Concurrence of spinodal decomposition and nano-phase precipitation in a multi-component AlCoCrCuFeNi high-entropy alloy

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The concurrence of spinodal decomposition and nano-phase precipitation in an AlCoCrCuFeNi high-entropy alloy produced by arc melting, spray casting and melt spinning was investigated in the present work. It is shown that the present high cooling rate cannot inhibit the concurrence of spinodal decomposition and nano-phase precipitation. In the solidification and annealing process, three typical structures including Cu-rich nano-precipitates of FCC structure, Al-Ni-rich plate of B2 structure, and Fe-Cr-rich plate of A2 structure were observed; meanwhile, the width of modulated plate decreased with the increase of the cooling rate. An interesting phenomenon was observed in the as-annealed microstructure that Al-Ni and Fe-Cr spinodal plates were weakened or vanished rather than strengthened, due to the atom diffusion and composition homogenization. Different from spinodal decomposition plates, the Cu-rich nano-precipitates grew into rod-like phase from point-like or oval phase in the whole process. The intersection angle of newborn rod-like nano-phases tended to 60°, following the K-S crystallographic relationship.

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1. Introduction

High entropy alloys (HEAs) that consist of five or more principal elements with equiatomic or near equiatomic composition have broken the concepts of traditional alloy design [1,2]. Since firstly proposed by Yeh et al., in 2004, HEAs have gained considerable attention [3–7], meanwhile the critical reviews of high entropy alloys and related concepts have been published [8–18]. Owing to small atomic size difference, high entropy effect and near-zero values of absolute enthalpy of mixing, HEAs tend to form a simple solid solution structure, for instance, face-centered cubic (FCC), body-centered cubic (BCC) or hexagonal-close-packed (HCP) structure [7,19–24]. Until now, some typical characteristics of HEAs have been summarized including...
good high-temperature stability, high low-temperature toughness, superior anti-irradiation swelling rate and distinct sluggish diffusion effect. Accompanying with those characteristics, several HEA systems are reported to have remarkable properties, such as high hardness, excellent resistance to softening, outstanding corrosion oxidation, wear, fatigue, and fracture toughness [7,25–34]. Properties of Al0.5CoCrCuFeNi high-entropy alloy have been widely studied. The effect of aging on the structure and properties of AlCoCrCuFeNi HEA was investigated by Zhang et al., and results showed that the annealed alloys had high strength and excellent ductility. Meanwhile with the increase of annealing temperature, the compressive strength decreased but the plastic strain increased. In the study of Al0.5CoCrCuFeNi HEA, good processing property and working hardening ability were observed during hot forging and cold rolling process, excellent fatigue properties also have been found in Hemphill’s research [34].

Understanding microstructure and phase composition of a material is significant for predicting its properties [35–44]. Synthesized under identical processing condition, the number of phases formed depends on the alloying elements in HEAs [35], while the different processing conditions, especially for the cooling rate and heat treatment, influence the structure and phase composition of HEAs. For quinary alloys such as CoCrCuFeNi, the formation of only one FCC solid solution phase was observed [8]. Several studies showed that additions of certain elements (such as Al) into HEAs could have strong effects on the crystalline structure, microstructural morphology and the subsequent mechanical properties [19,20]. In contrast, the six-element alloy AlCoCrCuFeNi formed a modulated structure composed of disordered (A2) and ordered (B2) BCC phases as a result of spinodal decomposition [1]. Subjected to the method of atom probe, Singh et al., revealed that the alloying elements in the Ni-Al-rich plate and Cr–Fe-rich interplates were not randomly distributed, but well-aligned with pronounced compositional fluctuations. The reported investigations only focused on the as-solidified structures under different cooling rate, but omitted the subsequent annealing heat treatment. Besides spinodal structure, Cu-rich precipitates of different morphologies (plate-like, spherical and rhombohedron-shaped) could also be found in the above alloys. These nano-precipitates are not randomly distributed, but kept some orientation relationships with the BCC matrix [44]. Yu et al., detected that those precipitates were nano-twins in AlCoCrFeNi and their growth direction followed the K-S crystallographic relationship: \( \{111\}_{\text{FCC}} \langle 110 \rangle_{\text{B2}} \) and \( \langle 110 \rangle_{\text{FCC}} \langle 111 \rangle_{\text{B2}} \) [45]. Subjected to anneals, the spherical nano-twins grew into rod-like grains. However, there were no reports on the formation and growth of the nano-twins and their correlation with the spinodal decomposition.

