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# Effect of heat treatment on microstructure and properties of Al<sub>0.5</sub>CoCrFeNi high entropy alloy fabricated by selective laser melting



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#### ABSTRACT

In this study, heat treatment as a post processing was used in order to improve the microstructures and mechanical properties of  $Al_{0.5}$ CoCrFeNi high entropy alloy (HEA), which fabricated by selective laser melting (SLM). Compared to the microstructure of SLM-ed  $Al_{0.5}$ CoCrFeNi HEA, the strengthening the weakening mechanisms of HEA at different heat treatment temperatures are figured out. Heated at 1073 K for 4 h, the SLMed  $Al_{0.5}$ CoCrFeNi HEA shows the 1419 MPa tensile strength. With increasing heat treatment temperature from 1073 K to 1673 K. The content of BCC phase decreases from 34.4% to 14.6%. The average size of BCC phase at grain boundaries increases from 0.497  $\mu$ m to 2.271  $\mu$ m, and the average size of BCC phase inside the grains increases from 0.037  $\mu$ m to 1.216  $\mu$ m. Moreover, dislocation network disappearance and recrystallization occur at 1173 K and 1373 K, respectively. The boundaries of the dislocation network, as the nucleation sites of precipitation, promote the formation of precipitated phases and form dislocation network wrapped by precipitated phases at 1073 K. The precipitated phases, and the dislocation density in the recrystallized grains change the morphology of the precipitated phases, and the aspect ratio of the BCC phases increases, which made the HEA still maintain a certain tensile strength at 1673 K.

# 1. Introduction

High entropy alloys (HEAs), have been developed in recent decades as a new type of alloy, which is contrary to the traditional alloy design concept. High entropy alloys are usually composed of four or more metallic elements, and the molar ratio of metal elements is adjusted to reduce the Gibbs free energy of the system and thus inhibit the production of intermetallic compounds. HEAs usually consist of single phase faced centered cubic (FCC), body centered cubic (BCC) or hexagonal close packed (HCP) structure. Owing to the unique design philosophy and basic effect, HEAs have the outstanding mechanical and functional properties, such as high strength, hardness, high temperature stability, wear and corrosion resistance, and excellent magnetic properties, which have great application prospects in aerospace, shipbuilding and other fields [1–4]. At present, HEAs are mainly fabricated by conventional casting, but this method has limitations of component segregation and shrinkage. Moreover, the secondary processing is required for HEAs to fabricate specific shapes, which increases costs in the field of industries. These problems have led to limitations in the industrial development of HEAs, so there is an urgent need to find a new forming method to prepare HEAs.

Selective laser melting (SLM) is a type of laser additive

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manufacturing technology. It is based on the principle of completely melting the metal powder in the selected area under the action of a high power energy laser beam, and metallurgically combining the melted powder to form high precision and high density metal parts [5,6]. SLM has an extremely fast cooling rate (about  $10^5$ – $10^6$  K/s), which can inhibit component segregation and the high near-net forming ability effectively avoids the waste of raw materials. The HEA fabricated by SLM has a finer microstructure and exhibit better mechanical properties compared to those obtained by other additive manufacturing. Therefore, SLM is considered suitable for the preparation of HEAS [5].

Optimizing the printing process can reduce the generation of defects, but this method can not effectively improve the microstructure of the sample [7-9]. Heat treatment is considered to be an effective way to improve the uneven microstructure and excessive residual stress of parts fabricated by SLM [10]. Recent studies have shown that the dislocation network, second phase and recrystallization of SLM-ed HEAs can be adjusted through appropriate heat treatment, and the mechanical properties of HEAs can be further improved, the effectiveness of the heat treatment has been confirmed in CoCrFeNi, AlCoCuFeNi, (FeCo-Ni)86Al7Ti7 HEA [11-13]. However, there are few systematic investigations into the effects of dislocation networks, second phases and recrystallization on the mechanical properties of SLM-ed HEAs. According to the recent studies, it is well-known that Al<sub>x</sub>CoCrFeNi is a typical high entropy alloy, its microstructure and mechanical properties have been widely studied [14-16]. Al<sub>0.5</sub>CoCrFeNi HEA has been successfully fabricated by SLM, and the HEA shows a good combination of strength and ductility [17].

