CoNiFe and CoNiFeCr alloys which had the FCC granular structure and the corrosion resistance of both alloys in 1 M H2SO4 was better than that of 304 stainless steel. However, the mechanical properties of CoNiFe MHAs at room temperature have been found to be not good enough [24]. Cold working by for example, forging, followed by recrystallization is one of the simple thermal mechanical processes (TMP) to control the strength and ductility balance. In fact, two-dimensional (2D) forging is a simple and industrially viable method that is an effective slight plastic deformation technique in contrast to severe plastic deformation (SPD) such as high-pressure torsion [25].

In this work, CoNiFe MEA samples are prepared by two-dimensional (2D) forging followed by heat treatment. Our objective is to study the effects of annealing on the microstructure and properties of cold-forged CoNiFe MEA to improve the mechanical properties, especially the ductility at room temperature. The relationship between annealing twins, dislocations as well as micro-shear bands in the grains and mechanical behavior is determined.

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2. Materials and methods

2.1. Experimental materials and the annealing process

The CoNiFe MEA samples were produced by vacuum arc melting under argon from 99.9% pure Co, Ni, and Fe metals. Before melting, the chamber was evacuated to a pressure of $1 \times 10^{-5}$ Torr and back-filled with argon to 500 Torr. High-purity Ti was used as a getterer prior to melting to mitigate contamination from residual oxygen and nitrogen. The ingots were remelted under electromagnetic stirring at least five times to enhance the uniformity of the chemical composition and then cooled naturally in the furnace.

Before forging, the samples with dimensions of 30 mm (length) × 20 mm (width) × 15 mm (height) were cut from the ingots. Then 2D forged CoNiFe MEAs samples were prepared on an industrial air pneumatic hammer machine at a load of 100 kg and hammer frequency of 180 times per minute. The schematic of the 2D forging procedure and heat treatment is shown in Fig. 1. The final forged samples had dimensions of 50 mm (length) × 40 mm (width) × 4.5 mm (height). The amount of strain (forging ratio) was derived by the reduced height or increased cross section increasing of the forged specimens as follows:

$$\varphi_f = \frac{S_1}{S_0} = \frac{H_0}{H_1}$$

where $S_0$, $H_0$ and $S_1$, $H_1$ are the cross sections and heights of the initial and final samples, respectively. The forging ratio $\varphi_f$ was 30% according to the above formula.

2.2. Microstructural characterization

The metallographic sections were prepared by standard mechanical polishing procedures. An Olympus metallurgical microscope was used to examine the grain morphology of the samples and the grain size was measured using the Nano-measurement software. The microstructure and composition of the alloys were determined by field-emission scanning electron microscopy (EF-SEM, FEI Sirion), energy-dispersive X-ray spectrometry (EDS) (Sirion), and transmission electron microscopy (TEM, FEI Tecnai G2 at 200 kV). Electron backscattering diffraction (EBSD) was performed on the SEM using an EDAX Hikari super EBSD camera in conjunction with the acquisition software EDAX TSL DC7 and analysis software a TSL OIM. Prior to TEM examination, the specimens were mechanically ground to a thickness below 100 μm with SiC paper, punched into 3 mm diameter disks, and then thinned by ion milling to electron transparency. The phases were determined by X-ray diffraction (XRD, DB-Discover, Germany and Bruker-AXS) using Cu Kα radiation ($\lambda = 1.54183$ Å) in the 2θ range of 20°–90° at a scanning speed of 8°/min, 40 kV, and 20 mA.

2.3. Determination of mechanical properties

The uniaxial tensile specimens with a gauge length of 8 mm were cut from the alloy by electrical discharge machining and the tensile tests were performed in triplicate on a CMT5105 universal electronic tensile testing machine at a strain rate of $1 \times 10^{-3}$ s$^{-1}$ at room temperature. The yield strength (YS), ultimate tensile strength (UTS), and elongation were determined from the tensile stress-strain curves.

Cylindrical samples 2 mm in diameter and 10 mm tall were cut from the alloy on an electrical discharge machine and the thermal expansion tests were performed by thermo-mechanical analysis (TMA) at a heating rate of 5 °C s$^{-1}$ from 0 °C to 1000 °C.

