

# Effect of Al Content on Microstructure and Mechanical Properties of CoCrFeNiMn High-Entropy Alloy

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## Abstract

In this study, CoCrFeNiMn high-entropy alloys (HEAs) with different aluminum (Al) contents were fabricated, and the effects of Al content on the microstructure evolution and mechanical properties were systematically explored. The microstructural characterization results indicated that the Al content exerted a crucial regulatory effect on the crystal structure of the alloy. With increasing Al content, shifts in the characteristic XRD peaks indicate lattice expansion of the alloy. Meanwhile, the phase structure continuously evolved from a single face-centered cubic (FCC) structure to an FCC/body-centered cubic (BCC) dual-phase structure, and then finally transformed into a BCC-dominated structure. Appropriate Al element addition could produce localized stress fields near dislocations and achieve prominent solid-solution strengthening, which effectively inhibited dislocation movement and further improved the yield strength, tensile strength, and hardness of the alloy. In contrast, excessive Al addition would break through the solid solubility limit of the alloy matrix, causing obvious phase separation and the precipitation of brittle B2-ordered NiAl-type intermetallic secondary phases. These brittle secondary phases easily induced crack initiation in the plastic deformation process, which significantly deteriorated the ductility, work-hardening ability, and impact toughness of the alloys.

**Keywords:** high-entropy alloys; Al content; mechanical properties; crystal structure



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## 1. Introduction

High-entropy alloys (HEAs) were first discovered and defined by Yeh et al. [1] and Cantor et al. [2] in 2004. HEAs are characterized by compositions comprising five or more principal elements in equimolar or near-equimolar ratios, with each element occupying an atomic percentage ranging from 5% to 35% [3–7]. This name refers to the new design concept of alloying by introducing more metal elements [8]. These alloys exhibit unique microstructures and properties, offering potential solutions to current material performance bottlenecks in engineering fields, and have garnered significant attention from researchers worldwide [9]. CoCrFeNiMn-based HEAs, in particular, demonstrate exceptional mechanical properties, high-temperature stability, and corrosion resistance, showing great promise for high-end applications [10–12]. However, the strength of CoCrFeNiMn high-entropy

alloy at room temperature is insufficient to meet the pursuit of strength and plasticity matching of structural materials [13]. Currently, introducing alloying elements to form secondary phases is the most straightforward and effective method to enhance the performance of single-phase FCC matrices [14–17].

Metal matrix composites (MMCs) produced by using high-entropy alloy (HEA) powders as reinforcements exhibit superior mechanical properties. Aluminum (Al), with its abundant availability, low cost, and ability to modify crystal structures, has been extensively studied as a dopant [18]. The larger atomic radius of Al induces significant lattice distortion when incorporated into the matrix, thereby improving yield strength [19]. Additionally, Al doping facilitates the formation of small amounts of hard and brittle secondary phases. These phases not only pin grain boundaries, restricting grain growth to achieve grain refinement strengthening, but also enhance wear resistance [20,21]. The findings indicate that HEA-reinforced Al7075 MMCs, with an ideal combination of strength, hardness, and corrosion resistance, are promising candidates for structural applications requiring superior mechanical properties [22]. Extensive investigations have systematically uncovered the microstructure and mechanical evolution of Al-alloyed CoCrFeNiMn Cantor alloys, laying solid theoretical foundations for compositional regulation of this classic FCC high-entropy alloy. He et al. first established the complete phase evolution law of  $\text{Al}_x\text{CoCrFeNiMn}$  alloys with broad Al concentration gradients, verifying that increasing Al content triggers a successive phase transition from single FCC to duplex FCC + BCC and finally to a fully BCC structure, accompanied by prominent strength elevation and ductility degradation at high Al fractions [23]. Focusing on the low Al doping range consistent with the present work, Pang et al. further confirmed that trace Al addition ( $\leq 6$  at.%) retains stable single FCC matrix, achieves obvious yield strength improvement without severe ductility loss, and simultaneously optimizes the aqueous corrosion resistance of Cantor alloy [24]. Distinct from conventional solid-solution strengthening behavior, Cheng et al. reported a unique solid-solution softening phenomenon in low-Al  $\text{Al}_{0.1}\text{CoCrFeMnNi}$  alloy, originating from the reduction in Peierls stress induced by minor Al solute atoms [25].

Nevertheless, nearly all of the above fundamental studies adopted vacuum arc melting casting as the fabrication route, while few reports concentrate on ultra-low Al-doped Cantor alloys consolidated via spark plasma sintering (SPS). The existing literature rarely systematically clarifies how trace Al content (0–2.5 wt.%) modulates the phase constitution, densification behavior, and mechanical performance of SPS-consolidated CoCrFeNiMn alloys. To fill this research gap, the present work systematically explores phase transformation, microstructural characteristics, and tensile performance of SPS-sintered CoCrFeNiMn alloys with an ultra-low Al content ranging from 0 to 2.5 wt.%, aiming to optimize the comprehensive performance of the base alloy.

