

# Effect of Microstructures and Mechanical Properties of Large Deformation High Entropy Alloy CoCrCuFeNi in Semi-solid Isothermal Heat Treatment

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## Abstract:

The semi-solid slurries of the CoCrCuFeNi high entropy alloy (HEA) were fabricated through the recrystallization and partial melting (RAP) process by cold-rolling and partial remelting. The temperature range of the semi-solid region and the relationship between the liquid fraction and the temperature were determined by the differential scanning calorimetry (DSC) curve. The effect of isothermal temperature and holding time on the evolution of the microstructure and mechanical properties of the rolled samples was analyzed. The results show that the microstructure was significantly deformed, and the tensile strength has been increased by 107% after 63% rolling deformation of the CoCrCuFeNi high entropy alloy (HEA). The high-entropy alloy after cold rolling was maintained at 1150 and 1300 °C for 20, 30, 60, and 120 minutes respectively, the plasticity has been improved compared with the rolled high entropy alloy. The optimal plasticity was reached 13.7% and 7.9% at 1150 °C and 1300°C for 30 minutes, respectively. After semi-solid isothermal heat treatment, the grain morphology changed from dendritic of as-cast or rolled to spherulite and the grain size increased significantly with time and the holding temperature increased.

**Keywords:** high entropy alloy; plastic deformation; semi-solid isothermal treatment; tensile strength; microstructure

## 1. Introduction

As a new alloy design concept, high-entropy alloy (HEA) has attracted much attention of many researchers in recent years. Different from the traditional concept of single-element based alloy, HEAs are the multi-component alloys with equimolar or near-equimolar compositions<sup>[1,2]</sup>. Therefore, high-entropy alloy is also known as multi-principal component high entropy alloy. Huang et al.<sup>[3]</sup> have prepared high entropy alloy AlCoCrCu<sub>0.5</sub>NiFe on single crystal silicon and glass by magnetron sputtering, which expanded the application prospect of high entropy alloy in terms of oxide film. Chen et al.<sup>[4]</sup> manufactured Al<sub>0.25</sub>CoCrFe<sub>1.25</sub>Ni<sub>1.25</sub> HEA coating on 45 steel surface by laser cladding, the results show that the surface hardness of cladding layer can reach 3.2 times of 45 steel due to the mutual solubility of high entropy alloy elements, the solution strengthening effect is produced. Qiu Jingwen, Fu Zhengfan<sup>[5]</sup> et al. prepared high entropy alloy reinforced AZ91D composite by laser cladding, which greatly

improved the hardness and wear resistance of magnesium alloy, and better applied in aerospace, chemical industry, vehicles and biomedical fields. Therefore, HEA was regarded as a promising structural material. In order to further improve the mechanical properties of HEA, many researchers used spark plasma sintering<sup>[6]</sup>, high-pressure torsion<sup>[7]</sup> and equal channel angular extrusion<sup>[8]</sup> to obtain high-strength HEA.

The semi-solid metal process (SSM), as the most promising material-forming process in the 21st century, combined with the advantages of solidification and plastic processing, such as the good flowing ability, low resistance to deformation, and easy formation of complex and high precision parts<sup>[9,10]</sup>. The key to the SSM process is to obtain a semisolid slurry with a uniform, small non-dendritic structure. The required spherical microstructure can be generated by either a liquid or a solid route. Solid-state path ways include strain induced melt activation (SIMA) method and recrystallization and partial melting (RAP)

method<sup>[11]</sup>. Some researchers have studied the effects of plastic deformation, isothermal temperature and holding time in an appropriate semi-solid temperature range on the microstructure evolution and tensile properties of A380 aluminum alloy through SIMA and RAP methods<sup>[12]</sup>. Chen et al.<sup>[13]</sup> pointed out that the SIMA process can produce ideal, fine semisolid tissues, in which spherical  $\alpha$ -Mg particles have almost no residual liquid. The relationship between the spheroidization degree, holding time and liquid fraction in isothermal treatment is also discussed. However, the research focuses on the low melting point of Al and Mg alloys, there are few reports on high melting point alloys, especially for HEA. Rogal<sup>[14]</sup> obtained the spherical microstructure of CoCrCuFeNi HEA required for the thixotropic process through RAP method. However, the influence of semisolid conditions (isothermal temperature and time) on microstructure evolution, mechanical properties and coarsening mechanism is not given. These explorations will be interesting and meaningful, which will expand the understanding and application of HEA.