Until now, spinodal decomposition and nano-precipitation has been studied independently in HEAs. This gives rise to two open questions. (1) Is there the concurrence of spinodal decomposition and nano-precipitation in multi-component AlCoCrCuFeNi HEAs (i.e., as-solidified and as-annealed structures)? (2) If so, what is the inherent relationship between spinodal decomposition and nano-phase in the concurrent spinodal decomposition and nano-precipitation processes? In a word, no enough studies have been done to elucidate the sequence of spinodal decomposition and nano-precipitation in multi-component AlCoCrCuFeNi HEAs, especially for the morphology, structure and composition after annealing treatment.

In the present paper, we aim to answer the above two questions. We investigated the spinodal decomposition, nano-twins formation and growth process of as-cast, spray-cast and melt-spun AlCoCrCuFeNi HEAs, followed by annealing. Experimental details and characterization techniques were given in Section 2. Specific results, including analysis of XRD pattern (Section 3), structure of spray-cast specimen (Section 3), structure of melt-spun specimen (Section 3) and structure of annealing samples (Section 3), were given in Section 3. Section 4 discussed the evolution of spinodal decomposition (Section 4.1) and Cu-rich nano-phase (Section 4.2). Finally, we made the conclusion in Section 5.

## 2. Experiments

High purity elemental Aluminum (99.99 wt.%), Cobalt (99.98 wt.%), Chromium (99.99 wt.%), Copper (99.99 wt.%), Iron (99.95 wt.%) and Nickel (99.95 wt.% ) bulk were chosen as raw materials to produce AlCoCrCuFeNi high entropy alloy. Few surface oxidation and negligible mass loss ensured the composition of the alloy to be accurate to 0.1 at. %. The equiatomic AlCoCrCuFeNi high entropy alloy were produced by arc-melting under a pure argon atmosphere in a circulating water-cooling copper crucible. To guarantee the chemical homogeneity of the alloy, repeated melting was carried out at least six times. Then the ingots were solidified at a cooling rate of 10–20 K s\(^{-1}\) with the size of 25 mm in diameter and 15 mm in thickness. The ingots were cut into small cubes which were remelted to produce spray-cast alloy and melt-spun alloy in Vacuum (6 × 10\(^{-4}\) Pa) in an electromagnetic melting furnace. Spray-cast alloy was solidified with a cooling rate of 10\(^{-5}\)–10\(^{-3}\) K s\(^{-1}\) in a copper mold and eventually formed a metal rod with a diameter of 6 mm and length of 100 mm. Melt spinning device allowed us to gain the ribbon with the cooling rate of 10\(^{6}\)–10\(^{7}\) K s\(^{-1}\) and the thickness of 50 µm. Both spray-cast alloy and melt-spun alloy were annealed at 873 K for 20 h in order to investigate the spinodal decomposition in alloys.

The as-cast, spray-cast and melt-spun alloys were characterized by different techniques, including XRD, SEM, TEM and DSC. The as-solidified samples were sectioned, polished and etched by using 30 ml HCl plus 10 ml HNO\(_3\). The microstructure observation was completed by Quanta\textsuperscript{TM} 250 scanning electron microscopy (SEM). The microstructures of specimens from spray-cast alloy and melt-spun alloy were characterized by a JEM-200 transmission electron microscope, equipped with an energy dispersive X-ray spectrometer (EDX) that was used for the chemical composition analysis. The detailed information of the TEM specimen preparation and characterization parameters was shown as follows. Thin discs about 0.3 mm in thickness were cut from the specimen’s center by wire-electrode cutting for TEM observation. These discs were made electron transparent using a MTP-1A jet electropolisher. The electrolyte used for the polishing was a solution of 97% ethanol and 3% perchloric acid.
with the electropolishing condition 253 K. The high-resolution transmission microscopy (HRTEM) images and the corresponding selected-area electron diffraction (SAED) patterns were performed using a TEM at an operating voltage of 200 kV. XRD spectra were examined with Cu Kα radiation from 10° to 90° of 2θ with 5 min⁻¹. DSC curves were measured in Al₂O₃ crucible with 30 K min⁻¹ from 373 K to 973 K.