As is well-known, powder metallurgy can produce bulk high-entropy alloys with nanoscale grains and uniform microstructures and compositions, thus significantly improving their mechanical properties. Spark plasma sintering (SPS) is an effective method for producing gradient structures, as layers consisting of powder mixtures are compacted by simultaneously applied pulsed currents and loads. As a result, materials with high densities can be produced during a short time. SPS is interesting for producing TBCs consisting of a superalloy, transition layers, and an external ceramic layer [26]. In this study, CoCrFeNiMn-Al (HEAs) were prepared via powder metallurgy using a spark plasma sintering (SPS) furnace, and the influence of different Al contents on their microstructure and mechanical properties was systematically investigated. Accordingly, an optimized process window with both efficiency and cost balance was determined, which also provides a theoretical basis for the engineering applications of other high-entropy alloys.

## 2. Materials and Methods

CoCrFeNiMn HEA powder (15–53  $\mu\text{m}$ , gas-atomized) and Al powder (5–25  $\mu\text{m}$ ) were adopted as starting materials. All raw powders possessed a purity of  $\geq 99.9$  wt%. The powders were weighed according to the designed molar ratio and homogeneously mixed via planetary ball milling (Miqi Instrument Equipment Co., Ltd., Changsha, Hunan, China.) for 4 h without process control agents, namely simple mixing. The obtained powder mixture was finally consolidated by spark plasma sintering. The high-entropy alloys investigated in this work were fabricated via spark plasma sintering using an SPS-20T-10 sintering furnace (Shanghai Chenhua Science and Technology Co., Ltd., Shanghai, China), where gradient Al contents of 0%, 0.5%, 1%, and 2.5% were introduced to prepare disk-shaped alloy samples with uniform sizes and consistent surface states. (The sintering process was carried out via spark plasma sintering under a vacuum atmosphere. The sintering temperature was set at 900  $^{\circ}\text{C}$ , with a heating rate of 100  $^{\circ}\text{C}/\text{min}$  and a holding time of 10 min. A uniaxial pressure of 50 MPa was continuously applied throughout the sintering process. Graphite mold was used to hold the powder samples during sintering.) The detailed chemical compositions of the designed CoCrFeNiMnAl<sub>x</sub> high-entropy alloys are listed in Tables 1–4. The original samples were cut into dog-bone tensile samples and metallographic samples using a BM400-type center-wire cutting machine (Suzhou Baoma Numerical Control Equipment Co., Ltd., Suzhou, China) to meet the requirements of room-temperature tensile mechanical testing, and the size of the tensile samples is shown in Figure 1 [27]. The tensile mechanical performances of the alloys were tested on a CMT5305 universal material testing machine (MTS Systems (China) Co., Ltd., Shanghai, China) under room temperature and atmospheric environment conditions, with a constant tensile strain rate strictly set at  $5 \times 10^{-5} \text{ s}^{-1}$ . To guarantee the reliability and repeatability of experimental data, three parallel specimens with identical component and preparation parameters were subjected to uniaxial tensile tests for each Al content group to characterize the mechanical properties systematically.

**Table 1.** Chemical compositions of CoCrFeNiMn-0%Al high-entropy alloys.

| Element | Nominal (wt%) | ICP-OES (wt%) | EDS (wt%)        |
|---------|---------------|---------------|------------------|
| Al      | 0.00          | 0.02          | $0.00 \pm 0.03$  |
| Co      | 20.00         | 19.92         | $20.15 \pm 0.42$ |
| Cr      | 20.00         | 19.95         | $19.86 \pm 0.38$ |
| Fe      | 20.00         | 19.88         | $19.91 \pm 0.35$ |
| Ni      | 20.00         | 19.90         | $19.83 \pm 0.40$ |
| Mn      | 20.00         | 19.94         | $20.25 \pm 0.36$ |

**Table 2.** Chemical compositions of CoCrFeNiMn-0.5%Al high-entropy alloys.

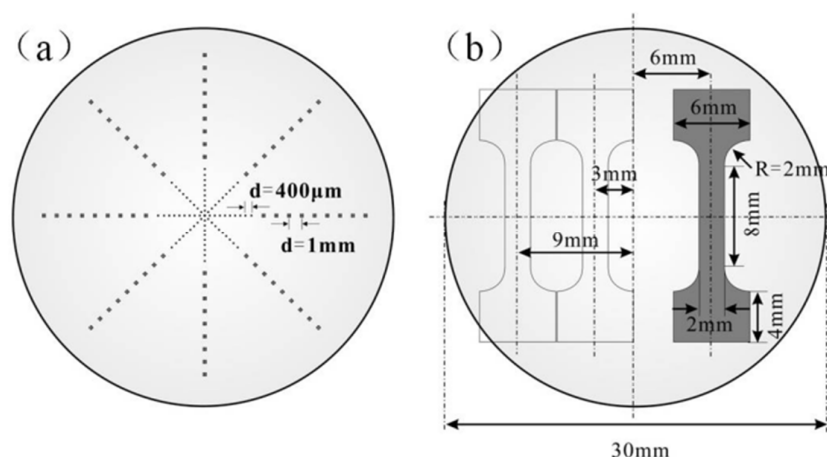
| Element | Nominal (wt%) | ICP-OES (wt%) | EDS (wt%)        |
|---------|---------------|---------------|------------------|
| Al      | 0.50          | 0.48          | $0.56 \pm 0.08$  |
| Co      | 19.90         | 19.86         | $19.72 \pm 0.45$ |
| Cr      | 19.90         | 19.89         | $19.98 \pm 0.33$ |
| Fe      | 19.90         | 19.83         | $19.80 \pm 0.39$ |
| Ni      | 19.90         | 19.85         | $19.94 \pm 0.41$ |
| Mn      | 19.90         | 19.87         | $19.81 \pm 0.34$ |