This work systematically investigates the microstructural evolution of SLM-ed Al<sub>0.5</sub>CoCrFeNi HEA after heat treatment and explains in detail the strengthening and weakening mechanism of HEA after different heat treatment temperatures. It is mainly caused by the effects of dislocation network, second phase and recrystallization as well as the changes in mechanical properties caused by the interaction of the all three. Based on the microstructure of the dislocation network, second phase and recrystallization network, second phase and recrystallization for the dislocation network, second phase and recrystallization network, second phase and recrystallization network, second phase and recrystallization, this study proposes an effective strategy to optimize the mechanical properties of SLM-ed HEA, which will help to design high performance SLM-ed HEA.

# 2. Materials and methods

This study used atmospheric atomized Al<sub>0.5</sub>CoCrFeNi high entropy alloy powder. Table 1 shows the content of each element of the powder. Al<sub>0.5</sub>CoCrFeNi HEA was fabricated by SLM equipment. The dimensions of 260  $\times$  260  $\times$  25 mm 316 stainless steel as the substrate, and the substrate was preheated to 100 °C before forming. The SLM-fabricated parameters were selected based on the previous exploration, among them, the laser power, scanning pitch, layer thickness and scanning speed are 200 W, 90 µm, 40 µm and 0.8 m/s respectively, laser rotation 67° between each layer. Then, the HEAs were heat treated at 1073 K, 1173 K, 1273 K, 1373 K and 1673 K for 4 h and subsequently cooled down to the room temperature with the furnace. The tensile test was performed at room temperature with a strain rate of  $5 \times 10^{-4}$ /s, and the gauge dimension of dog bone-shaped tensile specimens is  $50\times6\times1.5$ mm. The microhardness and phase structure of the HEA were tested and analyzed by Vickers hardness tester and X-ray diffractometer, respectively. Among them, the microhardness test load was 9.807 N for 10 s, the scanning speed and range of X-ray diffraction were 4°/min and 30°-90°, respectively. Optical microscopy (OM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) characterize the microstructure of SLM-ed and heat-treated HEAs. In this study,

#### Table 1

 $\underline{ Chemical \ compositions} \ of \ the \ Al_{0.5} CoCrFeNi \ high \ entropy \ alloy \ powder \ (wt.\%).$ 

|      | -     | •     |       |       |
|------|-------|-------|-------|-------|
| Al   | Co    | Cr    | Fe    | Ni    |
| 5.85 | 24.24 | 21.31 | 23.75 | 24.85 |
|      |       |       |       |       |

the BCC phase was measured in the width direction and its content was calculated using ImageJ software.

#### 3. Experimental results

#### 3.1. Microstructure of SLM-ed HEA after heat treatment

From Fig. 1a, it can be observed that the microstructure of the SLMed Al<sub>0.5</sub>CoCrFeNi HEA shows a clear molten pool boundary. The HEA is mainly composed of columnar crystals, which penetrate the molten pool boundary and exhibit obvious epitaxial growth, this phenomenon is mainly related to the preferred orientation of grain and the temperature gradient along the deposition direction during the SLM forming process [18]. As the temperature increases, the molten pool boundary gradually disappears. When the temperature is 1073 K, only a small amount of molten pool boundary exists and the fine precipitate phase along the columnar grain boundary can be observed (Fig. 1b). At 1173 K and 1273 K, many fine precipitate phases can be observed inside the grain (Fig. 1c and d). At 1373 K, a small amount equiaxial grains are found inside the HEA (The red arrow in Fig. 1e). When the temperature rises to 1673 K, large-sized equiaxed crystals are found in the interior of the HEA and the precipitate phase can be clearly observed along the grain boundary. The X-ray diffraction results show that the SLM-ed HEA exhibits a single-phase FCC microstructure while the heat-treated HEA is the FCC + BCC duplex structure (as shown in Fig. 2).

