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Effect of Al content on microstructure and wear properties of FeCrNiMnAlx high-entropy alloys

Xuewei Xing, Ying Liu, Jinkang Hu and Wei Li

Institute of Advanced Wear & Corrosion Resistant and Functional Materials, Jinan University, Guangzhou 510632, Guangdong, People’s Republic of China

E-mail: liuying2000ly@163.com

Abstract

A series of FeCrNiMnAlx (x = 0, 0.3, 0.5, 0.8, 1.0 in molar ratio) high entropy alloys (HEAs) were prepared by the vacuum arc melting method. The effects of Al content on the microstructure, mechanical and wear properties were investigated. For FeCrNiMn alloy, the microstructure was mainly a homogeneous structure with face-centered cubic (FCC) phase, whilst FeCrNiMnAl0.3 produced a dendritic microstructure consisting of a mixture of FCC + BCC + B2 phases, and the mixture BCC + B2 dendritic interdendritic microstructure appeared when the molar ratio of Al is beyond 0.5. The hardness and yield stress of the HEAs are effectively improved with the increased Al amount but the ductility is lowered. In this case, FeCrNiMnAl alloy showed decreased yield stress due to the deteriorated ductility. Moreover, the friction coefficient decreases, and the wear resistance improved with the increased aluminum content. FeCrNiMnAl0.8 HEAs have the best wear resistance due to the advantages of achieving a balance of strength and ductility.

1. Introduction

In recent years, high entropy alloys (HEAs) have attracted significant attention in materials science since Yeh et al developed the new design concept of HEAs in 2004 [1]. Different from the conventional alloys based on one or two principal elements such as iron or aluminum alloys, HEAs are a new type of metal materials comprised of five or more principal metallic elements with amounts in the range 5–35 at% and possess larger mixing entropies (∆S config ≥ 1.61R, R is the universal gas constant). Owing to the high mixing entropy effect, HEAs intend to form stable solid solutions such as BCC, FCC, or FCC + BCC structure [2–4]. Due to the four ‘core effects’ of high entropy, namely high entropy, sluggish diffusion, severe lattice distortion, and cocktail effects, HEAs exhibit some superior mechanical properties such as high hardness, strength, and ductility [5], exceptional thermal stability [3], excellent oxidation resistance at high temperature, good wear-resistant properties, and corrosion resistance, therefore HEAs become attractive materials for the modern industrial applications [5, 6].

To date, many high entropy alloy systems have been exploited in the past decade, and one of the most reported alloy systems contains Al [2, 7]. It was reported that Al modified the as-cast microstructure of Al5CoCrFeNi HEAs from the FCC structure for low Al content (x < 0.5) to FCC + BCC mixture for 0.5 (11.0 at% Al) < x < 0.9 (18.4 at% Al) and to BCC structure when x exceeds 0.9 [8]. Meanwhile, the BCC phases show a nano-scale two-phase structure due to spinodal decomposition and the as-cast Al0.9 alloy has a maximum hardness of HV 527. The similar phenomenon is seen in other studies [9, 10]. The (FeCoNiCrMn)1–xAlx (x = 0–20 at%) HEAs have single-phase FCC for x < 8 (8 at% Al), duplex BCC + FCC for 8 < x < 16, and BCC or BCC + B2 for x > 16 [7]. Along with the change of the structure, the hardness, tensile strength increase, and the ductility decrease with increasing Al [7]. The HEAs can be strengthened by solid solution hardening, ultratine grain strengthening, and precipitation strengthening. Lim et al [10] introduced a novel duplex Al12.9Co20.9Cr27.3Fe23.9Ni11.9 high-entropy alloy reinforced with B2 particles and found the alloy had an excellent tensile strength of 1031 MPa and acceptable tensile ductility. Al addition in Al5CoCrCuFeNi HEAs improved the hardness and the wear resistance by impeding plastic deformation and delamination as the
structure transforms from a single-phase FCC structure to BCC + FCC and then to single-phase BCC with increasing Al [11].