**Table 3.** Chemical compositions of CoCrFeNiMn-1%Al high-entropy alloys.

| Element | Nominal (wt%) | ICP-OES (wt%) | EDS (wt%)    |
|---------|---------------|---------------|--------------|
| Al      | 1.00          | 0.97          | 1.09 ± 0.10  |
| Co      | 19.80         | 19.78         | 19.65 ± 0.43 |
| Cr      | 19.80         | 19.81         | 19.92 ± 0.37 |
| Fe      | 19.80         | 19.75         | 19.76 ± 0.32 |
| Ni      | 19.80         | 19.79         | 19.88 ± 0.39 |
| Mn      | 19.80         | 19.76         | 19.70 ± 0.35 |

**Table 4.** Chemical compositions of CoCrFeNiMn-2.5%Al high-entropy alloys.

| Element | Nominal (wt%) | ICP-OES (wt%) | EDS (wt%)    |
|---------|---------------|---------------|--------------|
| Al      | 2.50          | 2.46          | 2.63 ± 0.12  |
| Co      | 19.50         | 19.43         | 19.31 ± 0.48 |
| Cr      | 19.50         | 19.47         | 19.54 ± 0.41 |
| Fe      | 19.50         | 19.41         | 19.38 ± 0.36 |
| Ni      | 19.50         | 19.45         | 19.49 ± 0.44 |
| Mn      | 19.50         | 19.42         | 19.36 ± 0.38 |

**Figure 1.** (a) The sintered sample and (b) the stretched sample. Reprinted from Ref. [8].

The microhardness of alloy samples with different Al doping contents was measured by an HVS-1000 micro Vickers hardness tester (Laizhou Huaxing Testing Instruments Co., Ltd., Laizhou, China). A diamond square pyramid indenter was adopted for the test, with a fixed loading force of 9.8 N and a holding time of 10 s during indentation to ensure sufficient indentation forming. For each sample, ten discrete testing positions were randomly selected to conduct microhardness measurement, avoiding surface defects and edge areas. The maximum and minimum values of the measured data were excluded to eliminate experimental errors, and the average value of the residual data was defined as the final microhardness of the sample.

The phase structural characteristics of the alloys were determined by an XRD-6000 X-ray diffractometer with 3 KW power (Shimadzu (China) Co., Ltd., Shanghai, China), equipped with Cu target K $\alpha$  radiation for high-precision phase scanning. The testing parameters were set as a tube voltage of 40 kV and a tube current of 30 mA, with a scanning angle range of 20–80° and a scanning speed of 4°/min. Prior to microstructure observation, all metallographic specimens were sequentially ground and mechanically polished to achieve a flawless mirror surface, followed by corrosion treatment with a mixed etching solution consisting of 4 mL HF, 6 mL HNO<sub>3</sub>, and 100 mL deionized water. A ZEISS optical microscope (OM) was utilized to observe the microstructural features of the etched

samples. The tensile fracture surface morphologies and microstructural characteristics of the specimens were further analyzed via a Hitachi TM4000PlusII scanning electron microscope integrated with EDS energy spectrum detector (Hitachi (China) Ltd., Beijing, China). The complete experimental workflow of this study is displayed in Figure 2.

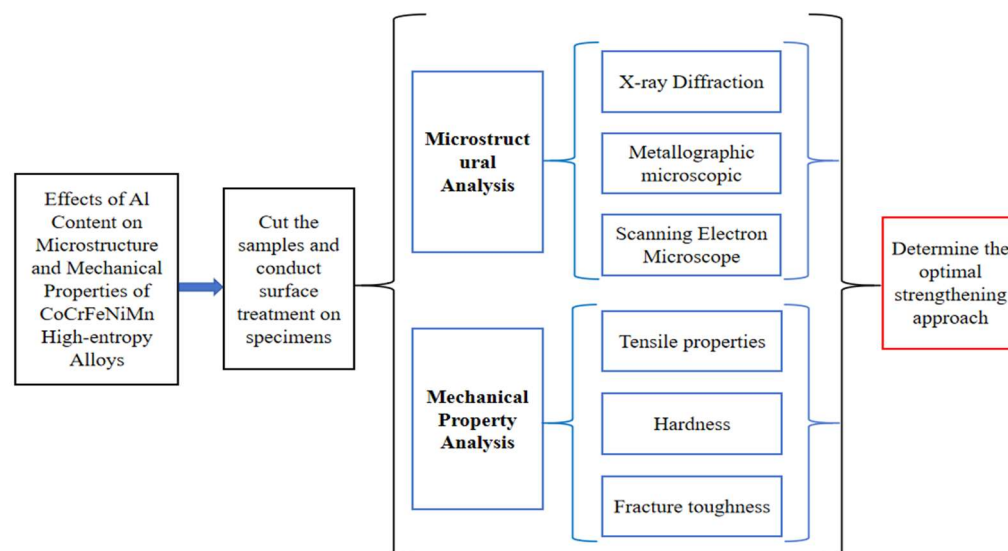


Figure 2. Overall flow chart.