The SEM image of the typical substructure of the SLM-ed HEA is shown in Fig. 3a. Several homogenously distributed BCC precipitates are found in the matrix of the HEAs after heat treatment (as shown in Fig. 3b–f). The plate-shaped BCC phase is found along the grain boundary, and oval or needle-shaped BCC phase is found in grains. With increasing heat treatment temperature, the size of the BCC phase inside the grains and at the grain boundary gradually increases, and the oval BCC phase gradually transforms into needle-shaped BCC phase (see Fig. 3 for details). Fig. 4 shows the SEM-BSE image of the HEA at 1073 K. At this temperature, fine BCC precipitates are found inside the grains of the HEA. In addition, BCC phases precipitate along the substructure boundaries are found inside the grain (Fig. 4a), and the  $\sigma$  phase is also found between the BCC precipitates and the matrix that is similar with the results reported in reference [19] (Fig. 4b).

As shown in Fig. 5, columnar and cellular substructures can be clearly distinguished in the grains of the SLM-ed HEA. The changes of substructural morphology depend on the direction of observation [11], and some researchers have also referred to the structure as a "dislocation network" [20]. There are a large number of dislocations inside the HEAs, which is determined by the rapid melting and cooling characteristics of SLM process (Fig. 5). In addition, a small amount of the precipitate phases is found at the individual dislocation network boundary, and the elemental analysis shows that Al–Ni elements are enriched at the precipitate phases (Fig. 6).

TEM results of the SLM-ed Al<sub>0.5</sub>CoCrFeNi HEA before and after heat treatment are displayed in Fig. 7. The clear dislocation network structure is found in the SLM-ed HEA, and elemental analysis of the dislocation network shows that the Al and Ni elements are enriched at the dislocation network boundary (Figs. 6 and 8). The diffraction spot results show that the matrix of SLM-ed HEA is FCC structure, while the Al-Ni precipitate phase is BCC structure (Fig. 7h, l). At 1073 K, a large amount of BCC phases are found at the boundary and inside the dislocation network, and the Cr-rich  $\sigma$ -phase is attached to the BCC phase (Fig. 7e-g and Fig. 9). Meanwhile, a set of inclined dislocations, which possess a certain angle to the boundary of the dislocation network (Fig. 7g). At 1173 K, the dislocation network and the  $\sigma$ -phase disappear (Fig. 7i-k and 10), only the BCC phase is visible in the HEA, and many dislocations can be observed around the BCC precipitates. Compared with the SLM-ed HEAs, the density of dislocations in the HEA decreases after heat treatment.



Fig.1. OM images of (a) SLM-ed HEAs and heat treatment HEAs at different temperatures for 4 h, (b)1073 K, (c)1173 K, (d)1273 K, (e)1373 K, (f)1673 K.





#### 3.2. Mechanical properties of SLM-ed HEA after heat treatment

Compared with the SLM-ed HEA, the tensile strength and yield strength of the HEA after 1073 K heat treatment increased by 563 MPa and 339 MPa, respectively, but the elongation decreased by 13.7% (As shown in Fig. 11a). When the heat treatment temperature is 1073 K–1373 K, with increasing temperature, the strength of the HEAs decrease, but the elongation increase. For the 1173 K–1273 K heat treated HEAs, the mechanical properties of the HEA do not change significantly. As the heat treatment temperature reaches 1373 K, the HEA exhibits the highest elongation. After the heat treatment at 1673 K, the tensile strength and elongation of the HEA are reduced. Fig. 11b shows the average tensile strength and elongation of HEA after printing and heat treatment. The Vickers hardness testing results of the HEAs show that the variation of hardness change is consistent with the change in tensile strength (Fig. 12). The evolution of mechanical properties are dependent upon the precipitate phase, dislocation network,

recrystallization and their interactions, as discussed in Section 4.4.