3. Experimental results

XRD patterns of as-cast, spray-cast and melt-spun equiatomic AlCoCrCuFeNi HEAs and Bragg peaks that correspond to different compositions are shown in Fig. 1. Both FCC and BCC phases could be observed. Two types of BCC phase with similar structure but different composition can be obtained, therefore the BCC phases are defined as BCC1 and BCC2 phases. Obviously, the intensity of diffraction peaks of BCC phases is stronger than that of FCC phase. By selecting the [111] peak for FCC phase and the [110] peak for BCC phase to estimate the volume fraction of the corresponding phase, it is shown that the volume fraction of FCC phase is far lower than that of BCC phase. The excursion of main peaks is displayed by the diffraction patterns at 2θ = 43°-46° (the magnified image in the inset of Fig. 1). The [110] peaks position of spray-cast and melt-spun alloy shift to the right with a tiny angle respectively, due to the different lattice distortion intensified by cooling rate.

Fig. 2 displays the structure of spray-cast equiatomic AlCoCrCuFeNi HEAs, including SEM image, TEM images and their corresponding SAED images. The typical dendritic microstructures with legible boundaries are present in Fig. 2a and b. The width of inter-dendritic area is about 1 μm, and edge of boundary has a narrow transition layer. The bright-field TEM image clearly shows the precipitate morphologies inside the dendrites (Fig. 2c). There are two types of plates (A and B) that arranged perpendicular to each other, aligning along the <110> matrix direction. The [001] zone axis diffraction pattern (Fig. 2e) shows the superlattice reflection generated by phase A and it corresponds to BCC structure. The Fig. 2f represents [001] zone axis diffraction pattern of plate-like phase B and superlattice reflection shows the structure of B2. There are some small dark precipitates (C) with different size and feature evolve in phase B. Superlattice reflection for [001] zone axis diffraction pattern of the oval dark precipitate (C) is given in Fig. 2g, indicating an FCC structure. The sizes of the phases are shown in Table 1, phase A has the width of 30 nm, phase B has the width of 38 nm and phase C has a size range from 4–33 nm. The inter-dendritic region (E) morphology is shown by bright-field TEM image in Fig. 2d, meanwhile the magnified image of dark precipitate (D) and the corresponding SAED pattern are displayed in the inset (Figs. 2h and i). Nano-precipitates have stratified structure that similar with nano-twins. The [112] zone axis of diffraction pattern presents the superlattice reflection of precipitate (red line) and inter-dendritic other region (white line). It is clearly revealed that the inter-dendritic region is of FCC structure and stratified precipitate has L1₂ structure.

The compositions of each phase are exhibited in Table 2. Similar to S. Singh’s research [27], phase A is enriched in Fe-Cr, phase B is enriched in Al-Ni, oval phase C is enriched in Cu and the Cu content is more than 85%. The precipitate phase D in the inter-dendritic region is also enriched in Cu, and other region of inter-dendrites is enriched Co-Cr-Fe-Ni.

The morphology of melt-spun AlCoCrCuFeNi HEAs is given in Fig. 3. The equiaxed grain could be observed in Fig. 3a. Typical precipitates that are clearly revealed in the spun alloy grain, including alternately arranged plates, small dark dot and ellipse precipitates are similar with those in spray-cast alloy. Though all of the precipitates share the similar structure, some differences still exist in the alloy. Vertical structure of two plates is not distinct and width of the plates is smaller than that in spray-cast alloy (Fe-Cr plate is 22 nm and Al-Ni plate is 30 nm, see in Table 1). Simultaneously, smooth grain boundary without transition layer is shown in Fig. 3c, width of the boundary is also smaller than that of spray-cast specimen. Fig. 3d is the magnified image of oval precipitate that generates from boundary. The crystal structure of Cu-rich oval phase is FCC, same with spray-cast alloy, but the structure of region nearby oval precipitate should be distinguished from crystal, that is, non-crystalline phase is observed in melt-spun specimen grain boundary (see inset in Fig. 3d).

Fig. 4 is the DSC curve of spray-cast AlCoCrCuFeNi HEA. The curve clearly reveals that endothermic peak occurs at 913 K. It indicates that phase transition may take place in the process of heating. Based on the understanding of spinodal decomposition found in AlCoCrCuFeNi HEAs, endothermic peak should be caused by degeneration or disappearance of spinodal decomposition structure. In order to clarify the stability of spinodal decomposition structure, nano-phases texture and their interrelation, spray-cast and melt-spun samples were annealed at 873 K for 20 h.