### 3. Results and Discussion

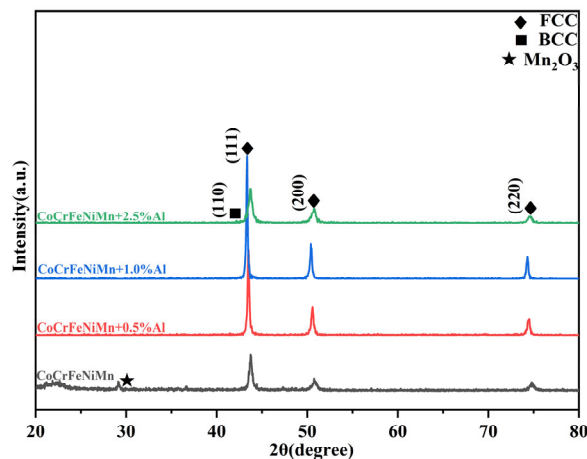
#### 3.1. Microstructure Analysis

Figure 3 shows the X-ray diffraction (XRD) patterns of CoCrFeNiMn-Al high-entropy alloys with different Al contents. As can be seen from the figure, the 0% Al (base alloy) and 0.5% Al alloys only exhibit characteristic diffraction peaks of a typical face-centered cubic (FCC) structure without any additional impurity peaks, indicating that the alloys maintain a single-phase FCC solid-solution structure and the Al elements are completely dissolved into the matrix as solute atoms without inducing phase transformation. For the 1.0% Al alloy, the FCC characteristic peaks remain dominant, while a weak body-centered cubic (BCC) phase (110) plane diffraction peak appears near  $2\theta \approx 44^\circ$ , indicating that the alloy begins to transform from a single-phase FCC to an FCC + BCC dual-phase structure. In the 2.5% Al alloy, the intensity of the BCC phase (110) diffraction peak increases significantly, while the peak intensity of the FCC phase decreases relatively. The alloy presents an FCC + BCC dual-phase coexistence structure and the proportion of the BCC phase further increases with the increase in Al content.

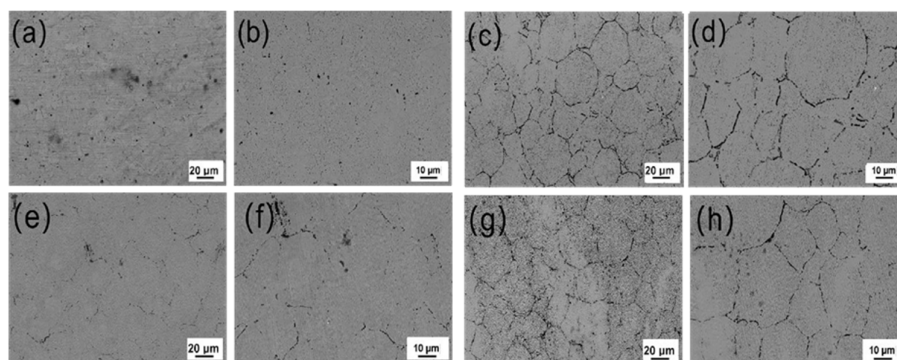
Combined with the phase formation law of high-entropy alloys, it can be concluded that Al is a typical BCC-stabilizing element. With the gradual increase in Al content, the stacking fault energy and phase stability of the alloy change, and the microstructure evolution follows the continuous transformation law of single-phase FCC  $\rightarrow$  dual-phase FCC + BCC  $\rightarrow$  single-phase BCC. In this study, when the Al addition is within 0.5%, Al is completely dissolved to maintain a single-phase FCC structure; when the Al content increases to 1.0% and above, the BCC phase begins to precipitate and form a dual-phase structure; and if the Al content is further increased, the BCC phase will gradually replace the FCC phase and finally achieve a complete transformation to the BCC structure, which is completely consistent with the phase regulation mechanism of Al on CoCrFeNiMn high-entropy alloys reported in the literature.

The microstructural evolution, grain size distribution, and mechanical properties of the alloys as a function of Al content are correlated in Figures 4, 5 and 8. From the optical

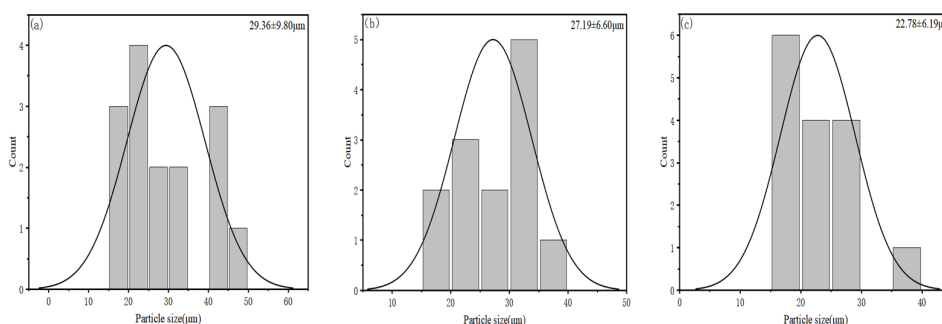
micrographs, the 0% Al alloy exhibits a featureless, homogeneous matrix with no clearly resolved grain boundaries, consistent with its high ductility (elongation of 0.52%) and moderate microhardness of 199.8 HV. The absence of distinct grain boundaries suggests a relatively uniform single-phase structure, which favors plastic deformation by reducing grain boundary-induced stress concentration.



