Effect of low temperature rolling on mechanical properties and corrosion resistance of CrCoNi medium entropy alloy

Jinliang Chen, Zhongxue Feng, Jianhong Yi and Jun Yang

1 Faculty of Materials Science and Engineering, Kunming University of Science and Technology, Kunming 650093, People’s Republic of China
2 College of Titanium & Vanadium, Panzhihua University, Panzhihua 617000, People’s Republic of China
E-mail: chenjinliang2011@126.com

Keywords: low temperature rolling, medium entropy alloy, mechanical properties, corrosion resistance

Abstract
For the casted CrCoNi medium entropy alloy melted by magnetic levitation, the deformation was carried out in 4 passes under the condition of liquid nitrogen temperature (−196 °C), the total reduction was 50%. The microstructure and properties were analyzed after liquid nitrogen low temperature rolled. The experimental data showed that the phase structure of the alloy was not changed under the low-temperature rolling. The grains, crushed and refined, were elongated along the rolling direction. With the increasing of passes and reduction, the tensile strength increased from 585 MPa to 1359 MPa, while the elongation decreased from 37.8% to 5.9%. With the increasing of work hardening, the tensile strength of the CrCoNi medium entropy alloy gradually increased, while the plasticity dramatically decreased. At the same time, the corrosion resistance of the CrCoNi medium entropy alloy was improved by low temperature cold rolled. The corrosion resistance of as-cast and rolled CrCoNi was much better than 304 stainless steel.

1. Introduction

Medium Entropy Alloys (MEAs) were based on the development from high-entropy alloys (HEAs), which melted by three or four metallic elements with equal atomic ratios. Similar to the HEAs, MEAs have unique ‘four effects’ [1]. Moreover, MEAs have more excellent strength and plasticity than HEAs, which attracted great attention from researchers [2]. The emergence and development of CrCoNi medium entropy alloy, which complemented the research field of high-entropy alloys and provided new options and support for the development of high-performance materials, particularly broaden the bottleneck of research applications field in low temperature extreme materials. Even though CrCoNi medium entropy alloy have great potential for low-temperature applications, but how to improve their performance in application and service under the low temperatures was an important issue for researchers [3]. It is well known that the application of CrCoNi medium entropy alloy was strictly limited due to its low yield strength. Rolling deformation is one of the most significant method to enhance the strength and refine the uniformity of the material. The low-temperature cold rolling deformation is the most efficient method, its effect on the mechanical properties and corrosion resistance changes in CrCoNi medium entropy alloys has not been deeply researched.

In this paper, the casted CrCoNi medium entropy alloy was rolled under the condition of liquid nitrogen temperature for four passes with 50% total deformation. Then, the phase composition, microstructure and mechanical properties of each pass of the alloy were analyzed, the polarization curve was measured by the electrochemical corrosion method. In short, this work can provide references for the study of mechanics and corrosion properties about medium entropy alloy.
Table 1. Rolling passes thickness parameters.

| Rolling passes thickness mm\(^{-1}\) | casted | n = 1 | n = 2 | n = 3 | n = 4 |
|--------------------------------------|--------|-------|-------|-------|-------|
|                                      | 2.000  | 1.700 | 1.400 | 1.200 | 1.000 |

2. Experimental and detection methods

2.1. Materials and experimental scheme

Ingots of equimolar CrCoNi were produced by magnetic levitation melting a mixture of high-purity elemental metals (>99.9% purity) in an argon (Ar) atmosphere. The CrCoNi medium entropy alloy repeatedly melted four times to ensure uniformity of chemical composition and microstructure. Then, the ingot is obtained by cooling to room temperature. The ingot was split into 2.0 mm thick billets using wire cutting. Before low temperature rolling, the samples were placed in liquid nitrogen for 15 min, then quickly rolled using a four-roller mill step by step for four passes, the final thick of product is 1 mm. After rolling, the rolled specimens were stored in liquid nitrogen. The rolling passes were marked n = 1, n = 2, n = 3, the detailed Rolling passes thickness parameters are shown in the table 1.

2.2. Detection method

The phase structure of the CrCoNi medium entropy alloy was examined by using an X’ Pert Powder type x-ray diffractometer. The instrument uses Ka-rays from a Cu target with a test voltage of 40 kV, a step size of 0.02°, a scanning speed of 6°/min and a scanning angle of 10° to 90°. In order to obtain engineering stress-strain curves, tensile tests were detected by using a universal tensile testing machine with model WDW-10E. In order to obtain fracture morphology map, a Gemini-SEM 300 field emission scanning electron microscope were used. In order to obtain metallographic structure diagram, granularity of 1000 ~ 2000 sandpaper was used for fine grinding, after polishing, electrolytic etching was followed by preparing metallographic samples, the electrolyte is 15% nitric acid alcohol solution, and the metallographic etching time was 50 seconds. The metallographic observation was carried out by using a LEICA-DM400 M optical microscope. In order to obtain corrosion rate of polarization curves, a single-channel electrochemical workstation model of CS350H was used. The reference electrode was a supersaturated potassium chloride solution, a graphite rod was used as an auxiliary electrode, and the corrosive liquid was configured 3.5% (mass fraction) NaCl solution. The alloy specimens were scanned for kinetic potential polarization curves with the parameters set in the range of −0.2 V to 1 V and a scanning frequency was 0.5 mV s\(^{-1}\). All data curves were plotted by using software of Origin.

