Effect of heat treatment on the microstructure and hardness of Al$_{0.3}$CoCrFeNi high entropy alloy

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Abstract-In this study, the cold-rolled Al$_{0.3}$CoCrFeNi high entropy alloys were heat treated at 900℃ for 30min and 1050℃ for 20min, respectively, to investigate the effect of heat treatment on the microstructure of the alloy. The results showed that grain refinement occurred in the 900℃/30min annealed sample, while remarkable equiaxial grains and twins appeared in the 1050℃/20min annealed sample. The hardness of samples showed a decrease trend following: as-rolled sample, 900℃/30min annealed sample, and 1050℃/20min annealed sample, which can be attributed to the dislocation elimination caused by recovery and recrystallization.

1. Introduction

The high entropy alloy has deviated the traditional design concept that the alloy is dominated by one or two elements and supplemented by a small number of other elements [1]. In recent years, high-entropy alloys have become a hot spot in the field of metal materials research because of their novel design concept, broad design space and unique performance characteristics [2]. The multi-principal components of high entropy alloys determine their unique atomic structure characteristics, which in turn affect the activation of different deformation mechanisms during the deformation process. The controllable microstructure often makes the high entropy alloy have excellent strength and plastic deformation ability [3].

In general, the hardness of BCC phase is higher than that of FCC phase, and the microstructure of high entropy alloy can be regulated by heat treatment at specific temperature and time, which also provides convenience for the study of hardness of high entropy alloy[4]. For example, in high entropy alloys, different molar ratios of certain elements will affect the phase composition of the material. The molar ratio of Fe element is the stabilizer of FCC phase in the alloy. With the increase of the molar ratio of Fe element, the difference of atomic size of different elements decreases, which promotes the formation of FCC phase and the disappearance of L12 precipitation, and then the hardness value of the material decreases [5]. The increase of molar ratio of Al will change the composition of the alloy phase with high entropy, and the hardness value of the alloy and the molar ratio of Al are found to conform to the Hall-Petch linear relationship [6]. TiAlFeCoNi high entropy alloy with super high hardness can be obtained by introducing nano-sized grains and high density dislocation through high pressure torsional treatment [7].

The high configurational entropy mixing of high entropy alloys is beneficial to the formation of solid solution rather than brittle intermetallic phase at high temperature. Therefore, different heat
treatment processes can regulate grain size and precipitate phase to realize fine grain strengthening and second phase strengthening [8, 9].

In this paper, the effects of different heat treatments on the microstructure and hardness of Al0.3CoCrFeNi high entropy alloy were studied through two different heat treatments on the cold-rolled Al0.3CoCrFeNi high entropy alloy.

2. Material and Experiments

The samples of Al0.3CoCrFeNi high entropy alloy are composed of Co, Cr, Fe, Ni and Al. In the high-purity argon atmosphere with titanium absorbing oxygen, the arc melting method was adopted for the melting. In order to ensure the uniform mixing of elements, each ingot was turned and melted at least 4 times. After the melting, the cold-rolled samples were kept in muffle furnace at 1050℃ for 20 minutes (CRS1050) and 900℃ for 30 minutes (CRS900), as shown in Fig. 1.

The cold-rolled samples were polished with 360#, 600#, 800#, 1500# and 2000# sandpaper, and then mechanically polished with diamond polishing fluid with particle sizes of 9 micron, 3 micron and 1 micron. Afterwards the cold-rolled samples were immersed in aqua regia and subjected to chemical corrosion to obtain the microstructure of the cold-rolled Al0.3CoCrFeNi high-entropy alloy. Firstly, the CRS1050 and CRS900 were polished with sandpaper, the diamond polishing solution was mechanically polished, and the 0.05 microns SiO2 polishing solution was vibrated to achieve the surface quality of the sample to achieve EBSD effect. Then, the EBSD was photographed by scanning electron microscope. Finally the grain orientation and texture of Al0.3CoCrFeNi high entropy alloy were obtained.

![Fig. 1 The heat treatment processes of high entropy alloy.](image)

3. Results and Discussion

It is seen from Fig. 2 that the grains of cold-rolled Al0.3CoCrFeNi high-entropy alloy are elongated along the rolling direction (vertical direction) and appear as long strips. In Fig. 2(b), a large number of grain boundaries perpendicular to the rolling direction (TD) are distributed inside the grain. The Vickers hardness of cold rolled Al0.3CoCrFeNi high entropy alloy was tested, and the average hardness value was 375.74(±17.07)HV. As can be seen from Fig. 3, the crystal structure of cold-rolled Al0.3CoCrFeNi high entropy alloy is single-phase FCC structure.
Fig. 2 Microstructure of Al\textsubscript{0.3}CoCrFeNi high entropy alloy after cold rolling: (a) low magnification; (b) high magnification