**Figure 3.** XRD patterns of CoCrFeNiMnAl alloys with different Al contents.



**Figure 4.** Microstructures of the alloy with different Al contents: (a,b) 0% Al; (c,d) 0.5% Al; (e,f) 1.0% Al; (g,h) 2.5% Al.



**Figure 5.** Particle sizes at different aluminum contents: (a) 0.5% Al; (b) 1.0% Al; (c) 2.5% Al.

With the addition of 0.5% Al, well-defined equiaxed grain boundaries become visible, and the corresponding grain size distribution shows an average grain size of  $29.36 \pm 9.80 \mu\text{m}$ . Accompanied by this microstructural change, the elongation drops sharply to 0.19%, while the microhardness decreases slightly to 196.8 HV. The reduction in ductility is primarily attributed to the formation of continuous grain boundaries, which act as preferential sites for crack initiation and propagation, thereby limiting plastic

deformation. At 1.0% Al, the grain boundaries become more pronounced, with some boundaries appearing discontinuous or slightly corroded. The average grain size decreases marginally to  $27.19 \pm 6.60 \mu\text{m}$ , and the elongation further reduces to 0.18%, while the microhardness remains stable at 197.6 HV. The subtle grain refinement at this Al level does not offset the negative effect of grain boundary features on ductility, resulting in a continued decline in plasticity. For the 2.5% Al alloy, the grain boundaries are the most clearly defined, forming distinct dark networks, and the average grain size is further refined to  $22.78 \pm 6.19 \mu\text{m}$ . However, despite the finer grain size, the elongation decreases to the lowest value of 0.12%, while the microhardness increases significantly to 210.1 HV. This indicates that the strengthening effect from grain refinement is overshadowed by the embrittling effect of severe grain boundary segregation/precipitation at higher Al contents, which increases the material's brittleness and hardness while drastically reducing ductility.

The addition of Al induces a clear transition from a ductile, featureless microstructure to a brittle, grain-boundary-dominated structure. The trade-off between grain refinement strengthening and grain boundary embrittlement governs the mechanical performance: increasing Al content continuously reduces elongation due to enhanced grain boundary cracking tendency, while microhardness first slightly decreases (0–1.0% Al) and then increases significantly at 2.5% Al, reflecting the combined effects of grain size reduction and grain boundary strengthening.

From the metallographic micrographs with different aluminum contents in Figure 4, the corresponding grain sizes can be measured. The metallographic micrographs were imported into ImageJ software (Version 1.54f), and the corresponding scale bars were set. Then, no less than 10 groups of data were selected for plotting and analysis using Origin, and finally the results shown in Figure 5 were obtained. Figure 5 shows the grain size distributions of the alloys with different Al contents, fitted with normal distribution curves, with the average grain size and standard deviation indicated in each plot. With increasing Al content from 0.5% to 2.5%, the average grain size decreases monotonically from  $29.36 \pm 9.80 \mu\text{m}$  to  $22.78 \pm 6.19 \mu\text{m}$ , accompanied by a gradual narrowing of the distribution range. The 0.5% Al alloy exhibits the broadest grain size distribution (15–50  $\mu\text{m}$ ) with the largest standard deviation, indicating significant microstructural heterogeneity. As Al content increases to 1.0%, the distribution becomes narrower (15–40  $\mu\text{m}$ ) and the standard deviation decreases, reflecting improved grain size uniformity. At 2.5% Al, the grain size is further refined to  $22.78 \pm 6.19 \mu\text{m}$ , with the narrowest distribution (10–35  $\mu\text{m}$ ) and the most homogeneous grain structure. This trend demonstrates that increasing Al addition not only refines the grains but also improves the uniformity of the grain size distribution.

This refinement can therefore be inferred to arise from two main factors: Al addition promotes the formation of fine intermetallic phases or solute segregation at grain boundaries, which pin grain boundaries and inhibit grain growth during solidification or heat treatment; and higher Al content may increase the number of heterogeneous nucleation sites, leading to a larger number of initial grains and thus a finer final microstructure.

The relationship between grain size and yield strength in polycrystalline materials is described by the Hall–Petch relationship:

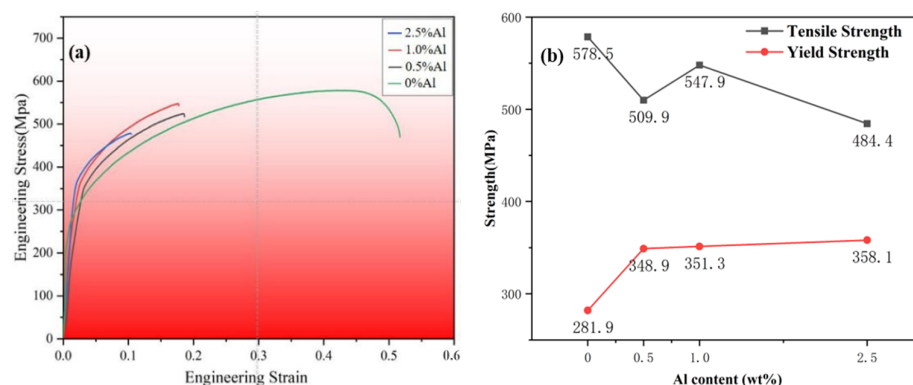
$$\sigma_y = \sigma_0 + \frac{k_y}{\sqrt{d}}$$

In this equation,  $\sigma_y$  is the yield strength,  $\sigma_0$  corresponds to the intrinsic resistance of the crystal lattice to dislocation motion,  $k_y$  is the Hall–Petch coefficient, and  $d$  is the average grain diameter. Grain refinement improves strength by increasing grain boundary density. These boundaries act as effective obstacles to dislocation propagation, causing

dislocations to pile up at grain boundaries. Consequently, higher external stresses are required to overcome these pileups and sustain plastic deformation, leading to the well-known grain-boundary-strengthening effect.

