The melt-spun equiatomic AlCoCuFeNi HEA with a large amount of nanoscaled twins about 20 nm disperse uniformly in the matrix. And these nanotwins keep the K-S crystallographic relationship: $\{111\}_{\text{FCC}} \parallel \{110\}_{\text{B2}}$, and $\langle 110 \rangle_{\text{FCC}} \parallel \langle 111 \rangle_{\text{B2}}$.

Nanotwins Formation and Growth in an AlCoCuFeNi High-Entropy Alloy

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Abstract: Nanotwins were formed in the AlCoCuFeNi high-entropy alloy produced by melt-spinning. The Cu-rich nanotwins have a face-centered-cubic (FCC) structure diffused in the ordered body-centered-cubic (B2) matrix. The nanotwins decompose from the matrix with the K-S crystallographic relationship: $\{111\}_{\text{FCC}} \parallel \{110\}_{\text{B2}}$ and $\langle 110 \rangle_{\text{FCC}} \parallel \langle 111 \rangle_{\text{B2}}$. After annealing, the spherical nanotwins grow into rodlike grains. The growth direction is parallel to the $\{111\}$ twin planes of the FCC phase. The hardness and elastic modulus change with the twin size, which is tested by nanoindentation. This study deepens the fundamental understanding of the phase transition in HEAs.

Keywords: High-entropy alloy; Nanotwin; K-S crystallographic relationship; Growth direction; Nanoindentation

The high-entropy alloys (HEAs) have been widely studied since firstly proposed by Yeh et al. in 2004 [1–8]. Till today, the HEAs with the face-centered-cubic (FCC), body-centered-cubic (BCC) or hexagonal-closed-packed (HCP) structure have been reported [2,4,5,9]. The different processing conditions influence the structure of HEAs, especially the cooling rate [3]. High cooling rates could suppress the decomposition of HEAs efficiently [3]. A rapid solidification rate greatly favors the formation of the solid-solution phase vs. undesired precipitated compounds by exploiting the incubation times of nucleation for various competing phases in the HEAs [10,11]. Meanwhile, the number of the phases formed, and their structures depend on the alloying elements in HEAs synthesized under identical processing conditions [12]. According to the alloying effect of elements on microstructural characteristics in stainless steels, elements can be classified into two types: one is the FCC stabilizer, such as Ni, Mn, Cu, C and N, and the other is the BCC stabilizer, such as Al, Cr, Mo, Si, and Nb [9]. It is a good case in noting that the phase of $\text{Al}_x\text{CoCrFeNi}$ changing from the single FCC, FCC + BCC to complete BCC phases with increasing the Al content [1,9,13]. The reports in the literature indicate that the Al addition promotes B2 ordering in HEAs (e.g., AlCrCuFeNi [9], AlCoCrCuFeNi [14], and $\text{Al}_{1.3}\text{CoCrCuFeNi}$ [15]). The Cu-Cu always forms a preferred nearest-neighbour pair in the alloy melt [13,15], and the Cu segregation occurs on different length scales, such as the interdendritic regions and the nanoscaled Cu-rich precipitates [1,12,15]. The nanoscaled phase separation by the Cu partitioning and local L_{12} ordering was observed in the as-spun $\text{CoCrFeCuNiAl}_{0.5}$ HEA [16].

In some HEAs with the precipitates, the different morphology with spinodal structures, such as the plate-like precipitates, the rhombohedron-shaped precipitates, and the nanoprecipitates decomposing from the BCC phase exist at low temperatures [3,15]. These precipitates are not randomly distributed, but keeping some orientational relationships with the BCC matrix [3]. For example, the Cu-rich plate-like precipitates are coherent with the BCC matrix in the AlCoCrCuFeNi HEA, and the edges of the rhombohedron-shaped precipitates are aligned along the $\langle 111 \rangle$ directions [3]. However, there is no reports of the nanotwin's formation, growth, and their orientational relationship with the BCC matrix. In fact, there are the nanoscaled twins at the earliest reference of HEA [1], named nanoprecipitates. However, they are not be realized to be nanotwins. Their formation and growth processes have not been studied. In the present work, we investigate the nanotwin formation, growth process, and their property variation of the AlCoCuFeNi HEA fabricated by melt-spinning, followed by annealing.