Fig. 5 gives the information of morphology features and orientation relationship of the annealed samples. After annealing, plate-like structure which caused by spinodal
decomposition in both spray-cast and melt-spun alloys disappeared. The oval Cu-rich precipitates grow into rod-like phase. Inset in Fig. 5b shows that the [011] zone axis SAED of precipitates and legible twin structure is emerged. Hence the new phase is proved to be twin phase. It is easy to find that the lengthwise direction and {111} twin plane normal are parallel to each other. Measuring result shows the intersection angle of two rod-like phases is 60°, which means that the intersection angle of two {111} twin planes is 60°, and the [111] zone axis SAED of B2 matrix phase could prove it. Cu-rich precipitates and non-crystalline phases in the boundary fade away and the grain boundary changes into clean smooth band (Fig. 5c). The [112] zone axis diffraction pattern (inset in Fig. 5c) shows the superlattice reflections generated by grain boundary of FCC structure. Comparing with SAED inset in Fig. 2d, weak superlattice reflections corresponding to a L1₂ structure are unavailable to be sought.

The hardness and indentation elastic modulus of as-cast, spray-cast and melt-spun HEAs are given in Table 3. Obviously, the nanohardness of as-cast alloy (534 Hv) is almost equal to that of melt-spun alloy (539 Hv), and as-cast alloy (500 Hv) is harder than spray-cast alloy (444 Hv). After annealing, hardness of spray-cast alloy displays a slight

| Table 1 – Width/size of each phase (nm) in AlCoCrCuFeNi HEAs. |
|--------------------------|---------------------|-----------------|---------------------|------------------------|
| Materials                | Fe-Cr plate         | Al-Ni plate     | Cu-rich             | Average of Fe-Cr plate and Al-Ni plate |
| As-cast[27]              | –                   | –               | 5–15                | 50                      |
| Spray-cast               | 30 ± 3              | 38 ± 3          | 4–33 ± 3            | 34                      |
| Melt-spun                | 22 ± 3              | 30 ± 3          | 4–26 ± 3            | 26                      |
Table 2 – Crystal structure and chemical position (at. %) of AlCoCrCuFeNi HEAs. Different phases marked in the spray-cast alloy (region A-E as marked in Fig. 2) are measured by TEM/EDX. Date of as-cast and melt-spun alloy are referring to [27].

<table>
<thead>
<tr>
<th>Symbols</th>
<th>Region enrich</th>
<th>Crystalline</th>
<th>Al</th>
<th>Co</th>
<th>Cr</th>
<th>Cu</th>
<th>Fe</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melt-spun</td>
<td>grains</td>
<td>B2</td>
<td>13.1±3</td>
<td>17.7±3</td>
<td>16.2±3</td>
<td>18.7±3</td>
<td>17.6±3</td>
<td>16.7±3</td>
</tr>
<tr>
<td>Spray-cast</td>
<td>A</td>
<td>Fe-Cr</td>
<td>BCC</td>
<td>3.9±3</td>
<td>19.2±3</td>
<td>41.8±3</td>
<td>3.1±3</td>
<td>27.2±3</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>Al-Ni</td>
<td>B2</td>
<td>31.1±3</td>
<td>17±3</td>
<td>3.9±3</td>
<td>10.±3</td>
<td>10.9±3</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>Oval precipitate</td>
<td>FCC</td>
<td>4.7±3</td>
<td>1.8±3</td>
<td>2.8±3</td>
<td>85.4±3</td>
<td>1.5±3</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>Cu</td>
<td>L12</td>
<td>5.0±3</td>
<td>1.7±3</td>
<td>2.5±3</td>
<td>86.3±3</td>
<td>0.2±3</td>
</tr>
<tr>
<td></td>
<td>E</td>
<td>Inter-dendrite</td>
<td>FCC</td>
<td>16.6±3</td>
<td>3.6±3</td>
<td>2.4±3</td>
<td>62.0±3</td>
<td>2.9±3</td>
</tr>
<tr>
<td>As-cast dendrite</td>
<td>Al-Ni</td>
<td>B2</td>
<td>25.8±3</td>
<td>17.9±3</td>
<td>3.0±3</td>
<td>10.4±3</td>
<td>12.1±3</td>
<td>30.8±3</td>
</tr>
<tr>
<td></td>
<td>Fe-Cr</td>
<td>BCC</td>
<td>2.2±3</td>
<td>20±3</td>
<td>43.2±3</td>
<td>0.3±3</td>
<td>29±3</td>
<td>5.3±3</td>
</tr>
<tr>
<td></td>
<td>Plate precipitate</td>
<td>L12</td>
<td>4.9±3</td>
<td>1.8±3</td>
<td>1.1±3</td>
<td>85±3</td>
<td>2.0±3</td>
<td>5.2±3</td>
</tr>
<tr>
<td></td>
<td>Inter-dendrite Cu</td>
<td>B2</td>
<td>7.6±3</td>
<td>2.9±3</td>
<td>1.3±3</td>
<td>77.1±3</td>
<td>2.5±3</td>
<td>9.1±3</td>
</tr>
<tr>
<td>Annealed spray-cast</td>
<td>matrix</td>
<td>BCC</td>
<td>14.5±3</td>
<td>17.4±3</td>
<td>27.1±3</td>
<td>6.8±3</td>
<td>20.2±3</td>
<td>14.0±3</td>
</tr>
<tr>
<td></td>
<td>rod-like phase</td>
<td>Nano-twins</td>
<td>4.8±3</td>
<td>2.4±3</td>
<td>2.6±3</td>
<td>81.4±3</td>
<td>2.1±3</td>
<td>6.7±3</td>
</tr>
</tbody>
</table>