### 3.2. Mechanical Properties Analysis

Figure 6 presents the room-temperature tensile engineering stress–strain curves (a) and the corresponding tensile strength and yield strength values (b) of the alloys with different Al contents. The results reveal a clear trade-off between strength and ductility as Al content increases, which is closely correlated with the microstructural evolution and grain size changes observed earlier.



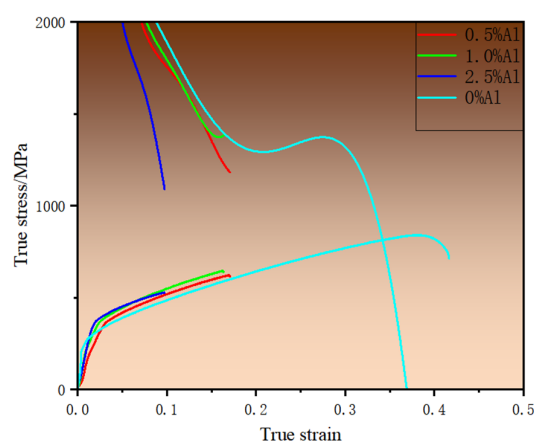
**Figure 6.** Tensile properties of specimens with different Al contents: (a) engineering stress–engineering strain curve; (b) Al content and tensile strength and yield strength.

For the 0% Al alloy, the stress–strain curve shows a long plastic stage, with a tensile strength of 578.5 MPa, yield strength of 281.9 MPa, and elongation of 0.52. This excellent ductility arises from its featureless, homogeneous single-phase microstructure, which minimizes grain boundary stress concentration and enables uniform plastic deformation. With 0.5% Al addition, the tensile strength drops sharply to 509.9 MPa, while yield strength rises significantly to 348.9 MPa, accompanied by a drastic reduction in elongation to 0.19. This is attributed to the formation of distinct grain boundaries and a heterogeneous grain structure, which act as preferential sites for crack initiation and propagation, severely limiting plastic deformation. At 1.0% Al, tensile strength slightly recovers to 547.9 MPa, while yield strength remains stable at 351.3 MPa, with elongation marginally decreasing to 0.18. The modest strength improvement is linked to moderate grain refinement and improved grain size uniformity, which partially counteracts the grain boundary embrittlement effect. For the 2.5% Al alloy, tensile strength decreases to 484.4 MPa, but yield strength continues to rise slightly to 358.1 MPa, while elongation reaches its lowest value of 0.12, showing nearly no plastic deformation. Despite significant grain refinement, severe grain boundary segregation/precipitation dominates the mechanical behavior, promoting premature crack initiation and brittle fracture, thus overriding the Hall–Petch strengthening effect.

In summary, as Al content increases from 0% to 2.5%, the yield strength increases monotonically from 281.9 MPa to 358.1 MPa due to the combined effects of grain refinement and grain boundary strengthening. In contrast, the tensile strength first decreases (0–0.5% Al), then slightly recovers (0.5–1.0% Al), and finally decreases again (1.0–2.5% Al), while the ductility shows a continuous decline. This behavior reflects the competition between the beneficial effects of grain refinement and the detrimental effects of grain boundary embrittlement induced by Al addition.

Figure 7 shows the true stress–strain curves and strain hardening curves of high-entropy alloy samples prepared at different Al contents. It can be seen from Figure 7 that

the slope of the elastic segment of the 0% Al alloy shows no significant difference from that of Al-containing alloys, indicating that the addition of a small amount of Al has little effect on the elastic modulus of the alloy. The yield strengths of the alloys with 0.5%, 1.0%, and 2.5% Al are significantly higher than that of the Al-free alloy, and the yield strength increases more obviously with increasing Al content: 2.5% Al > 1.0% Al > 0.5% Al > 0% Al. This phenomenon is attributed to the solid-solution strengthening effect of Al. Al atoms dissolve into the high-entropy alloy matrix as solute atoms, causing lattice distortion and impeding dislocation movement, thereby increasing the yield strength.