3. Results and discussion

3.1. Phase composition

The XRD patterns of casted and different passes rolled CrCoNi MEAs specimens are shown in figure 1. The characteristic peaks in specimens can be obviously identified. It using a plumb line in the peak position as the reference in casted CrCoNi MEAs. The results show that the CrCoNi consists of a single face-centered cubic (FCC) phase and no phase transformation was detected after four passes rolled, which is consistent with our previous study [1]. As can be seen from the figure 1, the intensity of (111) diffraction peak significantly increases while the intensities of (200) peaks decrease, it indicated that metal texture enhanced on the (111) crystal plane while (200) crystal plane was weakened. At the same time, the diffraction peak is obviously broadened after rolled, with the increase of rolling passes, the widening becomes more obvious. In addition, the diffraction peak shifts to the right, it was inferred that the grain size becomes smaller after rolling deformation [5,6]. The XRD patterns showed that CrCoNi MEAs rolled at liquid nitrogen temperature, and no new phase was generated, keeping a single FCC phase.

3.2. The microstructure

Figure 2(a) shows the casted metallographic structure of CrCoNi MEAs. In figure 2(a), it can seen that the grains were equiaxed which uniform distribution. Figures 2(b)–(e) shows the metallographic organization of the CrCoNi MEAs after low temperature rolled which n = 1, 2, 3 and 4 passes respectively. It can been seen that the grains were obviously elongated by rolling, the grains boundaries collapses under the rolling pressure. In addition, the grain deformation increases with the increase of rolling passes while producing obvious fibrous tissue in the rolling direction. In the last pass, when the rolling deformation is 50%, the grain boundaries became almost inconspicuous or even disappeared, forming a clear fibrous orientation, which may be related to the (111), (220) crystal plane in the XRD pattern [7,8].
3.3. Tensile mechanical properties and fracture morphology

When CrCoNi MEAs been rolled, all specimens were cutted into non-standard tensile samples with a pitch section size of $16 \times 5 \times 1$ mm, using a tensile speed of $1 \times 10^{-3}$ S$^{-1}$ to obtain the stress-strain curves in universal testing machine, the casted and different passes curves as shown in figure 3. It can be seen in figure 3 that the yield strength is only 259 Mpa while tensile strength is 585 Mpa of casted CrCoNi, but the elongation reached 37.8%.

The yield strength and tensile strength are signifcantly increased by 4 passes of cold rolling while the elongation reduced to 5.9%, at the moment, the yield strength and the tensile strength is 1280 MPa and 1359 MPa,

Figure 1. XRD patterns as cast and after cold rolled.

Figure 2. Microstructure of Crconi alloy in as-casted and after rolled.

3.3. Tensile mechanical properties and fracture morphology

When CrCoNi MEAs been rolled, all specimens were cutted into non-standard tensile samples with a pitch section size of $16 \times 5 \times 1$ mm, using a tensile speed of $1 \times 10^{-3}$ S$^{-1}$ to obtain the stress-strain curves in universal testing machine, the casted and different passes curves as shown in figure 3. It can be seen in figure 3 that the yield strength is only 259 Mpa while tensile strength is 585 Mpa of casted CrCoNi, but the elongation reached 37.8%.

The yield strength and tensile strength are signifcantly increased by 4 passes of cold rolling while the elongation reduced to 5.9%, at the moment, the yield strength and the tensile strength is 1280 MPa and 1359 MPa,
respectively. Compared with the casted CrCoNi, the yield strength and tensile strength increases by 394.2% and 132.3% after rolling, respectively. The reasons for this is due to CrCoNi MEAs have lower stacking fault energy, so it is more prone to produce dislocations and twinning during deformation at liquid nitrogen temperatures [9–12], which hinders deformation and increases the strength of the alloys. As the number of passes increased, the increasing of deformation resulted in increasing of dislocations density and resistance to deformation. Further resulting in increased strength and decreased toughness.

Figures 4(a) and (b) shows the fracture morphology and rectangular box enlarged map of casted CrCoNi MEAs, respectively. Figures 4(c) and (d) shows the fracture morphology and rectangular box enlarged map of rolled CrCoNi MEAs, respectively. As can be seen from the figure 4, the number of dimples in the casted fracture is more than that in the rolled fracture, a large number of microporous dimples are gathered on the tearing edge of the casted fracture. In contrast, there were no microporous dimples on the rolled fracture edge. It can be seen that the casted fracture has obvious characteristics of ductile fracture, the toughness is reduced by rolling deformation. At the same time, particles can be clearly seen in dimple from figure 4. EDS energy spectrum test
was carried out on the particles in the dimple, and the element content was shown in figure 5, combined with the previous XRD data, it can be analysed that the particles are oxides, not a second phase matter.