A two-phase FCC CoCrCuFeNi HEA was selected in this paper. Semi-solid slurry is produced by the RAP process through cold rolling and partial remelting. The microstructures and mechanical properties of cast, rolled and semisolid isothermal heat treatment alloys were studied. And the influence of isothermal temperature and holding time on microstructure evolution and tensile properties at room temperature were discussed.

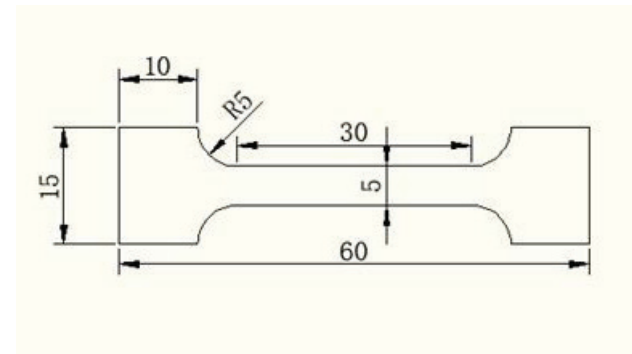
## 2. Experimental Procedures

In this experiment, five high-purity metals (Co, Cr, Cu, Fe and Ni) with higher than 99.9% (mass fraction) purity were selected as raw materials. Each element is weighed according to the equal molar ratio, with a total weight of 4 kg. CoCrCuFeNi high entropy alloy was obtained by melting in a vacuum suspension induction melting furnace protected by high purity argon. In the smelting process, the ingot was re-melted 4-5 times to ensure uniform smelting. The cylinder sample with a dimension of 90 mm in diameter and 70 mm in height was obtained.

The rectangular sample with a dimension of 70 mm×15mm×6 mm was cut from the as-cast button. Large deformation rolling high entropy alloy sheet with a thickness of 2.2mm was obtained by 8 passes of rolling treatment, in which the first 7 passes rolling reduction are all 0.5mm, and the last pass rolling reduction is 0.3mm. The rolled plate is cleaned with anhydrous ethanol and then vacuum sealed with quartz tube. The quartz tube is kept flat and put into YFFG40/13G-YC three-phase resistance furnace for semi-solid isothermal treatment and water quenching after treatment at different temperatures and holding times.

The microstructure was investigated by X-ray diffraction (XRD) with the CuK $\alpha$  radiation and optical microscope (OM). The compositions of phase were analyzed by energy dispersive spectroscope (EDS). The thermal analysis was performed by the differential-scanning calorimetry (DSC) with a constant heating rate

of 20 K/min. The mechanical properties were characterized by tensile behavior. The tensile samples with a total length of 60mm, a thickness of 2.2mm, a clamping end width of 15mm, a standard tensile distance of 30mm, a section width of 5mm and a radius of 5mm arc transition as shown in Figure1.