Fig. 13 shows the fracture characteristics of SLM-ed HEA with and without heat treatment. The SLM-ed HEA fracture surface has dimples and cleavage steps, exhibiting mixed tough-brittle fracture characteristics (Fig. 13a). At 1073 K, intergranular cracks appear on the fracture surface of HEA. After heat treatment at this temperature, the size of the precipitated phase at the grain boundaries of the HEA is larger and cracks are more likely to extend along the grain boundaries. At 1173 K–1373 K, many dimples on the fracture surface are ductile fractures. At 1673 K, continuous coarse BCC precipitates appear at the grain boundary of HEA. During the deformation process, the precipitated phase attached to the grain boundary obstructed the dislocation movement, and a large number of dislocations accumulated at the grain boundary, leading to the crack extension along the grain boundary. It shows obvious rock candy-like feature on the fracture surface.

# 4. Discussion

#### 4.1. The evolution of dislocation network

The dislocation network is a typical structure in the HEAs fabricated by SLM, which exists in the grain interior as columnar and cellular. It has been reported that the dislocation networks were found in IN625, IN718, Hastelloy X, 316L and Al-Si alloy fabricated by SLM [21-25]. In our work, the SLM-ed Al<sub>0.5</sub>CoCrFeNi HEA exhibit clear substructures (Fig. 5), and this structure is absent in Al<sub>0.5</sub>CoCrFeNi HEA fabricated by other technologies. However, the mechanism of the formation of this substructure is not clear, mainly because the solidification process could not be further observed and analyzed effectively due to the melt pool size and cooling rate during the forming process. Lin et al. [11] reported that the dislocation network structure consisted of many Geometrically Necessary Dislocations (GNDs), and in the process of SLM, the columnar crystals in the molten pool grow under the condition of rapid cooling until they contact with each other. The columnar crystals in contact with each other are deformed by stress along the width due to shrinkage. GND is generated in deformed grains in order to inhibit further deformation of the grains and to maintain continuity between the crystal lattices. It divides the grains into many small substructures, thus forming dislocation networks. Dislocation network is a major strengthening mechanism in SLM-ed HEA, which maintains the continuity of the crystal lattice and hinders the movement of other dislocations while not moving itself



Fig.3. SEM images of (a) SLM-ed HEAs and heat treatment HEAs at different temperatures for 4 h, (b)1073 K, (c)1173 K, (d)1273 K, (e)1373 K, (f)1673 K.



Fig.4. SEM-BSE images of HEA:(a) heat treatment at 1073K for 4h and (b) the magnified patterns of the black rectangle area in (a).



Fig.5. TEM images of SLM-ed HEA: (a) cellular substructure, (b) columnar substructure.



Fig.6. Elemental mappings of the precipitation at dislocation networks.



Fig.7. TEM images of (a-c) SLM-ed HEAs and heat treatment HEAs at different temperatures for 4 h, (d-f)1073 K, (g-i)1173 K.

under a driving force. Movable dislocations are plugged at the dislocation network, producing a significant strengthening effect on SLM-ed HEA [11]. With increasing heat treatment temperature, the dislocation network gradually annihilates (Fig. 7). This reduces the formation of micropores near the dislocation network due to dislocation plugging during deformation, which delays fracture and increases the total strain of HEA [11]. In previous studies [26,27], grain boundaries annihilation and dislocation reaction have been extensively studied using simulation methods such as phase field crystal (PFC). In order to reduce the distortion strain energy, the dislocation network boundaries undergo a low-angle rotation by the motion of dislocations (Fig. 7g) as well as interact with other dislocations, resulting in annihilation. This



Fig.8. Elemental mappings of dislocation network in SLM-ed HEA.



Fig.9. Elemental mappings of the HEA at 1073 K.

phenomenon was also observed in 316L stainless steel, IN718, and other HEAs [10,11,28]. In our current work, it is confirmed that the dislocation network of SLM-ed Al<sub>0.5</sub>CoCrFeNi HEA exhibits a tendency to annihilate at 1073 K, and above 1173 K the dislocation network disappears completely (Fig. 7g). The dislocation network structure changes significantly affect the mechanical properties of the samples. During the deformation process, the dislocation network hinders the movement of removable dislocations and produces a significant strengthening effect on the sample. Meanwhile, the disappearance of dislocation networks reduces the formation of micropores and increases the plasticity of the SLM-ed HEA.