3. Results

Fig. 2 illustrates the microstructural evolution of the as-cast CoNiFe MEA and after different annealing processes. The transformation from columnar crystals in the as-cast CoNiFe MEA to a heavily fragmented microstructure with deformation twins (DT) is presented in Fig. 5a–e and the grain size increases with annealing temperature. The mean grain sizes of the specimens annealed at 900 °C, 1000 °C, and 1100 °C are 42 μm, 74 μm, and 90 μm, respectively, as shown in Fig. 2f. Similar to the one annealed at 900 °C, the samples annealed at higher...
temperature show many annealing twins (AT). A similar temperature trend during grain growth was also observed by Sathiaraj et al. [26] from CoNiCr MEAs. Athiaraj et al. found that annealing at 700 °C yielded a fully recrystallized ultrafine grain microstructure with a large fraction of annealing twins and extensive grain coarsening occurred after annealing at 1100 °C. Chuang et al. [27] revealed a face-centered cubic (fcc) crystal structure and low stacking fault energy (SFE) are key to the production of alloys with a large density of annealing twins. Sathiaraj et al. [28] showed that the microstructure and texture of ternary alloys are different from those of quaternary and quinary alloys because CoNiFe MEAs are not low SFE alloys. The quinary and quaternary alloys with lower SFE can form more TBs during deformation and annealing produces greater microstructural fragmentation of refinement and texture transition. Pure metal or copper-type texture is observed from high to medium SFE alloys during the deformation state, whereas low SFE alloys exhibit a strong brass or alloy-type texture [29].

The EBSD maps (inverse pole figure, IPE) of the microstructures annealed at 800 °C, 900 °C, and 1000 °C for 1 h are shown in Fig. 3(a1), (b1), and (c1). The misorientation angle distributions curves of the various microstructures (Fig. 3 (a2), (b2), and (c2)) show that the misorientation angle distributions have a strong preference for 60°, indicating a large number of annealing twins (ATs) in the grains as shown by SEM (Fig. 3a, b, c). The 60° < 111 > and 38.9° < 110 > angle-axis misorientations corresponding to the Σ3 and Σ9 boundaries result in strong and weak peaks, respectively, implying that a lot of TBs exist in the forged-CoNiFe MEAs. The fraction of Σ3 (about 35%) in the sample treated at 900 °C is larger than those treated at 1000 °C (about 2%) and 1100 °C (about 6%). According to Sathiaraj et al. [29,30], annealing twins resulting in a large fraction of annealing twin boundaries (Σ3) are observed from CoCrFeMnNi HEAs with low SFE and Ni with medium SFE. The twin fraction of ternary CoNiFe MEAs is lower than that of the quinary HEAs but higher than that of pure Ni and it is consistent with the difference in the SFE values: Fe-CoNiCrMn(γSFE = 20 mJ m⁻²) < FeCoNi(γSFE = 70 mJ m⁻²) < Ni (γSFE = 130 mJ m⁻²) [31,32].

The grain boundary characteristic distributions (GBCDs) of the forged FeCoNi MEAs annealed at different temperature show that the fraction of low-angle grain boundaries (LAGBs) such as the Σ1 boundaries (misorientation across them in the range of 2°–15°) is quite large and increases with annealing temperature. The evolution of LAGBs is in good agreement with the general tendency of the proportion of LAGBs to increase and high energy grain boundaries to decrease during grain growth [33]. The reason is that the Σ1 boundaries have relatively low energies. Because grain growth reduces the total interfacial area, more grain boundaries are eliminated rather than created. Dillon et al. [34] showed that higher-energy grain boundaries were preferentially eliminated from the network during grain growth thus producing a larger relative population of low energy grain boundaries. Besides, the motion and impact of the incoherent Σ3 formed during annealing lead to the formation of Σ1 which improves the fraction of LAGBs. The EBSD maps (inverse pole figure, IPE) of the microstructures annealed at different temperature show that the fraction of low-angle grain boundaries (LAGBs) such as the Σ1 boundaries (misorientation across them in the range of 2°–15°) is quite large and increases with annealing temperature. The evolution of LAGBs is in good agreement with the general tendency of the proportion of LAGBs to increase and high energy grain boundaries to decrease during grain growth [33]. The reason is that the Σ1 boundaries have relatively low energies. Because grain growth reduces the total interfacial area, more grain boundaries are eliminated rather than created. Dillon et al. [34] showed that higher-energy grain boundaries were preferentially eliminated from the network during grain growth thus producing a larger relative population of low energy grain boundaries. Besides, the motion and impact of the incoherent Σ3 formed during annealing lead to the formation of Σ1 which improves the fraction of LAGBs. The motion and impact of the incoherent Σ3 formed during annealing lead to the formation of Σ1 which improves the fraction of LAGBs.