**Figure1.** Dimensional drawing of tensile samples (mm).

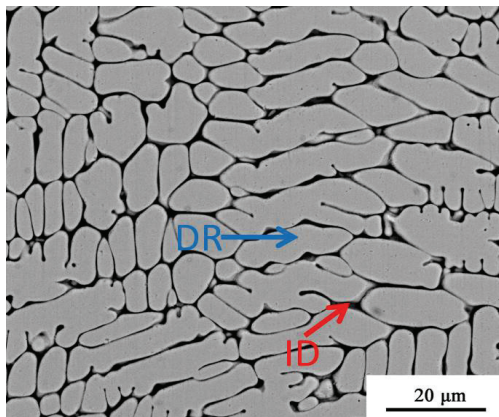
## 3. Results and Discussions

### 3.1. SEM of as-cast materials and thermodynamic results

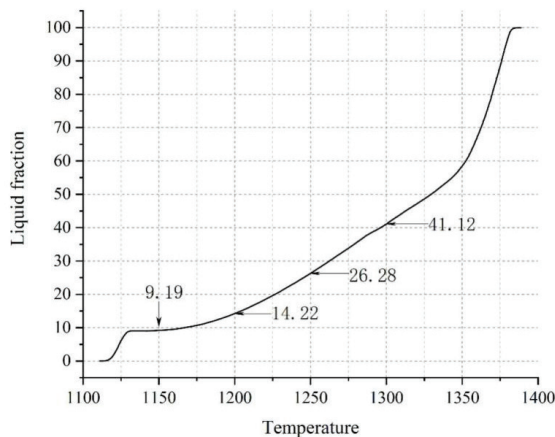
The as-cast CoCrCuFeNi HEA has typical dendrite (DR) and interdendrite (ID) structures as shown in Figure 2. The chemical compositions of different phases were determined by SEM energy dispersion spectrometer (EDS) at the points of dendrite (DR) and interdendrite (ID) respectively. The DR structure was FCC2 matrix phase with high volume fraction. In the DR region, the ID phase with a low volume fraction is FCC1 phase. The chemical composition of FCC1 and FCC2 phases indicates that FCC1 phase is Cu rich phase. However, the concentration of Co Cr, Fe and Ni in FCC2 is similar as shown in Table 1. The reason leading to a strong segregation of Cu in the FCC1 phase from the EDS results is the positive mixing enthalpy of Cu-Cr, Cu-Co, Cu-Fe, and Cu-Ni<sup>[15]</sup>. The volume fraction of the FCC2 phase was about 87%.

Figure 3 shows the DSC curves of as-cast and rolled CoCrCuFeNi HEA. There are two exothermic peaks in the as-cast alloy and the rolled alloy, and the positions of the exothermic peaks are basically the same, which indicates that the internal composition of the alloy has not changed after rolling. The first exothermic peak appears at about 1114 °C, the integral area of the peak is small and the temperature point is close to the melting point of copper (1083 °C). Combining DSC curve, EDS test and volume fraction calculation results, it could be judged that this peak represented FCC1 phase, and the second peak represented FCC2 phase. The alloy began to melt partially at about 1114°C and the crystal structure changed, the second exothermic peak appeared at about 1343°C and ended at about 1388°C, indicating that the alloy was completely melted at this time. The semi-solid holding temperature of the as cast sample is obtained by integrating the DSC curve in Figure 3. In the liquidus rate curve as shown in Figure 4, the liquidus rate is about 9.2% at 1150 °C, which is

relatively low, and there is a rapid increase of liquid phase ratio before 1150 °C. In combination with DSC curves, the FCC1 phase has been completely melted at 1150 °C, and the liquid phase ratio increases slowly with the increase of temperature. When the temperature reached 1350 °C, the liquid phase ratio curve increased rapidly, indicating that the FCC2 phase began to melt, and the liquid phase ratio approached 60%. It is very difficult to get accurate liquid phase ratio in the two regions where the liquid phase ratio changes rapidly, finally the liquid phase ratio changes rapidly and the solid phase ratio is easy to lose stability. When the temperature is higher than 1350 °C, the melting of FCC2 phase leads to the high liquid ratio of materials, which is easy to cause the deformation and melting and cannot maintain the macroscopic structure of the sheet metal during the semi-solid heat preservation treatment. Therefore, the semi-solid treatment temperature should be between 1133 °C and 1343 °C. Therefore, in this experiment, 1150 °C with a liquid phase ratio of 9.2% and 1300 °C with a liquid phase ratio of about 41% were selected as semi-solid insulation temperature.