# 4.2. Recrystallization

The presence of a large number of dislocations inside SLM-ed HEA is mainly due to the change of material vacancy energy before and after powder solidification, the vacancy energy of the solid is higher than that in the liquid molten pool. The vacancies in molten pool should be filled during the solidification process [11], however, the rapid cooling characteristics of SLM and the sluggish diffusion effect of HEAs lead to numerous of vacancies inside the SLM-ed HEA, which are further translated into dislocations [29,30]. Therefore, the structure of the SLM-ed HEAs is similar to that of the work-hardened sample after deformation, and both of them have a high dislocation density (Fig. 5). This provides conditions for recrystallization during the subsequent heat treatment. The grain morphology of HEA is changed after the heat treatment at 1373 K. Many fine equiaxed crystals appears inside the HEA (Fig. 1e), the partial recrystallization of SLM-ed Al<sub>0.5</sub>CoCrFeNi HEA occurs at this temperature. With increasing temperature, the proportion of recrystallized grains increases. When the temperature is 1673 K, all the columnar crystals inside the HEA are converted to equiaxial crystals, and the equiaxial crystals have been coarsened and grown at this



Fig.10. Elemental mappings of the HEA at 1173 K.



Fig.11. Tensile properties of the HEAs (a) stress-strain curves (b) Average tensile strength and elongation.



Fig.12. Average microhardness of the HEAs heat treated at different temperatures.

temperature (Fig. 1f).

#### 4.3. The evolution of precipitate phase

It has been reported that the traditional casting Al<sub>0.5</sub>CoCrFeNi HEA has a duplex FCC + BCC structure [19,31]. While the BCC phase is suppressed under the rapid cooling condition, and the SLM-ed Al<sub>0.5</sub>CoCrFeNi HEA exhibits a single phase FCC structure [17]. However, in our current work, trace BCC phases exist inside the SLM-ed HEA, and they are distributed at some dislocation network boundaries (Fig. 6), which may be related to the thermal cycling during the SLM process. During the layer-by-layer processing of SLM, the thermal input from the subsequent processed layers leads to elemental segregation in the formed part, and BCC phase is formed at the boundary of the dislocation network. During the heat treatment, elements are redistributed inside the HEA, which leads to several BCC phases found in FCC matrix of the HEA after the heat treatment. The size of BCC phase increases with increasing heat treatment temperature (Figs. 14 and 15), because higher temperature will promote the diffusion of elements [12]. Elemental analysis of the precipitation shows that the BCC precipitate is an Al-Ni rich phase (Fig. 10). It can be explained using the mixing enthalpy of alloy elements. It is well known that the mixing enthalpy of Al and Fe, Co, Cr elements are -11 kJ/mol, -19 kJ/mol, and 10 kJ/mol, respectively, while the mixing enthalpy of Al and Ni elements is -22



Fig.13. Fracture surface of (a) SLM-ed and heat treatment HEAs at different temperatures for 4 h, (b)1073 K, (c)1173 K, (d)1273 K, (e)1373 K, (f)1673 K.



Fig.14. The size distribution of precipitation along grain boundaries after different heat treatment temperature: (a)1073 K, (b)1173 K, (c)1273 K, (d)1373 K, (e) 1673 K.

kJ/mol [32]. It can be indicated that Al and Ni have high binding energy, and segregation will occur during heat treatment to form BCC phase. The proportions of BCC phases in the matrix at different heat treatment temperatures are listed in Table 2, which are in good agreement with the relevant thermodynamic calculations given by Aizenshtein et al. [19]. As the heat treatment temperature increases, some precipitates dissolve and the BCC phase content in HEA decreases. Aizenshtein et al. [19] validated the effectiveness of the thermodynamic model through experiments, and obtained the phase composition and content of  $Al_{0.5}$ CoCrFeNi HEA after heat treatment at different temperatures through thermodynamic calculations. The results show that the phase composition of  $Al_{0.5}$ CoCrFeNi HEA is related to the heat treatment temperature, the BCC phase was partially dissolved. They also predicted the temperature