As Cobalt is expensive, the inexpensive Co-free HEAs are interesting. Two high-entropy alloys (HEAs) Al$_x$CrFe$_{1.5}$MnNi$_{0.5}$ (x = 0.3 and 0.5) were designed by Chen et al [12] and microstructures and properties were investigated. Al$_{0.3}$CrFe$_{1.5}$MnNi$_{0.5}$ alloy has a dual-phase structure of FCC phase and BCC phase, and Al-Ni rich precipitates of B2-type BCC structure disperse in the BCC phase. And the Al$_{0.5}$CrFe$_{1.5}$MnNi$_{0.5}$ alloy has a matrix of BCC phase with Cr-rich particles of BCC structure and Al-Ni rich of B2 phase. Both alloys display a significant high-temperature age-hardening phenomenon. The Al$_{0.3}$CrFe$_{1.5}$MnNi$_{0.5}$ alloy can attain the highest hardness of 850 HV by aging at 600 °C for 100h, and Al$_{0.5}$CrFe$_{1.5}$MnNi$_{0.5}$ can get a even higher hardness of 890 HV. It was reported that Al$_{x}$CrFeMnNi (x = 0.5–0.8) high-entropy alloys with trimodal distributions of coherent B2 precipitates exhibit a good combination of the high compressive yield strength (1091–1200 MPa) and large plasticity (> 45%) [13]. Adjusting the Al content slightly changed the average size and volume fraction of the precipitates [13]. Stepanov et al [14] studied microstructure and mechanical properties of the (Fe$_{38}$Mn$_{25}$Cr$_{20}$Ni$_{15}$)$_{100-x}$Al$_x$ high entropy alloys with a different Al content (x = 1–14 at%). It was found that the addition of a small amount of Al (x = 2–6) increase the fraction of the BCC phase to 26% and formed fine B2 precipitates with Ni-Al of the BCC phase. At higher amounts of Al (x = 10 and x = 14), the microstructure consisted of coarse BCC matrix grains with the B2 precipitates inside. The addition of Al content from 0 to 10 at% tends to strengthen the alloys but further increase in Al concentration did not influence strength considerably. Wear is the main performance of the metal material failure forms and HEAs can be designed and expected to acquire excellent wear properties. Joseph et al [1] observed the wear rate of Al$_{0.3}$CoCrFeNi remains constant above 600 °C, which was attributed to the strengthening effect of B2 precipitates. Chen et al [5] found that FeCrNiMnAl HEAs coating had a microhardness value of 432.2 HV, which had a lower friction coefficient compared with the substrate by the 0.55 and exhibited superior wear resistance. As less is still known about the wear properties of FeCrNiMnAl series HEAs, the present work aims to study as-cast microstructure, mechanical and wear properties of the FeMnCrNiAl$_x$ HEAs changed with Al contents. Of particular interest was appropriate alloying with Al could improve the wear resistance in the HEAs.

2. Materials and methods

Five FeCrNiMnAl$_x$ (x = 0, 0.3, 0.5, 0.8 and 1.0 in molar ratio) alloys were synthesized by arc melting under a Ti-gettered high-purity argon atmosphere in a water-cooled copper crucible. The pure particle of Fe (99.9%), Cr (99.9%), Ni (99.9%), Mn (99.9%), and Al (99.9%) were used as raw materials. All ingots were flipped and remelted 7 times under electromagnetic stirring to ensure homogeneity. The size of the ingot was approximately $\Phi$ 35 mm $\times$ 12 mm. The specimens for microstructural characterization, mechanical testing and friction testing were cut from the produced ingots using electric spark cutting machine. Samples for testing were prepared by 320#, 800#, 1000#, 1500#, 2000# SiC paper and careful mechanical polishing with 2.5 μm and 1 μm polishing paste. The polished samples were processed by ultrasonic, and finally dried for use. All treated samples need to have a dry, pollution-free surface.