Fig. 3 – The structure of melt-spun equatomic AlCoCrCuFeNi HEA. (a) TEM bright-field image of an equiaxed grain structure; (b) and (c) TEM bright-field image of dendrites and inter-dendrites; (d) the magnified image of precipitate in the inter-dendrites region. The inset displays a non-crystalline structure of region near precipitate.

increase. Nevertheless, the indentation elastic moduli of melt-spun alloy (105 GPa) is far lower than that of as-cast alloy (182 GPa).

4. Discussion

The microstructural studies show that the main phases formed in the AlCoCrCuFeNi HEAs are Al-Ni-rich phase, Fe-Cr-rich phase and Cu-rich phase. Referring to S. Singh’s investigation [27], the formation of Al-Ni-rich phase can be attributed to the largest negative mixing entropy [46] which is −22 kJ mol⁻¹ (see in Table 4). Large amounts of Co, Cr, Fe and Cu are detected in Al-Ni-rich plates, the assumption that Co and Cr take up Ni sites, whereas Fe take up Al sites can be used as a reasonable explanation. Nevertheless, Fe-Cr-rich plates are formed in disparate mechanism [47].
Fig. 4 – DSC curve of spray-cast AlCoCrCuFeNi HEA. Distinct endothermic peak is shown around 913 K.

4.1. Evolution of spinodal decomposition and its disappearance

During the process of alloy solidification, concurrence of spinodal decomposition and nano-phase formation took place in the AlCoCrFeNi HEAs. A description of spinodal decomposition has been given in Appendix A.

According to Appendix A and experimental results, the size of pinodal decomposition plates follows the above rules, as shown in Table 1. It should be noted from Eq. (11) and Figs. 2–3 that no matter what amount of cooling rate above is, the occurrence of the spinodal decomposition could not be completely inhibited. As-cast alloy (cooling rate 10–20 K s⁻¹) with the average size of 50 nm, spray-cast alloy (cooling rate 10²–10³ K s⁻¹) with the average size of 34 nm and melt-spun alloy (cooling rate 10⁶–10⁷ K s⁻¹) with the average size of 26 nm, in other words, plate width of as-cast alloy > spray-cast alloy > melt-spun alloy.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Hardness (HV)</th>
<th>Nanohardness (HV)</th>
<th>Elastic modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-cast [27]</td>
<td>500</td>
<td>534</td>
<td>182</td>
</tr>
<tr>
<td>Melt-spun [27]</td>
<td>444</td>
<td>539</td>
<td>105</td>
</tr>
<tr>
<td>Spray-cast</td>
<td>460</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Annealed spray-cast</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

![Fig. 5](image) – The structure of equiatomic AlCoCrCuFeNi HEAs after annealing. (a) TEM bright-field image of annealing spray-cast alloy. The rod-like phases with the intersection angle of two [111] planes are 60°. The corresponding electron diffraction of [111] zone axis in the inset displays BCC structure of matrix. (b) TEM bright-field image of annealing melt-spun alloy. The rod-like phases with intersection angle of two [111] planes are 60° and the inset is the [011] zone axis SAED pattern of twins structure. (c) Microstructure of inter-dendrites region in spray-cast alloy. The corresponding SAED pattern of [112] zone axis in the inset displays FCC structure of inter-dendrites region.)
Table 4 – The mixing enthalpy of binary alloys.