### 3.1. Mechanical properties of CoNiFe MEAs

Fig. 5a shows the engineering stress–strain curves of the forged-CoNiFe MEAs after annealing at different temperature. Compared to the...
untreated one, the annealed samples have much improved ductility. The fracture surface is analyzed to determine the fatigue characteristics such as crack initiation sites, crack propagation, and final fracture. The unannealed sample shows brittle fracture characteristics according to Fig. 5d, but the annealed samples exhibit ductile failure as shown in Fig. 5(e, f, g). As the annealing temperature is increased from 800 °C to 1100 °C, the ultimate tensile strength $\sigma_{UTS}$ decreases from 540 MPa to 430 MPa and tensile ductility $\sigma_y$ decreases from 50% to 40%. The yield strength values are 276, 217, and 201 MPa after annealing at 900, 1000, and 1100 °C, respectively. The sample annealed at 900 °C shows superior ductility in comparison with similar HEAs reported in the literature [24].

According to the true stress-strain curves, the strain-hardening rates (d$\sigma$/d$\varepsilon$) versus true strain curves of the forged-CoNiFe MEAs annealed at different temperature are presented in Fig. 5b. The strain-hardening rates of the annealed alloys exhibit similar trends that can be separated into two stages. In stage I, the strain-hardening rates decrease linearly and in stage II, the strain-hardening rates diminish with increasing strain. Heterogeneous deformation caused by grain size and substructure is generally believed to be the reason and the alloy annealed at 900 °C shows excellent work-hardening ability ($\sigma_{UTS} - \sigma_y = 246$ MPa, $\sigma_{UTS}/\sigma_y = 0.5$). The higher work-hardening rate can be ascribed to twin boundaries which can pin the dislocations and promote dislocation accumulation for strain hardening [35]. The outstanding work-hardening ability is crucial to the reliability in engineering applications because its ensure a large safety margin against fracture.

4. Discussion

4.1. Relationship between mechanical behavior and microstructure

According to the tensile test, the forged CoNiFe MEA treated at 900 °C possesses excellent mechanical properties. Fig. 6 shows the TEM micrographs and corresponding SAED patterns of the forged-CoNiFe MEA treated at 900 °C. The rings in the SAED pattern (Fig. 5a) suggest a [011] zone axis for the FCC structure consistent with XRD (Fig. 4) and based on the interlunar spacing in the SAED pattern, the lattice parameter is calculated to be 3.60 Å. The TEM image and corresponding SAED patterns of the annealing twins are shown in Fig. 6c. Annealing twins are common in cold-working face-centered cubic metals and affect the mechanical properties and corrosion behavior [36]. Many models have been proposed to explain the formation of annealing twins.
and Mahajan [43] suggested that twinning was only in boundary migration distance and velocity. Gleiter [42] designed a Meanwhile, the twin density has a strong tie with both the grain moting the generation of annealing twins in the growth accident model. Previous research [41] has indicated that the migration distance second glide of partial dislocations takes place on the successive {111} surfaces. In FCC materials, it is generally accepted that twinning is initiated by pre-existing dislocations that dissociate into partial dislocations. After the first glide of partial dislocations requiring the maximum stress, the second glide of partial dislocations takes place on the successive (111) plane. Previous research [41] has indicated that the migration distance and velocity of the grain boundary migration are two key factors promoting the generation of annealing twins in the growth accident model. Meanwhile, the twin density has a strong tie with both the grain boundary migration distance and velocity. Gleiter [42] designed a formula which could accurately determine the annealing twin density and Mahajan [43] suggested that twinning was only influenced by the temperature due to the effects on grain size. Jin et al. [41] presented evidence that the annealing twin density increased during recrystallization but decreased during grain growth and the observation is consistent with ours.