The target alloy used in the present work has the nominal composition of AlCoCuFeNi (in atomic proportion). The alloys were melted five times by arc-melting in a Ti-gettered high-purity argon atmosphere. The specimen was then crushed into an appropriate size for single-roller melt-spinning with a wheel tangential speed of 15 m/s. The width and thickness of the ribbons are about 1 – 1.5 mm and 15 μm , respectively. The ribbons were annealed at 873 K for 60 min. The nature of phase transitions was examined by the x-ray diffraction (XRD) using the Cu $K\alpha$ radiation from 20° to 100° of 2θ with $2^\circ/\text{min}$. The working voltage and current are

40 kV and 40 mA, respectively. We grind the as-spun ribbons into powders to conduct the XRD experiment. The transmission-electron-microscopy (TEM) observations were performed at 200 kV in a JEM-2010 microscope equipped with an energy-dispersive X-ray (EDX) spectrometer. Thin specimens for TEM observations were prepared by dimpling and ion-beam milling with a low energy ion beam (0.5 keV) to avoid damage at the latter milling stage. The nanoindentation test employed the Hysitron Triboindenter (TI-900) with the load increased up to the maximum load, $P_{\max}$, of 7,000 μN at a loading and unloading rates of 2,000 $\mu\text{N/s}$. The data were averaged in groups of five.

Figure 1 displays the structure of the melt-spun equiatomic AlCoCuFeNi HEA, including the XRD pattern, TEM images, and their corresponding selected-area-electron-diffraction (SAED) patterns. Figure 1a shows the XRD pattern of the melt-spun equiatomic AlCoCuFeNi HEA. The blue dots display the original data, and the red line is the fitting curve with the program Maud [17]. The difference ($I_{\text{exp}} - I_{\text{fit}}$) curve is also shown. I_{exp} and I_{fit} are the experimental diffraction intensity and fitting curve intensity, respectively. In the pattern, the XRD peaks corresponding to ordered BCC (B2) and FCC phases are observed. The lattice parameters of the B2 and FCC phases are 2.872 Å and 3.618 Å, respectively. According to the fitting results, the volume fractions of the FCC and BCC phases are 21.5% and 78.5%, respectively.

The bright-field TEM image in Fig. 1b indicates the typical microstructure of a polycrystalline material with abundant small precipitates. Inset is the SAED pattern for the matrix. The $\bar{1}11$ zone axis SAED of the matrix verifies that it is a BCC phase.

To display the small precipitates clearly, a higher magnification image was made in Fig. 1c. In this figure, a large amount of nanoscaled precipitates about 20 nm disperse in the matrix. In the SAED patterns (see the inset of Figure 1c), the bright reflections can be indexed along the [001] zone axis of an ordered BCC phase for the (100) ordered diffraction spot indicated by the white arrow, and two directions nanoprecipitates are clearly displayed by weak diffraction spots. The high-resolution TEM (HRTEM) image of a nanotwin is shown in Fig. 1d, and Fig. 1e displays the corresponding its fast Fourier transforms (FFT) patterns. The twinning relations are clearly labeled in the FFT patterns. The FFT patterns were stretched for existing stacking faults between twins, which could be confirmed by the enlarged Fourier-filtered HRTEM (Fig. 1f). The twin boundaries are marked by black dashed lines, and the twin angle of 70.7° is determined. The twin thicknesses are 2 ~ 5 nm. Therefore, twins and stacking faults coexist in the precipitates. It seems that the directions of nanotwins are not randomly in Fig. 1d. The {111} twin planes of all grains are along two vertical directions. In order to clarify the orientational relationship and the nanoscaled twins growth, the spun samples were annealed at 873 K for 60 min.