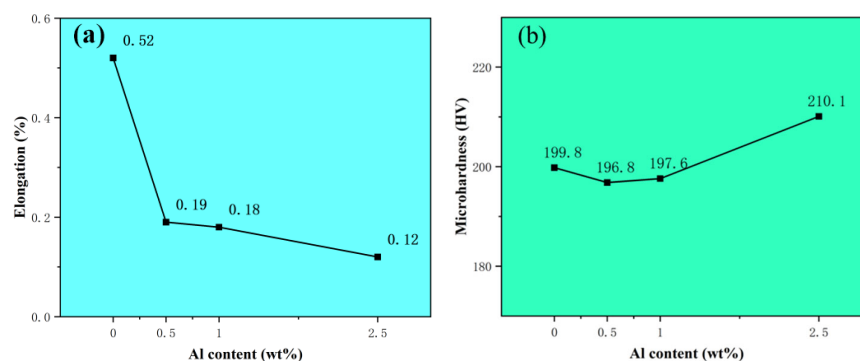


**Figure 7.** Strain hardening curves of high-entropy alloys.

The work-hardening rate of Al-containing alloys is slightly higher than that of the Al-free alloy at the initial deformation stage, indicating that Al enhances the initial work-hardening ability of the alloy. This directly reflects the negative effect of Al addition on the ductility of the alloy: the higher the Al content, the worse the uniform elongation and the earlier the fracture occurs. Solid-solution strengthening induced by Al is the main reason for the strength improvement. The atomic radius of Al is significantly different from those of the matrix elements in the high-entropy alloy, such as Fe, Co, Cr, and Ni. After dissolving into the matrix, Al causes strong lattice distortion, hinders dislocation slip and multiplication, and thus greatly improves the yield strength and tensile strength.

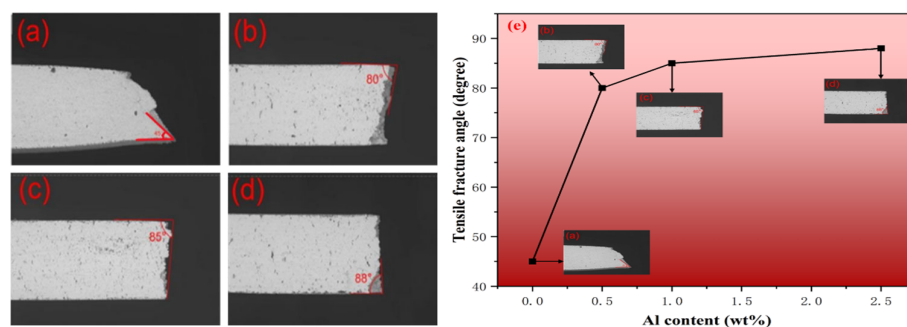
Figure 8 illustrates the influence of Al content on the elongation and hardness of the CoCrFeNiMn high-entropy alloys. As observed in Figure 8a, the elongation of the alloy decreases with increasing Al content due to the superior plasticity of the FCC phase and the inherent brittleness of the BCC phase. As the Al content increases, the phase structure of the alloy transitions from a single face-centered cubic (FCC) phase to a dual-phase (FCC + BCC) structure and ultimately evolves into a body-centered cubic (BCC) structure, resulting in the continuous reduction in elongation.

The hardness trends of alloys with different Al contents are shown in Figure 8b. Compared to the Al-free sample, the 0.5% Al and 1.0% Al alloys exhibit a slight decrease in hardness. Although aluminum (Al) is a known strengthening element that enhances strength and hardness by forming finely dispersed phases in the alloy, its addition also modifies microstructural features, such as grain size and phase transformations, which may counteract these strengthening effects. However, with further increases in Al content, the hardness progressively rises, reaching its peak in the 2.5% Al sample. This enhancement is attributed to the formation of BCC (body-centered cubic) phases, which induce secondary-phase strengthening, combined with solid-solution strengthening from Al atoms occupying lattice sites.



**Figure 8.** Deformation capacity of samples with different Al contents: (a) plasticity—elongation; (b) rigidity—hardness.

Figure 9 displays the variation in tensile fracture angles across different Al contents. As the Al content increases, the fracture angle gradually increases from  $45^\circ$  (0% Al) to  $88^\circ$  (2.5% Al). This behavior is consistent with reports on Cu-Ag and Cu-Zn alloys, where macroscopic failure similarly occurs via shear fracture with angles exceeding  $45^\circ$ , mirroring the observations in this study [28,29].



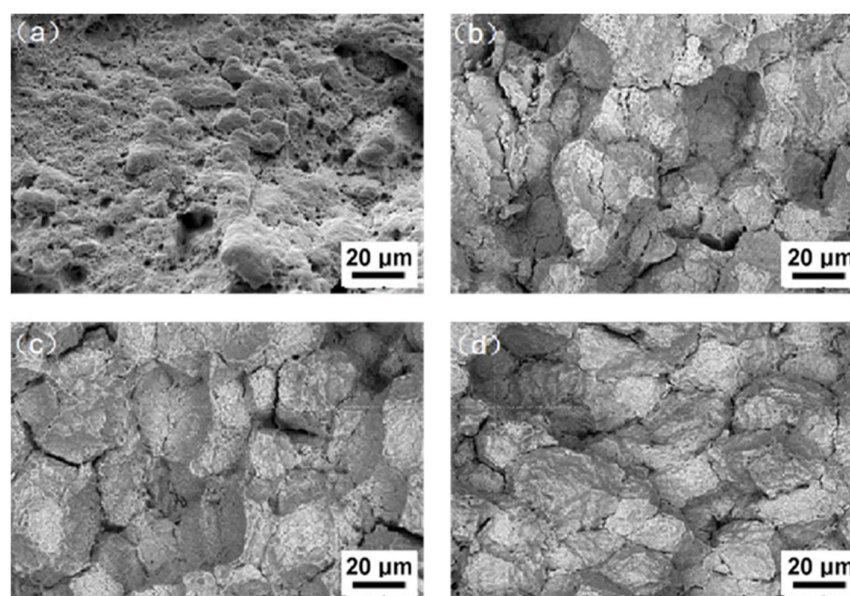
**Figure 9.** Different Al contents of (a) 0% Al; (b) 0.5% Al; (c) 1.0% Al; and (d) 2.5% Al; and (e) angle difference diagram.