range of 873 K–1133 K for the presence of  $\sigma$  phase in HEA by thermodynamic modeling. The experimental results showed that the  $\sigma$  phase precipitated in the conventionally cast Al<sub>0.5</sub>CoCrFeNi HEA after the 1073 K heat treatment. The  $\sigma$ -phase was also found in the SLM-ed HEA after heat treatment of 1073 K in our present work (Fig. 9).

As shown in Fig. 7e-g, the dislocation network and precipitation are found in the HEA at 1073 K. A large number of precipitated phases is formed at the boundaries of the dislocation network, forming a dislocation network wrapped by the precipitate phase. On the one hand, the boundary of the dislocation network is in a high energy and unstable state, which is easier to form precipitate phase. On the other hand, element Al has a large atomic radius and in order to reduce the distortion energy of the system, Al and Ni are separated at the boundary of the dislocation network [13] (Fig. 8). Therefore, the dislocation network



Fig.15. The size distribution of precipitation inside grains after different heat treatment temperature: (a)1073 K, (b)1173 K, (c)1273 K, (d)1373 K, (e)1673 K.

 Table 2

 The proportion of BCC phase in the HEAs at different heat treatment temperatures.

| Temperature,K | BCC,%  |
|---------------|--------|
| 1073          | 34.354 |
| 1173          | 21.474 |
| 1273          | 20.655 |
| 1373          | 18.265 |
| 1673          | 14.62  |

promotes the formation of the precipitate phase. With increasing heat treatment temperature, the dislocation density of the HEA decreases (Fig. 7), such that the change of dislocation density leads to the variation of the morphology of the precipitated phase. With decreasing dislocation density around the BCC phase, the atomic diffusion capacity decreases, and the BCC phase grows according to the preferred orientation [33]. The morphology gradually changes from oval to long strips, and the average aspect ratio of the BCC phase increases (Fig. 16). When the temperatures are 1373 K and 1673 K, the HEAs are partially recrystallized and completely recrystallized, respectively. The dislocation density of the recrystallized grains decreases, and the average aspect ratio of the BCC phase increases significantly. Overall, the dislocation network



Fig.16. The aspect ratio distribution of the BCC phase inside the grains after different heat treatment temperature: (a)1073 K, (b)1173 K, (c)1273 K, (d)1373 K, (e) 1673 K.

promotes the formation of the precipitate phase, and the occurrence of recrystallization helps to change the morphology of precipitated phase. The content and aspect ratio of the BCC phase will change the mechanical properties of SLM-ed HEA. However, in our study, the dislocation network disappearance and recrystallization occur at 1173 K and 1373 K, respectively. The dislocation network is completely annihilated when recrystallization occur inside the HEA. The interaction between dislocation network, recrystallization, and precipitated phase can not be studied.

#### 4.4. Strengthening and softening mechanism

Compared with the traditional casting Al<sub>0-5</sub>CoCrFeNi HEA, the dislocation network and higher dislocation density usually enable the SLM-ed HEAs to show higher strength. In order not to break the continuity between lattices, the dislocation network does not move under the action of external forces. During the deformation process, the dislocation network hinders the movement of other dislocations that are plugged in the dislocation network and hinder subsequent dislocations [11]. Therefore, the dislocation network is an important way to reinforce the SLM-ed HEAs.