3.4. Corrosion resistance

The blue curve in figure 6 shows the polarization curve of rolled CrCoNi MEAs, The red and black curves shows the polarization curve of casted CrCoNi MEAs and 304 stainless steel, respectively. The instrument of CS3SOH electrochemical workstation is used for perform Tafel curve linear fitting for CrCoNi alloy and 304 stainless steel, respectively. In order to obtain self-etching voltage value (Ecorr), corrosion current density value (Icorr) and Corrosion rate value through curve fitting, the values are shown in table 2. The corrosion rate of metal is judged by the density of corrosion current, the lower the corrosion current density is, the lower the corrosion rate is, otherwise, the greater. The higher the corrosion voltage is, the lower the corrosion rate is, otherwise, the greater. It is not hard to see from figure 6 and table 2, the corrosion rate of casted CrCoNi alloy is less than that of

![Figure 5. Particle and EDS spectra shows elements content in marked particle.](image1)

![Figure 6. Tafel curves of 304 stainless steel, casted CrCoNi MEAs and rolled CrCoNi MEAs.](image2)

| Simples   | Icorr(A.cm²) | Ecorr(V) | Corrosion rate(mm/a) |
|-----------|-------------|---------|----------------------|
| 304 steel | $1.550 \times 10^{-5}$ | -0.626  | 0.182                |
| casted    | $6.013 \times 10^{-7}$  | -0.649  | 0.071                |
| rolled    | $9.102 \times 10^{-7}$  | -0.522  | 0.010                |
304 stainless steel, the rolled CrCoNi MEAs has the lowest corrosion rate. CrCoNi MEAs has better corrosion resistance than 304 stainless steel, the corrosion resistance of CrCoNi MEAs can be improved by low temperature rolling.

4. Conclusions

(1) CrCoNi MEAs rolled at liquid nitrogen temperature, and no new phase was generated, keeping a single FCC phase.

(2) Contrast with the casted CrCoNi MEAs, rolled under the condition of liquid nitrogen temperature, the yield strength and tensile strength are increased from 259 MPa and 585 MPa to 1280 MPa and 1359 MPa, respectively.

(3) CrCoNi MEAs has better corrosion resistance than 304 stainless steel, the corrosion resistance of CrCoNi MEAs can be improved by low temperature rolling.

Acknowledgments

The authors are grateful for the financial support by the Science and Technology Planned Project of Yunan Province, China (No. 908075156031) and the Science and Technology Planned Project of Panzhihua City, China (No. 2020ZD-G-10).

Conflict of interest

The authors declare that they have no conflict of interest.

Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

ORCID iDs

Jinliang Chen https://orcid.org/0000-0002-1839-2968

References

[1] Yeh J W 2013 Alloy design strategies and future trends in high-entropy alloys JOM 65 1759–71
[2] Gludovatz B et al 2016 Exceptional damage-tolerance of a medium-entropy alloy CrCoNi at cryogenic temperatures Nat. Commun. 7 10602–5
[3] Laplanche G et al 2017 Reasons for the superior mechanical properties of medium-entropy CrCoNi compared to high-entropy CrMnFeCoNi Acta Mater. 128 292–303
[4] Cantor B et al 2004 Microstructural development in equiatomic multicomponent alloys Materials Science & Engineering 103 213–8
[5] Farm K Y et al 2011 Electrical, magnetic, and hall properties of AlxCoCrFeNi high-entropy alloys Journal of Alloys and Compounds 509 1607–14
[6] Zijiao Z et al 2017 Dislocation mechanisms and 3D twin architectures generate exceptional strength–ductility–toughness combination in CrCoNi medium-entropy alloy Nat. Commun. 8 1530–45
[7] Han B et al 2021 Additively manufactured high strength and ductility CrCoNi medium entropy alloy with hierarchical microstructure Materials Science & Engineering 820 141545 (https://sciedirect.com/science/article/abs/pii/S0921509321008145)
[8] Sinha S et al 2020 Deformation mechanisms and ductile fracture characteristics of a friction stir processed transformative high entropy alloy Acta Mater. 184 164–78
[9] Laplanche G et al 2019 Achieving ultra-high strength and ductility in equiatomic CrCoNi with partially recrystallized microstructures Acta Mater. 165 496–507
[10] Bin Gan J M et al 2019 Superb cryogenic strength of equiatomic CrCoNi derived from gradient hierarchical microstructure Journal of Materials Science & Technology 35 957–61
[11] Guana B et al 2021 Comprehensive study of strain hardening behavior of CrCoNi medium-entropy alloy J. Alloys Compd. 882 160623
[12] Huang H et al 2018 Critical stress for twinning nucleation in CrCoNi-based medium and high entropy alloys Acta Mater. 149 388–96