Material fracture can be generally divided into brittle fracture and ductile fracture according to the overall deformation characteristics. According to the crack propagation path inside the material, fracture modes can be further subdivided into transgranular fracture, intergranular fracture, and mixed transgranular–intergranular fracture. In transgranular fracture, cracks propagate directly through the interior of grains, often accompanied by obvious plastic deformation and usually corresponding to ductile fracture characteristics. In contrast, in intergranular fracture, cracks preferentially propagate along grain boundaries, which is usually related to grain boundary weakening, segregation or embrittlement, and tends to exhibit brittle fracture characteristics.

In the present alloys, the gradual increase in fracture angle with Al addition indicates a transformation in the fracture mechanism. The increase in Al content enhances solid-solution strengthening and restricts dislocation movement, which reduces overall ductility and changes the direction and path of crack propagation. As a result, the fracture mode gradually deviates from the typical  $45^\circ$  shear fracture and approaches a near-normal fracture mode, reflecting the combined effect of Al addition on the plastic deformation capacity and crack growth behavior of the CoCrFeNiMn high-entropy alloy.

Figure 10 shows the fracture morphologies at different aluminum contents. The fracture surface of the Al-free CoCrFeNiMn alloy exhibits relatively rough fracture characteristics due to the absence of secondary-phase particles (e.g., BCC) or specific microstructural features to provide effective crack deflection and propagation resistance. The fracture sur-

face is relatively rough, lacking visible dimples or ligament structures, indicating limited plasticity and toughness. Upon Al addition, the fracture morphology begins to change. The introduction of Al promotes the formation of secondary-phase BCC particles, which create observable features on the fracture surface, such as fine dimples or particulate structures. These features suggest improved plasticity and toughness, as the BCC particles enhance resistance to crack propagation and induce crack deflection. With the Al content increased to 1%, the fracture morphology further improves, showing a higher density of fine dimples and secondary-phase particles, indicating enhanced ductility. This demonstrates that the increased fraction of BCC particles aids in energy dissipation during crack propagation, thereby improving overall toughness. In the 2.5% Al alloy, the fracture surface displays the most pronounced dimples and particulate features, signifying superior plasticity and toughness. The abundance of BCC particles effectively hinders crack propagation and increases deformation capacity prior to fracture. Additionally, complex fracture characteristics, such as river patterns, dimples, and fibrous structures, are observed, which are typical indicators of high-toughness alloys.



**Figure 10.** Fracture morphology of the alloy with different Al contents: (a) 0% Al; (b) 0.5% Al; (c) 1.0% Al; (d) 2.5% Al.

#### 4. Conclusions

In this experiment, Co, Cr, Fe, Ni, Mn, and Al were used as raw materials, and the samples were prepared by spark plasma sintering. The phase composition and microstructure of the alloy were analyzed, and a series of mechanical properties of the samples were tested. The following conclusions were drawn:

- (1) The alloy transitions from a single FCC phase (0–0.5 wt.% Al) to a mixed FCC + BCC dual-phase structure (1.0–2.5 wt.% Al), with the BCC phase becoming progressively dominant at higher Al additions. This phase evolution is critical for tailoring performance, as FCC phases typically offer high ductility, while BCC phases enhance strength and hardness.
- (2) With increasing Al content, the hardness of the alloy increases continuously, which can be attributed to the lattice distortion of the solid-solution matrix and the formation of second-phase particles induced by Al addition, and higher hardness reflects stronger deformation resistance and wear resistance of the material. This trend directly translates to improved deformation resistance and wear performance, making higher-Al

- variants promising candidates for components subjected to abrasive wear or high-contact loads, such as industrial tooling or structural parts requiring surface durability.
- (3) Tensile strength exhibits a non-monotonic, fluctuating trend with Al addition, governed by competing microstructural effects. While solid-solution strengthening and BCC phase formation can boost strength, excessive Al-induced grain boundary segregation or brittle intermetallic precipitation may degrade it. This balance requires careful composition optimization to meet specific structural load-bearing requirements, such as in aerospace or automotive components where consistent tensile performance is critical.
  - (4) Contrary to hardness, elongation decreases continuously with increasing Al content, reflecting a transition from ductile to brittle fracture behavior. The FCC-dominated low-Al alloys retain excellent plastic deformability, which is essential for forming operations (e.g., rolling, stamping) and for applications requiring tolerance to impact or overload. In contrast, high-Al alloys with reduced ductility are more suited for static, low-stress environments, where high hardness and wear resistance are prioritized over formability or toughness.

Overall, these findings highlight that Al addition provides a versatile route to tailor the balance between strength, hardness, and ductility in CoCrFeNiMn high-entropy alloys. For practical applications, low-Al ( $\leq 0.5$  wt.%) compositions are preferable for forming processes and ductility-critical structural uses, while higher-Al variants offer enhanced hardness and wear resistance for wear-resistant components. Future work should focus on optimizing Al content and processing routes to mitigate the ductility trade-off, enabling the development of high-performance high-entropy alloys for a broader range of industrial applications.

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