**Figure 2:** The SEM of as-cast sample.



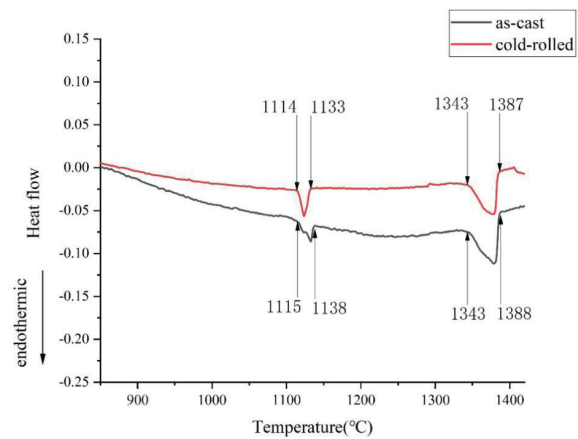
**Figure 4:** Liquid phase ratio curve of as-cast.

**Table 1.** Contents of each element at two regional points in the as-cast microstructure of CoCrCuFeNi high-entropy alloy (wt. %).

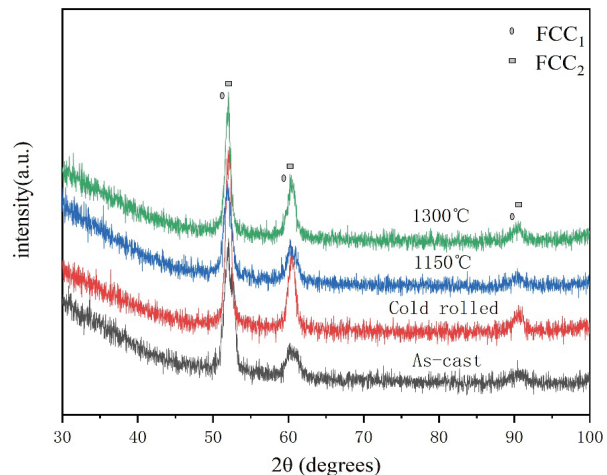
Sampling point	Co (%)	Cr (%)	Cu (%)	Fe (%)	Ni (%)
DR region	23.89	21.57	11.66	21.63	21.25
ID region	9.81	10.36	56.03	10.04	13.76

### 3.2. XRD diffraction

Figure 5 shows the X-ray diffraction patterns of samples in different states. Comparison before and after semi-solid isothermal treatment, the positions of each diffraction peak did not shift, and they were all combinations of FCC1 phase and FCC2 phase. The phase composition structure of CoCrCuFeNi high-entropy alloy did not change, indicating that CoCrCuFeNi high-entropy alloy had good thermal stability. In the subsequent analysis, the changes in material properties could be excluded the factors of phase structure change.