The features and orientational relationships of the annealed alloy are shown in Fig. 2. After annealing, the spherical nanotwins grow into rodlike grains. The length grow from ~ 20 nm to ~ 100 nm, and the width remains nearly unchanged. It can be seen clearly that the lengthwise direction is parallel to the {111} twin plane. Except for the vertical relationship between two {111} twin planes, another relationship was found

that the intersection angle of two $\{111\}$ twin planes is 60° in Fig. 2a. In fact, the $\{111\}$ planes with the 60° intersection angle are parallel to (110) and (101) planes of the B2 phase, respectively, demonstrated by the trace analysis with the $[\bar{1}\bar{1}1]$ zone axis SAED of the B2 phase in Fig. 2a. The perpendicular relationship of two $\{111\}$ twin planes are parallel to the $(\bar{1}10)$ and $(1\bar{1}0)$ of the B2 phase according to the $[001]$ zone axis SAED of the B2 phase in Fig. 2b. Therefore, the nanoscaled twinned FCC phase is transformed from the B2 matrix phase. It keeps an orientational relationship: $\{111\}_{\text{FCC}} \parallel \{110\}_{\text{B2}}$ for their similar crystalline interplanar spacing. The spacings of $\{111\}_{\text{FCC}}$ and $\{110\}_{\text{B2}}$ planes are $2.032 \text{ \AA}$ and $2.088 \text{ \AA}$, respectively.

To further illustrate the orientational relationship between the FCC and B2 phases, the HRTEM and SAED of the two-phases interface were shown in Fig. 3. The grain boundary of two phases were indicated by a dotted black line (the B2 phase on its left and the FCC phase on its right) in Fig. 3a. The grain of the FCC phase shows a twin structure in which the twin boundaries and twinning relations are marked with dashed red lines. The SAED patterns of the B2 (strong spots connected with solid yellow lines) and FCC phases (weak spots connected with dotted blue and red lines, which indicate a twin structure) were the indexed $[\bar{1}\bar{1}1]$ and $[011]$ zone axes shown in Fig. 3b. The $\langle 111 \rangle$ and $\langle 110 \rangle$ orientations of the B2 and FCC phase grains are strictly parallel to the electron beam, respectively, which indicates two-zone-axes parallel relationship. The parallel relationship between FCC and B2 phases could be demonstrated by HRTEM and their SAED pattern clearly. This orientation relationship obeys Kurdjumov-Sachs (K-S) crystallographic relationships [18]:

$\{111\}_{\text{FCC}} // \{110\}_{\text{B2}}$ and $\langle 110 \rangle_{\text{FCC}} // \langle 111 \rangle_{\text{B2}}$ by which the martensite phase transformation followed when the carbon content is lower than 1.4 wt.%. The chemical analysis by EDX/TEM shows that the FCC phase is the Cu-rich phase, and the B2 phase is rich in Al (see Table 1). The content of the Cu element increases in the FCC phase, and the Al content decreases after annealing. Whereas the contents of the Cu and Al elements in the B2 phase present the opposite results, this phenomenon means that the growth of nanotwins is accompanied by the Cu-elemental gathering.

The sample is produced by the melt-spinning device at a cooling rate of the order of $10^5 - 10^6$ K/s, which is lower than the splat-quenched AlCoCrCuFeNi HEA ($10^6 - 10^7$ K/s) [3]. Therefore, the growth of equilibrium phases could not be prevented that the Cu element separates and forms the Cu-rich phases at a lower cooling rate [11,19]. The formation of the Cu-rich precipitates is the result of the phase decomposition. The Cu element is prone to separating and forming Cu-rich phases for its strong repulsive interaction with the other elements, since Cu has the highest positive enthalpy of mixing with Fe, Co, and Ni [20]. In addition, the lattice difference between the FCC and BCC phases introduces a stress leading to the formation of the twin structure and stacking faults in the FCC phase.