<table>
<thead>
<tr>
<th>Binary alloys</th>
<th>Mixing enthalpy (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-Co</td>
<td>–19</td>
</tr>
<tr>
<td>Al-Cr</td>
<td>–10</td>
</tr>
<tr>
<td>Al-Cu</td>
<td>–1</td>
</tr>
<tr>
<td>Al-Fe</td>
<td>–11</td>
</tr>
<tr>
<td>Al-Ni</td>
<td>–22</td>
</tr>
<tr>
<td>Cu-Co</td>
<td>+6</td>
</tr>
<tr>
<td>Cu-Cr</td>
<td>+12</td>
</tr>
<tr>
<td>Cu-Fe</td>
<td>+13</td>
</tr>
<tr>
<td>Cu-Ni</td>
<td>+4</td>
</tr>
<tr>
<td>Ni-Co</td>
<td>0</td>
</tr>
<tr>
<td>Ni-Cr</td>
<td>–7</td>
</tr>
<tr>
<td>Ni-Fe</td>
<td>–2</td>
</tr>
<tr>
<td>Co-Cr</td>
<td>–4</td>
</tr>
<tr>
<td>Co-Fe</td>
<td>–1</td>
</tr>
<tr>
<td>Cr-Fe</td>
<td>–1</td>
</tr>
</tbody>
</table>

After annealing, spinodal decomposition plates fade away. Fig. 6 displays the annealing morphology of as-spray-cast alloy. No more obvious plates can be seen in bright-field TEM image in Fig. 6a, except nano-twins. Another corresponding regulated TEM image of the same region with Fig. 6a is given in Fig. 6b. It reveals that the Fe-Cr-rich region is unstable and a new decomposition can be detected in the Fe-Cr-rich phases [52]. Subjected to heat treatment from 773 K, Fe-Cr-rich phases ultimately decompose into Fe-rich region and Cr-rich region, then Al and Ni concentrations are diluted by diffused Fe and Cr, hence the plates are slaked and homogenized. The comparison of chemical concentration in original phases and annealed phases in spray-cast AlCoCrCuFeNi HEAs are shown in Table 5. It can be speculated that elements diffusion leads to the attenuation of spinodal decomposition plates which can be verified further by the endothermic peak near 913 K showed in DCS curve. For the region where spinodal decomposition phases disappeared entirely, comparing to matrix composition in Table 2, Al-Ni-rich phases mingle with Fe-Cr-rich phases by means of atom diffusion and finally all the elements except Cu achieve a homogeneous state.

4.2. Evolution of Cu-rich nano-phase accompanying spinodal decomposition and disappearance

Cu-rich phases with different morphology and size within the dendrites and inter-dendrites in both spray-cast and melt-spun AlCoCrCuFeNi HEAs can be observed. There is a concurrence relationship with spinodal decomposition phase. In the original specimens, due to its negative mixing entropy with Al, nano-Cu phases are mainly present in the Al-Ni-rich regions, as shown in Table 4 [27]. Other Cu is squeezed out of dendrites and enriches in inter-dendrites, which may be influenced by relatively positive mixing entropy between Cu and other five elements. After annealing, almost all Cu atoms in inter-dendrites diffuse into matrix. Therefore, the clean smooth grain boundary emerges. Meanwhile, with the uniform distribution of Al, Co, Cr, Fe and Ni, Cu grows to rod-like phase. Also owing to the homogenization of matrix, nano-twins are easy to form in the region with low stacking fault energy [6]. Recent studies showed that Cu-rich nano-twins decomposed from the matrix with K-S crystallographic relationship: (111)_{BCC}//(110)_{B2} and <110>_{BCC}//<111>_{B2} by which the martensite phase transformation followed when

![Fig. 6 – TEM image of the spray-cast AlCoCrCuFeNi HEAs. (a) TEM bright-field image of matrix with shallow linear trace which remained by spinodal decomposition structure; (b) Corresponding regulated TEM bright-field image of (a). White strips exhibit original form of spinodal plates, and pilotaxitic feature could be observed in those plates.](image)

Table 5 – Chemical position (at. %) of original spinodal decompositidon phases and anneal phases in spray-cast AlCoCrCuFeNi HEAs.