Heat treatment provides an opportunity for vacancies to be refilled, reducing the dislocation density and softening the samples. In our current work, the dislocation density of HEA decreases with increasing heat treatment temperature (Fig. 7), but the mechanical properties of the SLM-ed HEA change significantly after the heat treatment, which can not be explained by a single heat treatment softening mechanism. In this work, it indicates that heat treatment has an effect on dislocation networks, precipitate phases and recrystallization. At the same time, the dislocation networks and recrystallization interact with the precipitation, which leads to more complex changes in mechanical properties. However, different heat treatment temperatures determine the strengthening the weakening mechanism of the HEA. At 1073 K, dislocation network, hard and brittle BCC and  $\sigma$ -phase precipitation are present inside the HEA. The dislocation network boundary serves as the nucleation site of the precipitated phases and promotes the formation of the precipitated phases. At this temperature, a large number of precipitated phases are formed at the boundaries of the dislocation network, forming a dislocation network wrapped by the precipitated phases. The percentage of BCC phase in HEA is 34.4%, in which the average size of grain boundary and grain internal precipitated phase is 0.497 µm and 0.037 µm, respectively. During the deformation process, the dislocation network shape does not change. Both the dislocation network boundary and the fine hard and brittle precipitated phase strongly obstruct the dislocation motion. The dislocations are heavily plugged at the dislocation network boundary and precipitated phase. The strength of SLMed HEA is significantly enhanced by both dislocation network strengthening and precipitation strengthening. Compared with SLM-ed HEA, the tensile strength of HEA is increased by 65.8% after heat treatment at this temperature. However, the accumulation of a large number of dislocations at dislocation network boundary and precipitated phase under the forces can lead to the formation of micropores. Compare to SLM-ed HEA, the HEA heat treated at 1073 K is prone to premature fracture. During the heat treatment at 1073 K, the dislocation network promotes the formation of the precipitated phase, forming a dislocation network wrapped by the precipitated phases. Therefore, hard and brittle precipitation plays a dominant role in the strengthening of HEA after heat treatment at this temperature. At 1173 K-1273 K, the dislocation network and  $\sigma$ -phase of HEA disappear. With increasing heat treatment temperature, the content of BCC precipitate phases decreases and the size increases. Compared with 1073 K, the content of BCC phases decreases by 12.4% and 13.2% after heat treatment at 1173 K and 1273 K, respectively. The BCC phase size inside the grains increases by 0.15 µm and 0.36 µm, and the BCC phase size at the grain boundaries increases by 0.07 µm and 0.26 µm, respectively. It results in a weakening

of the precipitation strengthening effect of the BCC phases, while there is no dislocation network and  $\sigma$  phase strengthening at this stage. Compared with the HEA treated at 1073 K, the HEA strength at this stage is significantly reduce. However, the annihilation of the dislocation network and the change of the precipitate phase delay the formation of micropores during deformation and increase the total strain at fracture. Due to the disappearance of dislocation network and  $\sigma$ -phase, the change of HEA mechanical properties at this stage mainly depends on the change of BCC phase. As the temperature increases from 1173 K to 1273 K, the content of BCC phase decreases slightly (0.8%). The average size of precipitated phase increases by 0.16  $\mu$ m and 0.21  $\mu$ m for grain boundary precipitated phase and grain internal precipitated phase, respectively. The content of BCC change little, and the HEA strength decrease slightly after 1273 K heat treatment. At 1373 K, fine equiaxed crystals appear inside the HEA and partial recrystallization occurs. The dislocation density inside the recrystallized grains is lower, and the dislocation strengthening effect is weakened. At the same time, the content of BCC phase at this temperature is 18.3%. Compared with the HEA treated at 1273 K, the BCC content is reduced by 2.4%. The average size of precipitated phase increases by 0.16 µm and 0.02 µm for grain boundary precipitated phase and grain internal precipitated phase, respectively. The precipitation strengthening effect is weakened. The elongation of HEA increases to 24% due to recrystallization softening and reduced precipitation strengthening. The change of BCC content is small, and the weakening effect of precipitation strengthening is limited. Therefore, recrystallization after heat treatment at this temperature plays a dominant role in the softening of HEA. The dislocation density of HEA decreases after recrystallization, and the average aspect ratio of the BCC phase inside the grains increases by 35.3%. It results in the strength of HEA after heat treatment at this temperature being essentially the same as that of HEA after heat treatment at 1273 K [33]. Compared to 1373 K heat treatment, the HEA is completely recrystallized and the recrystallized grains grow after 1673 K heat treatment. The growth of recrystallized grains reduces the number of grains per unit volume of HEA. The number of grains that can participate in deformation under the external forces is reduced. The deformation can not be dispersed into more grains, and plastic deformation is not uniform, producing a larger stress concentration. Therefore, the elongation of HEA is reduced after 1673 K heat treatment. At the same time, the coarse hard and brittle BCC phase at grain boundary is prone to cracking during deformation, and the crack expand along the grain boundary, leading to fracture of HEA along the grain boundary. The total strain of HEA decreases. Compared to 1373 K, the BCC phase content of HEA decreases and the size increases after heat treatment at 1673 K. Also, the dislocation density of HEA decreases after recrystallization. The weakening effect of precipitation strengthening and dislocation strengthening leads to the reduction of the strength of HEA after 1673 K heat treatment. However, complete recrystallization causes a sharp decrease in the dislocation density inside the HEA grains, which leads to an increase in the average aspect ratio of the BCC phase inside the grains to 5.62. which make the HEA still maintain a certain strength [33].