**Figure 3.** DSC curves of as-cast and rolled CoCrCuFeNi HEA.



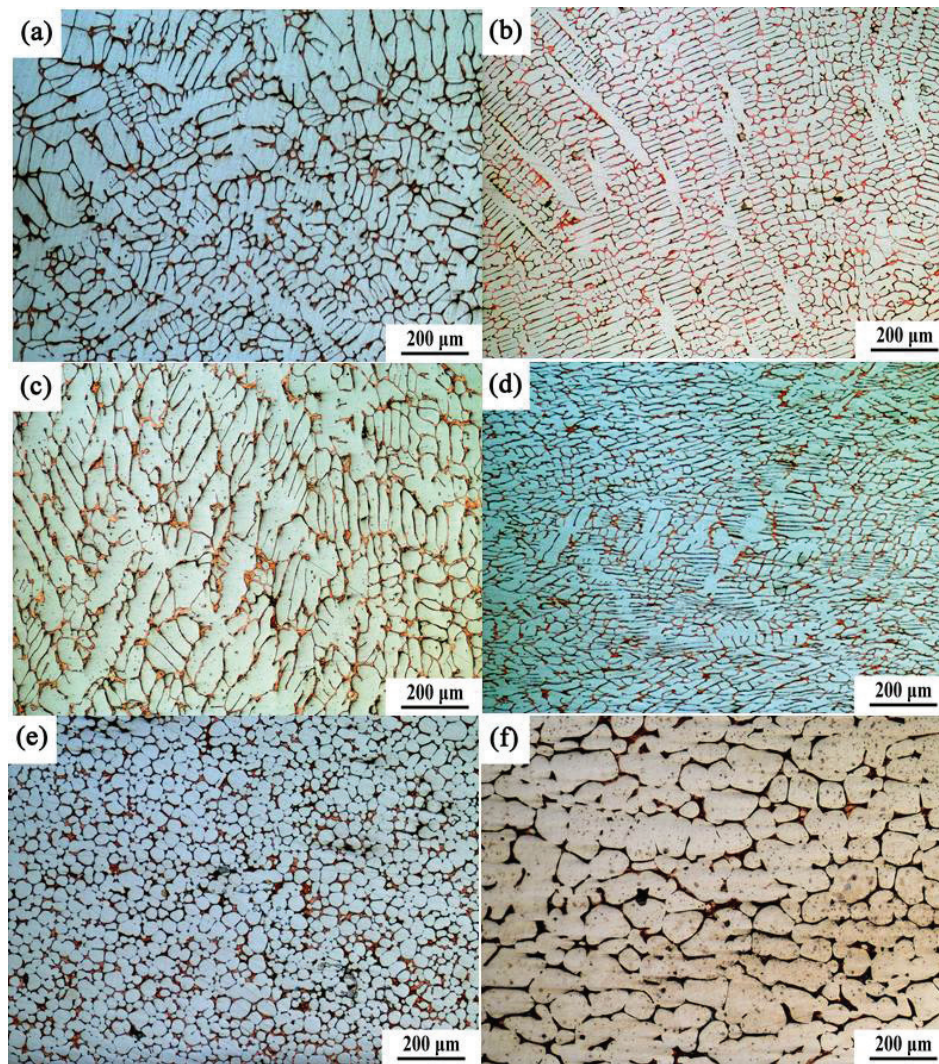
**Figure 5:** X-ray diffraction patterns of samples in different states.



### 3.3. Microstructure

As shown in Figure 6, the (a) and (b) are the metallographic diagrams of ingots in different areas, (a) is the upper ends of all the stretch sheet areas cut on the ingots, i.e the clamping area of the stretch sheet, (b) is the central area of the ingot, where the basic stretch sheet deformation area. The dendrite size in (b) region is more uniform and smaller than (a), which makes the tensile effect more stable. (c) shows the microstructure of the parallel rolling direction of the rolled plate. Compared with the as cast structure, it can be seen that the dendrites have obvious deformation, the secondary dendrite arm spacing is reduced, the dendrites have bending deformation, and even have dendrite fracture. (d) shows the microstructure in the vertical direction of

rolling. Compared with as cast samples, dendrites also have obvious extrusion deformation. (c) and (d) show that rolling makes the microstructure of the plate have a very large internal stress that can promote the grain boundary remelting in the semi-solid isothermal treatment, there are also a lot of dislocation energy in the crystal. (e) and (f) were the microstructure of the semi-solid isothermal treatment at 1150°C for 120min and 1300°C for 120 min respectively. Compared with the as-cast and rolled state, the morphology changed from dendrite to spherulite, and the grain size became smaller and evenly distributed, which indicated that the internal stress had been basically released. The higher the temperature of semi-solid isothermal treatment is, the larger the manager size is.



**Figure 6.** Metallographic photograph: (a) the upper area of the ingot;(b) central region of the ingot (c) parallel rolling direction (d) vertical rolling direction (e) 1150°C, 120min;(f) 1300°C, 120min.

Figure 7 shows the metallographic structure photos of semi-solid isothermal treated CoCrCuFeNi high-entropy alloy. The upper side(a), (c), (e) and (g) are the microstructure treated at 1150°C for 20min, 30min, 60min and 120min respectively, while bottom column (b), (d), (f) and (h) are the microstructure treated at 1300°C for 20min,

30min, 60min and 120min respectively. At 1150°C for 20 minutes, the grain size of FCC2 phase is still relatively small, the morphology and size of primary dendrite remain unchanged, and the secondary dendrite was partially remelted and peeled off to form small spherulites. For 30 minutes, the number of spherulites increased gradually and

the primary dendrite dissolved and fractured. When the temperature of semi-solid isothermal treatment is 1300°C, the grain size increases obviously, and with the increase of treatment time, the larger the grain size is.