<table>
<thead>
<tr>
<th>Symbols</th>
<th>Al</th>
<th>Co</th>
<th>Cr</th>
<th>Cu</th>
<th>Fe</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Cr</td>
<td>3.9 ± 3</td>
<td>19.2 ± 3</td>
<td>41.8 ± 3</td>
<td>3.1 ± 3</td>
<td>27.2 ± 3</td>
<td>4.8 ± 3</td>
</tr>
<tr>
<td>Annealed Fe-Cr</td>
<td>13.8 ± 3</td>
<td>18.4 ± 3</td>
<td>29.8 ± 3</td>
<td>2.7 ± 3</td>
<td>20.5 ± 3</td>
<td>14.8 ± 3</td>
</tr>
<tr>
<td>Al-Ni</td>
<td>31.1 ± 3</td>
<td>17 ± 3</td>
<td>3.9 ± 3</td>
<td>10 ± 3</td>
<td>10.9 ± 3</td>
<td>27.2 ± 3</td>
</tr>
<tr>
<td>Annealed Al-Ni</td>
<td>20.4 ± 3</td>
<td>18.7 ± 3</td>
<td>15.6 ± 3</td>
<td>8.4 ± 3</td>
<td>16.3 ± 3</td>
<td>20.6 ± 3</td>
</tr>
</tbody>
</table>
the carbon content is lower than 1.4 wt. % [45]. Orientation relationship between Cu-rich nano-twins with FCC structure and BCC matrix that found in AlCoCrCuFeNi HEAs also obeys the rule. Thus the intersection angle of two rod-like phases (60°) is confirmed.

In conclusion, from the early stage of solidification, spinodal decomposition takes place in AlCoCrCuFeNi HEAs prematurely, leading to the formation of Al-Ni-rich phase and Fe-Cr-rich phase. Owe to mixing enthalpy, Cu tends to segregate in grain boundary and Al-Ni plates in the form of point-like or oval phase (Figs. 2 and 3). After annealing, obvious spinodal decomposition plates are weakened, followed by morphological change of Cu-rich precipitates (Fig. 5). The small oval Cu-rich nano-phases grow into rod-like phases with the intersection angle of 60°. That is to say, the concurrence of spinodal decomposition and nano-phase precipitation in multi-component AlCoCrCuFeNi high-entropy alloy occurs not only in the as-solidified stage but also in the as-annealed stage. Finally, the concurrence of spinodal decomposition and nano-phase precipitation observed during solidification by three different processing conditions and subsequent annealing are summarized and presented schematically in Fig. 7.

5. Conclusion
The concurrence of spinodal decomposition and nano-phase precipitation in AlCoCrCuFeNi high-entropy alloy produced by arc melting, spray casting and melt spinning was investigated in the present work. The main conclusion can be given as follows:

1. It is shown that concurrence of spinodal decomposition and nano-phase precipitation still occurred subjected to high cooling rate of \(10^2-10^3 \text{ K s}^{-1}\).
2. In the solidification and annealing process, three typical structures including Cu-rich precipitates of FCC structure, Al-Ni-rich plate of B2 structure, Fe-Cr-rich plate of BCC structure were observed, meanwhile, the width of modulated plate decreased with the increase of cooling rate, subjected to the above three solidification pattern.
3. An interesting phenomenon was observed in the as-annealed microstructure that, Al-Ni and Fe-Cr spinodal plates were weakened or vanished rather than strengthened, due to the atom diffusion and composition homogenization.
4. Different from spinodal decomposition plates, the Cu-rich nano-precipitates grew into rod-like phase from point-like or oval phase in the whole process. The intersection angle of newborn rod-like nano-phases tended to 60°, following with K-S crystallographic relationship.

Conflicts of interest
The authors declare no conflicts of interest.
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Appendix A.

According to the classical solidification theory, solidification need a degree of undercooling (ΔT) to overcome the additional interfacial energy that result from new born solid-melt interface in the system [48]. Whereas crystal nucleus formation demands a certain value of ΔT to surmount the energy barrier ΔG*,

$$\Delta G^* = \frac{16\pi \sigma^3 T^3 m}{3\Delta H^5 \Delta T^2}$$  \hspace{1cm} (A1)

where σ is solid-melt interfacial tension, Tm is melting point and Hs is crystalization latent heat. Keep other conditions unchanged, ΔT increases, ΔG* will decrease and crystalization will be more likely to occur.