The formation of nanotwins in materials usually improve the mechanical properties, and the size of nanotwins has impacts on their performance [21]. Therefore, the hardness and elastic modulus were tested by nanoindentation for the as-spun and as-annealed samples. Figure 4 shows the load-displacement curves of the as-spun and as-annealed AlCoCuFeNi HEAs for nanoindentation. The hardness and elastic

modulus are calculated to be about 3.2 and 43.6 GPa for the as-spun HEA, and 2.1 and 40.2 GPa for the as-annealed alloy, respectively. From the nanoindentation test results, the hardness and elastic modulus decrease slightly for the growth of nanotwins. Nanoscaled spherical twins in the matrix have a function of dispersion strengthening, whereas the function weakens, when the twins grow up during annealing. The hardness and modulus could be improved by smaller nanotwins. Therefore, the property of HEAs could be adjusted by controlling the growth of the nanotwins.

In summary, the equiatomic AlCoCuFeNi HEA produced by melt-spinning (with cooling rates between 10^5 and 10^6 K/s) was investigated by XRD, TEM, and EDX/TEM. The XRD and TEM images indicate the Cu-rich nanotwinned FCC phase dispersed uniformly in the B2 phase matrix. The formation of the nanotwins with the FCC structure is the reason of the lattice distortion of the transformation from the B2 to the FCC structures. The FCC phase and B2 phase keep the K-S crystallographic relationship: $\{111\}_{\text{FCC}} \parallel \{110\}_{\text{B2}}$, and $\langle 110 \rangle_{\text{FCC}} \parallel \langle 111 \rangle_{\text{B2}}$. The nanotwins grow to rodlike grains during annealing, and the growth direction is parallel to the $\{111\}_{\text{FCC}}$ twin planes. The hardness and elastic modulus decrease during annealing for the growth of nanotwins.

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Figure captions

Fig. 1 The structure of the melt-spun equiatomic AlCoCuFeNi HEA. (a) The XRD pattern indicates the ordering B2 and FCC phase; (b) TEM bright-field image showing a polycrystalline structure with nanoscaled precipitates, and the inset is the $\bar{1}11$ zone-axis SAED; (c) high-magnification bright-field image of nano-precipitates, and the inset is the $[001]$ zone-axis SAED; (d) HRTEM of a nanotwin in (c); (e) The corresponding FFT pattern of (d), in which the twinning relation is labeled; (f) the enlarged Fourier-filtered HRTEM image of (d), in which the twin boundaries and twinning relations are marked with dashed black lines.

Fig. 2 TEM images of the melt-spun equiatomic AlCoCuFeNi HEA after annealing: (a) the rodlike grains with the intersection angle of two $\{111\}$ planes is 60° , and the inset is the $\bar{1}11$ zone-axis SAED of the B2 phase; (b) the rodlike grains with the intersection angle of two $\{111\}$ planes is 90° , and the inset is the $[001]$ zone-axis SAED of the B2 phase.

Fig. 3 (a) Fourier-filtered HRTEM of the interface between FCC and B2 phases, in which the twin boundaries and twinning relations are marked with dashed red lines. (b) The corresponding SAED patterns of the FCC and B2 phases, in which solid yellow lines indicate B2 phase and the twinning relations of FCC phase are labeled with dashed red and blue lines.

Fig. 4 Load-displacement curves of nanoindentation in the as-spun and as-annealed AlCoCuFeNi HEAs.

Figure 1

Figure 2

Figure 3

Figure 4

Table 1
The chemical composition (in at.%) of the as-spun and as-annealed AlCoCuFeNi
HEAs are measured by EDX/TEM.

Material	Crystal	Al	Cu	Co	Fe	Ni
As-spun	FCC	9.28 ± 3	35.15 ± 3	20.23 ± 3	18.31 ± 3	17.05 ± 3
	B2	26.30 ± 3	8.48 ± 3	20.10 ± 3	22.46 ± 3	22.66 ± 3
As-annealed	FCC	5.59 ± 3	68.27 ± 3	7.13 ± 3	5.84 ± 3	13.17 ± 3
	B2	27.84 ± 3	4.44 ± 3	23.48 ± 3	20.93 ± 3	23.32 ± 3