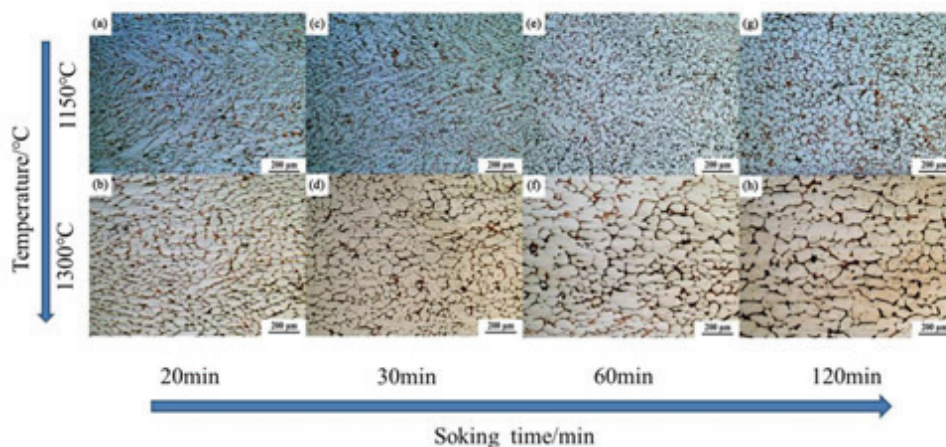
It can be seen that at 1150°C or 1300°C, the distribution of grains is uniform and the grain size is small when the time of semi-solid isothermal treat is 30 minutes. After 30 minutes, the grains grow with the increase of holding time; The average grain diameter is 50μm and 180μm at 1150°C and 1300°C for 120 minutes respectively, which indicated that the temperature has a key effect on grain growth.

The variation of grain size can be explained by growth kinetics. In the RAP process of manufacturing CoCrCuFeNi HEA semi-solid slurry, remelting heat provides energy to support dendrite fuse and spheroidization, while pre deformation stores internal energy. During reheating, recrystallization occurs, and with the formation of liquid phase, spherical grains are easy to form. Driving force of solid recrystallization is produced by the reduction of free energy due to the reduction of elastic storage energy (i.e. bit error energy)<sup>[16]</sup>. During the whole isothermal process

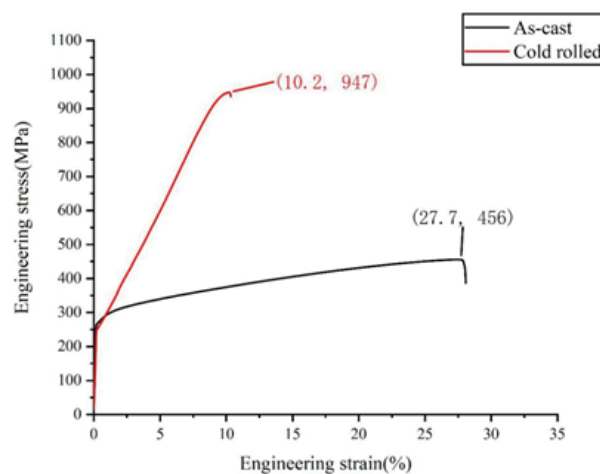
of semi-solid remelting, the sharp angle of solid-state FCC2 grains is engulfed by the liquid phase first, and then the grains become larger and rounder.

### 3.4. Tensile properties

Figure 8 shows the stress-strain curves of as-cast and rolled alloys. As you can see, the mechanical properties of the alloy has significant improvement after rolling compared to as-cast alloy, Tensile strength increased from 455MPa to 945MPa, and Young's modulus is also greatly improved, which in accordance with the previous rolling sample that causes the lattice fracture and grain refinement of the alloy to increase the strength and hardness. However, the elongation after fracture is much lower than that of as cast alloy, which may be due to: (1) Severe plastic deformation causes lattice fracture, grain refinement makes the strength of the alloy increase significantly and decrease the plasticity; (2) Rolling treatment leads to a certain degree of stress concentration in the alloy, which causes some defects, such as cracks, etc., in the process of drawing, which makes the alloy fracture rapidly and leads to low elongation.