Fig. 3 The X-ray diffraction (XRD) of Al\textsubscript{0.3}CoCrFeNi high entropy alloy in cold rolled state. After annealing at 900°C, the microstructure of cold-rolled Al\textsubscript{0.3}CoCrFeNi high-entropy alloy is shown in Fig. 4. Fig. 4(a) shows that the CRS900 sample has equiaxed grains and the average grain size is about 2 microns. As shown in Fig. 4(b), a mass of granular precipitates are distributed in CRS900, and the distribution is relatively uniform. The XRD results show that the granular precipitated phase is BCC structure named B2 precipitation\textsuperscript{[10]}. Granular B2 precipitation is only several hundred nanometers in size and embedded in the grains. The average Vickers hardness of CRS900 is measured to be 270.28(±3.05) HV, and the Vickers hardness of CRS900 decreases significantly compared with that of cold-rolled Al\textsubscript{0.3}CoCrFeNi. The grain of cold-rolled Al\textsubscript{0.3}CoCrFeNi high-entropy alloy has been refined after heat treatment at 900°C for 30 min. However, the improvement of the hardness due to the grain refinement is not enough to offset the decrease of the hardness because of the decrease of dislocation density caused by the recovery recrystallization\textsuperscript{[11-13]}. It can be seen from Fig. 4(c) that there is only a small amount of deformation inside the CRS900 grains, reflecting the low dislocation density of CRS900 sample.
Fig. 4 Microstructure of Al$_{0.3}$CoCrFeNi high entropy alloy after heat treatment at 900°C for 30min (CRS900). (a) The Inverse Pole Figure(IPF) map; (b) Image Quality(IQ) +phase map; (c) Kernel Average Misorientation (KAM) map; (d) The distribution of high-angle boundary and low-angle boundary map.

After annealing at 1050°C for 20min (CRS1050), the average grain size of the cold-rolled Al$_{0.3}$CoCrFeNi alloy is about 46.3 microns, compared with that of 900°C for 30min. CRS1050 exhibits a typical heterogeneous structure, with homogeneous grain distribution and a mass of annealing twins. As can be seen from Fig. 5(b), CRS1050 is a single-phase organization with FCC structure. The average Vickers hardness of CRS100 is 141.86(±5.97) HV, while the Vickers hardness of CRS1050 is much lower than that of CRS900, which is speculated to be due to two main reasons. The degree of recrystallization of CRS1050 is higher than that of CRS900, and the dislocation density is lower. The grain size of CRS900 is much smaller than that of CRS1050. According to the above, the grain boundary strengthening effect of CRS900 is stronger than that of CRS1050, and the precipitation of B2 phase in CRS900 exists. Fig. 5(d) shows that the length of high-angle crystal boundaries and low-angle boundary per unit area of CRS1050 are much smaller than that of CRS900. In addition, the ratio of the length of the low-angle boundary to the length of the high-angle crystal boundaries in CRS1050 is higher than that in CRS900.
Fig. 5 Microstructure of Al0.3CoCrFeNi high entropy alloy after heat treatment at 1050℃ for 20min. 
(a) The Inverse Pole Figure(IPF) map of CRS1050. (b) Image Quality(IQ) +phase map of CRS900. 
(d) The distribution of high-angle boundary and low-angle boundary map of CRS1050.

It is shown in the pole figure (Fig. 6) that the texture intensity of CRS900 is higher than that of CRS1050, indicating the recrystallization and recovery effect of CRS1050 is stronger than that of CRS900. After annealing at 1050℃ for 20min, the deformation texture intensity of cold-rolled Al0.3CoCrFeNi high entropy alloy reduced remarkably, and there was almost no preferred orientation. Fig. 7 shows the grain size distribution of CRS900 and CRS1050 of Al0.3CoCrFeNi high entropy alloy after two different heat treatments. The grain size of CRS900 is concentrated between 2 microns and 8 microns. While the grain size of CRS1050 is mainly between 20 micron and 80 micron. Thus, for the cold-rolled high entropy alloy Al0.3CoCrFeNi, sufficient recrystallization does not occur at 900℃, while sufficient recrystallization has occurred at 1050℃. It is speculated that there is a suitable temperature between 1050℃ and 900℃ that can fully recrystallize the cold rolled high entropy alloy.
Fig. 6 The pole figure Al0.3CoCrFeNi high entropy alloy after 900℃/30min heat treatment and 1050/20min heat treatment. (a) The {001} polar figure of CRS900. (b) The {111} polar figure of CRS900. (c) The {101} polar figure of CRS900. (d) The {001} polar figure of CRS1050. (e) The {111} polar figure of CRS1050. (f) The {101} polar figure of CRS1050.

Fig. 7 The grain size distribution of Al0.3CoCrFeNi high entropy alloy after heat treatment at 900℃/30min and 1050/20min.

Figure 8 shows that the Vickers hardness value of Al0.3CoCrFeNi high entropy alloy decreases significantly as the annealing temperature increases. It indicates that the degree of recovery and recrystallization of Al0.3CoCrFeNi high entropy alloy increased, and the dislocation density of the material decreased, resulting in the decrease of the hardness value of the material. In addition, the hardness of CRS1050 decreased evidently compared with that of CRS900, which may be related to the effects of recrystallization and grain growth [9].
4. Conclusion
In this work, the effects of two typical heat treatments on the microstructure of the Al$_{0.3}$CoCrFeNi high entropy alloy were studied. The following conclusions have been obtained:

(1) After heat treatment at 900°C for 30min, significant grain refinement occurred and granular B2 precipitates were formed in the Al$_{0.3}$CoCrFeNi HEA.

(2) The hardness of Al$_{0.3}$CoCrFeNi HEA after 900°C-30min annealing (CRS900) is lower than that of as-rolled Al$_{0.3}$CoCrFeNi high entropy alloy. Although CRS900 had fine grain and precipitates acting as strengthening contribution, the decrease of strain hardening led to the decrease of hardness after annealing.

(3) After the annealing at 1050°C for 20min (CRS1050), the HEA exhibited much larger grain size than that of CRS900, corresponding to a lower hardness than that of CRS900. And the grain boundary length per unit area of CRS1050 is also significantly lower than that of CRS900. The pole figure of CRS1050 remained similar distribution, but the texture intensity decreased.

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