Annealing twins have a large effect on the motion of dislocations. A high density of dislocations is observed from the areas adjacent to the TBs (Fig. 6d) indicative of strong interactions between the dislocations and TBs [44]. Lu et al. [45] reported that strengthening and work hardening of alloy were attributed to high-density TBs interfering with or obstructing dislocation propagation consistent with our results (Fig. 5b). Lu et al. investigated the influences of twin thickness, grain size, as well as strain rate on the work-hardening behavior and found that decreasing twin thickness or increasing grain size and increasing strain rate or decreasing deformation temperature might enhance work-hardening ability and subsequent mechanical performance. With regard to the forged-CoNiFe MEA treated at 900 °C for 1 h, because the twin volume fractions are relatively large, their contributions to the total tensile strain are larger. Moreover, the new twin boundaries that form during straining ("dynamic Hall-petch") play an important role in providing steady strain hardening which delays the onset of neck and enhances uniform elongation before fracture [46].

Excellent work-hardening strain is observed from the forged-CoNiFe MEAs due to dislocation accumulation near the TBs as observed during the experiments conducted at room temperature. The BF TEM images in Fig. 6d to show the morphology and state of dislocations in the boundaries. A large density of extended dislocations accumulates and piles up at the boundary forming dislocation wall. The long and straight dislocations and high density of dislocation walls suggest strong interactions in the multiple slip system at room temperature [47]. The simultaneous movement, intersection, and entangling of dislocations on the two active (111) planes lead produce volume structural defects which retard dislocation movement and increase the strength and strain hardening capacity of alloy [48,49].

The shear band also plays a critical role in plastic deformation. Previous studies [50] show that the shear bands occur on planes oriented roughly at 45° to the principal stress. Cui et al. [51] reported that the work-hardening capability was linked to the shear bands and an alloy with a large shear band density and critical shear offset exhibit better plasticity in general. The shear band in the forged-CoNiFe MEAs treated at 900 °C examined by TEM is shown in Fig. 5e.

### 4.2. Fracture mechanism

The fracture surfaces of the samples treated at 900 °C for 1 h undergo tensile tests and the results are presented in Fig. 7. Fracture starts approximately in the geometrical middle of the tensile specimens and ends at the specimen edge. Based on the crack propagation and fracture characteristics, the fracture surface can be divided into three regions (Fig. 7a). The crack origin is shown in region "I" and many microvoids appear in region "II" (Fig. 6b1). The crack originates from these microvoids and propagate from the center to outside. Cracks are usually initiated at defects on the surface or at the corner of the regions which favor crack nucleation [52]. The fracture surface in region "II" (Fig. 7c) exhibits typical ductile fracture with dimples. Many uniform oval dimples can be observed from Fig. 7c(3). Since the obvious neck behavior occurs during the tensile process, region "II" is the final fracture plane.
propagation area thus indicating a ductile fracture mechanism. The characteristics of shear tearing are shown in region “II” and the fracture and major stress have a 45° angle. Our results suggest that annealing twins and dislocation slips are the main factors for the exceptional ductility achieved from the forged-CoNiFe MEAs treated at 900 °C for 1 h.

4.3. Thermomechanical behavior

Fig. 8 shows the thermal expansion rate of the forged-CoNiFe MEAs annealed at different temperature. The thermal expansion rate increases almost linearly with temperature. The CTE is a temperature-dependent property and for most metals and alloys, gradually increases with temperature. However, the coefficient shows discontinuities as phase changes occur. For example, a sharp contraction occurs as heated iron-based materials go through the ferrite to austenite transition. It is because the crystal changes from body-centered cubic to the more compact face-centered cubic structure [53]. There are no peaks or discontinuities in the thermal expansion rate-temperature curve (Fig. 8) suggesting absence of phase transformation with increasing temperature. Therefore, it can be inferred indirectly that the forged-CoNiFe MEAs annealed at different temperature are stable at high temperature.

The thermal expansion coefficient (CTE) of the forged-CoNiFe MEAs annealed for 1 h at 900 °C, 1000 °C, and 1100 °C are $14.5 \times 10^{-6}$ K$^{-1}$, $14.0 \times 10^{-6}$ K$^{-1}$, and $12.1 \times 10^{-6}$ K$^{-1}$, respectively, which decrease slightly compared with the untreated one ($15 \times 10^{-6}$ K$^{-1}$). The CTE of the sample annealed at 1000 °C is relatively small compared to traditional stainless steel which generally has CTE between 14.4 and $16 \times 10^{-6}$ K$^{-1}$.