Based on the above analysis and discussion, the schematic diagram of the microstructure evolution of the SLM-ed Al<sub>0.5</sub>CoCrFeNi HEA under different heat treatment temperatures can be obtained and shown in Fig. 17. The dislocation networks are distributed inside the grains of the SLM-ed HEA, and a small amount of BCC phases are found at the dislocation network boundaries. At 1073 K, a large amount of precipitations are found at the boundaries and inside the dislocation networks. The dislocation network boundaries undergo low angle rotation, showing a tendency to disappear. When the temperature is 1173 K–1273 K, the dislocation networks and  $\sigma$ -phase disappear, the precipitate phase size increases and the content decreases. When the temperature is 1373 K, the precipitated phase transition trend remains unchanged, and the HEA is partially recrystallized. At 1673 K, the HEA is completely recrystallized and the grains are roughened.



Fig.17. Schematic diagram for microstructure evolution of SLM-ed Al<sub>0.5</sub>CoCrFeNi HEA at different heat treatment temperatures.

#### 5. Conclusion

Heat treatment has a significant effect on the microstructure and mechanical properties of Al<sub>0.5</sub>CoCrFeNi HEA fabricated by SLM. With increasing heat treatment temperature, the content of BCC precipitate phases decreases and the size increases. At 1073 K, the dislocation network wrapped by the precipitated phase and the precipitation inside the dislocation network have a significant strengthening effect to the HEA. At 1173 K–1273 K, the dislocation network and  $\sigma$ -phase disappear, and the mechanical properties of the HEA at this stage are mainly affected by the changes of the precipitation. The recrystallization is found in the HEA at temperature above 1373 K.

The dislocation network boundaries serve as the nucleation sites of the precipitation to promote the formation of the precipitate phases, and form a dislocation network wrapped by the precipitate phases. When the recrystallization and precipitated phases coexist, the low dislocation density inside the recrystallization grains causes the morphology of the precipitate phases to change. At 1373 K and 1673 K, the aspect ratio of the BCC phase increase significantly. It is worth noting that, the dislocation network annihilation temperature of HEAs is different, and the dislocation network of the  $Al_{0.5}$ CoCrFeNi HEA fabricated by SLM has been annihilated before recrystallization. There is no coexistence state of dislocation network and recrystallization on the precipitate phase is only discussed in this study. The interaction between dislocation network, precipitate phase and recrystallization and the influence on mechanical properties will be our future research direction.

#### CRediT authorship contribution statement

Yuhui Du: Conceptualization, Investigation, Methodology, Formal analysis, Writing – original draft. Chunhuan Guo: Project administration, Writing – review & editing. Fengchun Jiang: Resources, Supervision. Yanchun Li: Visualization. Xiaojing Sun: Visualization. Qianfei Sun: Visualization. Hexin Zhang: Visualization. Tao Dong: Visualization. Sergey Konovalov: Visualization.

#### Declaration of competing interest

No potential conflict of interest was reported by the authors.

# Data availability

Data will be made available on request.

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