**Figure 7.** Metallographic photograph: (a) 1150°C, 20min;(b) 1300°C, 20min;(c) 1150°C, 30min;(d) 1300°C, 30min;(e) 1150°C, 60min;(f) 1300°C, 60min;(g) 1150°C, 120min;(h) 1300°C, 120min.



**Figure 8.** Stress-strain curves of as-cast and rolled alloys.



Figure 9 and Figure 10 show the stress-strain curves of four groups of tensile experiments treated at 1150°C and 1300°C for 20min, 30min, 60min and 120min, respectively. As can be seen from Figure 9, the tensile strength of the alloy was 350MPa when the alloy was isothermally treated at 1150°C for 20min, and the tensile strength increased to 365MPa when the alloy was kept heat preservation for 30min. However, the tensile strength decreased to 335MPa and 305MPa after the isothermal treatment for 60min and 120min. In FIG.10, the tensile mechanical properties of the alloy treated at 1300°C have the same tend as those of the alloy treated at 1150°C. The tensile strength was 330MPa at 20min of heat preservation, and slightly increased to 335MPa after 30min of heat preservation.

This shows that the mechanical properties of CoCrCuFeNi high entropy alloy will change with the holding time when the temperature of semi-solid isothermal treatment remains unchanged. When the semi-solid isothermal treatment time is less than 30 min, the mechanical properties of CoCrCuFeNi high entropy alloy become better with the increase of semi-solid isothermal treatment time. When the semi-solid isothermal treatment time is more than 30 min, the mechanical properties of CoCrCuFeNi high entropy alloy become worse with the increase of semi-solid isothermal treatment time.

When the time of semi-solid isothermal treatment is constant, it can be seen that the tensile strength of the alloy at 1300°C is lower than that at 1150°C from Figure 9 and 10. The results show that the optimal properties of CoCrCuFeNi high entropy alloy appear in the semi-solid isothermal treatment at 1150°C for 30min, which is the same as the conclusion obtained in the previous metallographic structure analysis. It may be due to the high degree of grain refinement and microstructure homogenization after treatment at 1150 °C for 30min, so the strength of CoCrCuFeNi alloy is better at this time. After the heat preservation, the copper rich FCC1 phase cannot be supplemented by the liquid phase, resulting in shrinkage or porosity.

On the one hand, the composition has changed because of the exchange of elements in the two phases during the semi-solid isothermal heat treatment. According to the similar study in L.J. Zhang<sup>[17]</sup>, the content of Cu in low melting point FCC1 phase increased to about 83% and the content of CoCrFeNi decreased after semi-solid treatment. The enrichment of copper in FCC1 phase results in dendrite segregation, and the difference of composition and structure between the two phases becomes larger. The formation of positive mixing enthalpy between Cu and other four components, which indicated that it can repel the other four elements and reduce the affinity of two-phase structure, so the overall plasticity of the sample is reduced<sup>[18]</sup>; on the other hand, the solid phase of FCC2 grows up slowly and contacts with each other, the liquid phase of FCC1 is enclosed by the solid phase of FCC2 into a closed region. At the end of heat preservation, the copper rich FCC1 phase will produce shrinkage cavity and porosity due to the lack of liquid supplement during the

water-cooling solidification process. Under the action of semi-solid isothermal treatment, the shrinkage cavity and porosity changes into crack shown in Figure 11, and the higher the holding temperature is, the more obvious the crack is, resulting in an obvious drop of plasticity.