5. Conclusion

Effective slight plastic deformation - two dimensional (2D) forging and subsequent annealing at different temperature are conducted to investigate the microstructure and properties of the CoNiFe medium entropy alloy (MEA). The as-cast and forged CoNiFe MEA samples have a face-centered cubic (FCC) crystal structure. As the annealing temperature is raised from 800 °C to 1100 °C, the ultimate tensile strength $\sigma_{UTS}$ decreases from 540 MPa to 430 MPa and tensile ductility $\delta$ decreases from 50% to 40%. The mechanical properties depend on the grain size and annealing twins affect the dislocation motion. The Σ3 annealing TBs corresponding to misorientation distribution at $60' < 111 >$ are observed from the annealed CoNiFe MEAs. For the CoNiFe MEA sample annealed at 900 °C for 1 h, the efficiency of grain refinement by recrystallization is enhanced and the annealing twins, dislocations, as well as micro-shear bands inside the grains are responsible for the outstanding ductility and work hardening ability. The CTE of the forged-CoNiFe MEA sample annealed at 1000 °C is relatively low compared to traditional stainless steel that generally has CTE between 14.4 and $16 \times 10^{-6}$ K$^{-1}$.

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References

[25] S. Praveen, J.W. Bae, P. Asghari-Rad, et al., Ultra-high strength nanocrystalline CoCrNi equi-atomic medium entropy alloy processed by high-pressure
A.J.S. Mukul Kumar, Wayne E. King, Microstructural evolution during grain
Y. Jin, B. Lin, M. Bernacki, et al., Annealing twin development during re-
S.J. Dillon, G.S. Rohrer, Mechanism for the development of anisotropic grain
P.J. Humphreys, A network mod for recovery and recrystallisation, Scripta Mater.
Q. Li, J.R. Cahoon, N.L. Richards, On the calculation of annealing twin density,
K.H. Song, Y.B. Chun, S.K. Hwang, Direct observation of annealing twin formation

[26] W.S.G. Dan Sathiaraj, Aurimas Pukenas, Rolf Schaarschuch, R. Jose Immanuel,
evolution during annealing of equiatomic CoCrFeMn high-entropy alloy, J. Alloy.
grain boundary character distribution in pure nickel, Scripta Mater. 56 (1) (2007)
[31] S. Huang, W. Li, S. Lu, et al., Temperature dependent stacking fault energy of
[32] S.J. Dillon, G.S. Rohrer, Mechanism for the development of anisotropic grain
boundary character distributions during normal grain growth, Acta Mater. 57 (1)
[33] Q. Li, J.R. Cahoon, N.L. Richards, On the calculation of annealing twin density,
[34] B.B. Rath, M.A. Imam, C.S. Pande, Nucleation and growth of twin interfaces in fcc
[35] V. Jin, B. Lin, M. Bernacki, et al., Annealing twin development during recrystallization
[36] A.J.S. Mukul Kumar, Wayne E. King, Microstructural evolution during grain
boundary engineering of low to medium stacking fault energy fcc materials, Acta
[37] K.H. Song, Y.B. Chun, S.K. Hwang, Direct observation of annealing twin formation
[38] Q. Li, J.R. Cahoon, N.L. Richards, Effects of thermo-mechanical processing para-
eters on the special boundary configurations of commercially pure nickel, Mater.
[39] Y. Jin, B. Lin, M. Bernacki, et al., Annealing twin development during re-
295–303.
1421–1428.
[42] Y. Ma, F. Yuan, M. Yang, et al., Dynamic shear deformation of a CrCoNi medium-
407–418.
stress for twinning in the CrMnFeCoNi high-entropy alloy, Acta Mater. 118 (2016)
152–163.
entropy alloys with balanced strength and ductility in a wide temperature range,
of the high-entropy alloy CrMnFeCoNi, Nat. Commun. 6 (2015) 10143.
[47] I. Moravcik, J. Cizek, Z. Kovacova, et al., Mechanical and microstructural charac-
terization of powder metallurgy CoCrNi medium entropy alloy, Mater. Sci. Eng.,
Glasses Containing In-Situ Formed Ductile Phase Dendrite Dispersions, (2000).
[49] J.W. Cui, R.T. Qu, F.F. Wu, et al., Shear band evolution during large plastic de-
formation of brittle and ductile metallic glasses, Phil. Mag. Lett. 90 (8) (2010)
573–579.
[50] M.A. Hemphill, T. Yuan, G.Y. Wang, et al., Fatigue behavior of Al0.5CoCrFeNi high
for the thermal expansion coefficient of metals and alloys at elevated temperatures,