Nucleus formation is also a process that is realized by atomic migration and is therefore a kinetic process. When ΔT is large enough, free energy for the system can be lessened by liquid phase separation. In addition, spontaneous spinodal liquid phase separation could happen if the conditions are fulfilled and both the microstructure and morphology will be kept eventually in the subsequent solidification [49]. For melting alloy, liquid-state spinodal decomposition priciple is similar with solid-state spinodal decomposition which is mainly influenced by component fluctuation and energy fluctuation. Atoms in undercooled alloy diffuse and aggregate in the way of uphill diffusion, alloy component develops with sinusoidal fluctuation and the component fluctuation divide the liquid-state alloy into two phases: X-rich phase L1 and Y-rich phase L2 [50]. Obviously, as for AlCoCrCuFeNi high-entropy alloy, the two phases are Al-Ni-rich phase and Fe-Cr-rich phase. Assuming that composition variation is one-dimensional, when diffusion coefficient D has no relation with concentration C and distance x, there is a diffusion equation,

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$  \hspace{1cm} (A2)

where D (\(= M (\frac{\partial^2 G}{\partial C^2})\)) is diffusion coefficient, G is Gibbs free energy, M is mutual migration rate. Obviously, sign of D is determined by \(\frac{\partial^2 G}{\partial C^2}\). If \(\frac{\partial^2 G}{\partial C^2} < 0\), little component fluctuation will decrease the free energy for the system and spinodal decomposition will take place.

In Cahn’s opinion [50], in earlier stage of spinodal decomposition, component deviation and concentration gradient make the chemical potential lower, and variation of chemical potential Δμ is proportional to, \(-\frac{\partial^2 G}{\partial x^2}\)

$$\Delta \mu = \frac{\partial G}{\partial C} - 2k \frac{\partial^2 C}{\partial x^2} + \cdots$$  \hspace{1cm} (A3)

$$J = -M \frac{\partial}{\partial x} \left( \frac{\partial G}{\partial C} - 2k \frac{\partial^2 C}{\partial x^2} \right) = M \left( \frac{\partial^2 G}{\partial C^2} - 2k \frac{\partial^2 C}{\partial x^2} \right)$$  \hspace{1cm} (A4)

in which J is diffusion flux, K is constant. Introduce J into diffusion equation, a new equation is established [51],

$$\frac{\partial C}{\partial x} = -\frac{J}{\frac{\partial C}{\partial x}} = M \left( \frac{\partial^2 G}{\partial C^2} - 2k \frac{\partial^2 C}{\partial x^2} \right)$$  \hspace{1cm} (A5)

Suppose component fluctuation to be \( C - C_0 = A' \cos(2\pi x/\lambda) \), solution of the equation is,

$$C - C_0 = A' (\beta, t) \cos(2\pi x/\lambda)$$  \hspace{1cm} (A6)

where C0 is average composition, A' (β, t) is a function of time t and wave number β (= 2π/λ), with λ as the wave length), and A' (β, t) = A’ (β, 0) exp(R (β) t), with A’ (β) as component fluctuation amplitude, R (β) amplification factor, then two evolutionary equations can be obtained [51],

$$R (\beta) = -M \beta^2 \left( \frac{\partial^2 G}{\partial C^2} + 2\beta^2 K \right)$$  \hspace{1cm} (A7)

$$R (\lambda) = -M \frac{4\pi^2}{\lambda^2} \left( \frac{\partial^2 G}{\partial C^2} + \frac{8\pi^2 K}{\lambda^2} \right)$$  \hspace{1cm} (A8)

Only when R (λ) > 0, spinodal decomposition could proceed. Calculation shows that minimum wavelength \(\lambda_{\min}\) and maximum wavelength \(\lambda_{\max}\) meet the following relationship

$$\lambda_{\max} = \sqrt{2\lambda_{\min}} \hspace{1cm} [47],$$

$$\lambda^2_{\min} = -8\pi^2 K / \left( \frac{\partial^2 G}{\partial C^2} \right)$$  \hspace{1cm} (A9)

$$\lambda^2_{\max} = -16\pi^2 K / \left( \frac{\partial^2 G}{\partial C^2} \right)$$  \hspace{1cm} (A10)

Introduce unit interaction distance \(\psi\), \(\lambda_{\max}\) can also be presented as the following equation,

$$\frac{\lambda_{\max}}{\psi} = [C (1 - c)]^{1/2} [(T_s - T) / T_s]^{1/2}$$  \hspace{1cm} (A11)

where \(T_s\) is spinodal decomposition start temperature, \(T_c\) is melt point with composition of C. Under normal conditions, \(\lambda_{\max}\) is the finally wavelength of spinodal decomposition texture [49]. Another information observed from the equation is that \(\lambda_{\max}\) is influenced by numerical value of \(T_s - T\), and that means the higher \(\Delta T\) is, the smaller \(\lambda_{\max}\) will be.

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