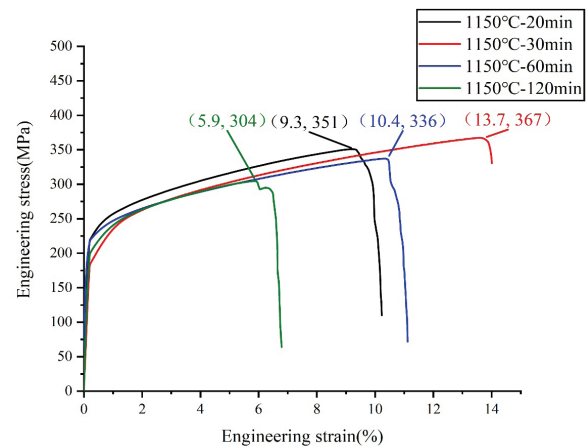


Figure 9. Tensile stress-strain curves of four groups at 1150°C.

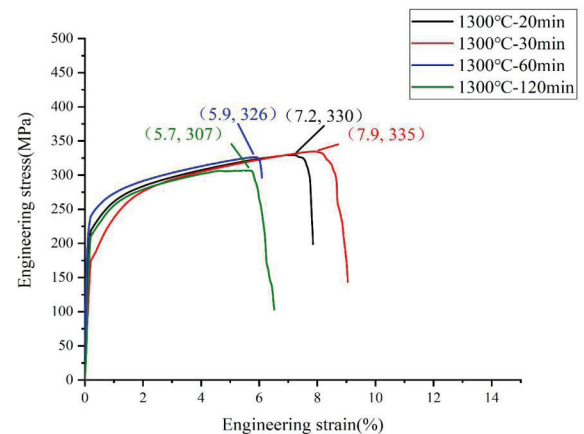


Figure 10. Tensile stress-strain curves of four groups at 1300°C.

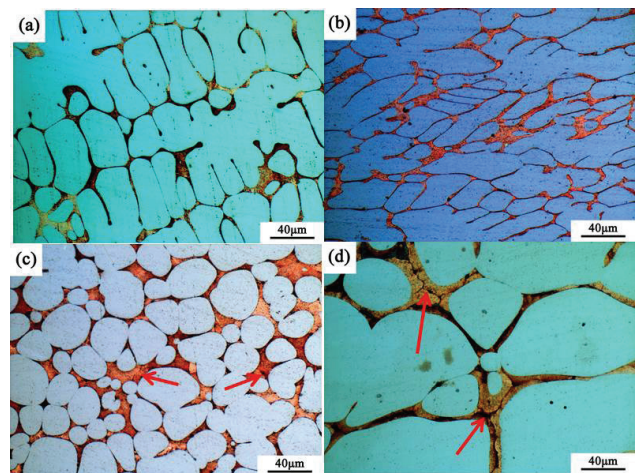


Figure 11. (a) high power in casting state (b) high power in rolling state (c) high power in 1150°C for 120min (d) high power in 1300 °C for 120min.

## Conclusions

1) The as-cast CoCrCuFeNi high-entropy alloy has two simple FCC phases, which exists in the form of intercrossing between dendrites and dendrites. The phase structure is not changed by rolling and semi-solid isothermal treatment. The as-cast alloy has 28% excellent plasticity.

2) After cold rolling with 63% deformation, the strength of CoCrCuFeNi high entropy alloy increased about 107%. Cold rolling pre deformation destroys the continuous distribution of dendrites, and the deformation energy accumulates at the grain boundary. In the stage of remelting and heat preservation, the release of stored internal energy can promote the melting of grain boundary, increase the proportion of liquid phase and improve the dendrite fuse.

3) The orthogonal experiment of semi-solid isothermal treatment was carried out on the rolled CoCrCuFeNi high entropy alloy. The results show that for the same holding time, with the increase of holding temperature, the microstructure grains become larger and the mechanical properties decrease; with the same holding temperature, the holding time of the optimal tensile properties is 30min, and the optimal semi-solid isothermal treatment parameters are 1150°C, 30min. The corresponding optimum elongation plastic variable is 13.7%, and the strength is 365MPa.

4) The tensile strength and plasticity of the high entropy alloy after isothermal treatment in solid state are lower than that in as-cast. The reason is that the micro cracks in rolling and the oxidation of the cracks in the process of isothermal treatment form, which results in the mechanical properties of the alloy after isothermal treatment is inferior to that of the as cast alloy. More experiments are needed to find other ways to strengthen the high entropy alloy.

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