The Crystal structures were analyzed by x-ray diffraction (XRD) (Ultima IV, Rigaku, Tokyo, Japan) with the 2θ ranging from 30° to 110° at a speed of 8°/min. The microstructure and chemical composition were examined by Nova Nano SEM430 scanning electron microscope equipped with an energy dispersive spectrometer (EDS). The hardness was measured using an HVS-1000 hardness tester with a loading force of 200 GF for a dwell time of 15 s. More than six points were measured in a sample and the average value was calculated. Room temperature compressive tests were performed on a cylinder specimen with the size of $\Phi$ 5 mm $\times$ 10 mm on an MTS E45.305...
electronic universal material testing machine at a loading speed of 1 mm min$^{-1}$. Compression mechanical tests were performed using samples of the alloys in the as-cast condition. Samples for this test were prepared by careful mechanical polishing in order to avoid the impact of cutting marks on the samples. The photo of the compression samples is shown in figure 1(a).

The friction and wear properties of the FeCrNiMnAl$_x$ HEAs were evaluated using a reciprocating tribometer (Rtec Co. Ltd, the USA) with a configuration of ball-on-plate at room temperature in air atmosphere. The schematic diagram of reciprocating ball-on-plate was shown in figures 1(b), (c). Before the testing, the test surface of samples were ground by 600#, 1000#, 2000# SiC paper and polished with 3$\mu$m suspension, and had a surface roughness ($S_a$) of 0.034$\mu$m. The YG6 carbide ball (94%WC and 6%Co) with a hardness of 89.5 HRA and a diameter of 6 mm was used as the counterparts. The test conditions were set as the applied load of 5 N, duration of 40 min, a sliding stroke of 5 mm, reciprocating frequency of 5 Hz, and a total slide distance of 120 m. To ensure repeatability, each test was repeated three times. After tribological tests, the 3D surface profiles of the wear tracks on plates were measured by the 3D profiler (Rtec, the USA). The wear traces of the samples were analyzed by using a Nova Nano SEM430 scanning electron microscope. The wear rates ($W_s$) were calculated using the following formula:

$$W_s = \Delta V / (p \cdot d)$$

Here $\Delta V$ is the volume loss, $p$ is the applied load and $d$ is the total sliding distance.

### 3. Results and discussion

#### 3.1. Microstructural characteristics

Figure 2 shows the XRD patterns of the five FeCrNiMnAl$_x$ HEAs ($x = 0, 0.3, 0.5, 0.8, 1.0$). The results indicate that three cubic crystal structures of FCC, BCC and ordered BCC phases (B2) are found, which have different lattice parameters of 0.365 nm, 0.290 nm and 0.289 nm, respectively. As the characteristic B2 superlattice reflections can be detected as primitive cubic with lattice parameters and the B2 phase can be recognized as the AlNi compound by the peaks known from the ICDD/JCPDS card (PDF-#20–0019). FeCrNiMn alloy show peaks corresponding to the main FCC structure, while FeCrNiMnAl$_{0.3}$ exhibits FCC + BCC + B2 structure with the intensity of FCC peak gradually decrease and the intensity BCC and B2 peak increase, and the higher Al HEAs (FeCrNiMnAl$_{0.5}$, FeCrNiMnAl$_{0.8}$ and FeCrNiMnAl$_{1.0}$) exhibit BCC + B2 structure. It means the FCC phase gradually disappears and converts to the BCC and B2 phase with increasing Al content. The result is consistent with Zhang et al [13], Stepanov et al [14] and Joseph et al [15], etc. The same alike structure evolution is found by Joseph et al [15] on Al$_{1-x}$CoCrFeNi alloys in which the FCC phase gradually disappears and converts to the BCC and B2 phase with increasing Al content. Wang et al [16] explained the shifting trend of FCC to BCC by Al addition in Al$_{1-x}$CoCrFeNi alloy as topological instability caused by lattice distortion. Al has a large atomic
radius, so more Al enters into the lattice of FCC promotes lattice distortion and causes some atoms to be squeezed out, thus obtaining a new lattice form of BCC. Some semiempirical thermodynamic criteria have been studied to predict the stability of high entropy alloys. Guo et al [17] points out that the FCC phases could develop in HEAs when $\text{VEC} > 8$, BCC phases can develop when $\text{VEC} < 6.87$, and both FCC and BCC phases could develop when $\text{VEC}$ ranges between 6.87 and 8.0. Table 1 gives the calculated thermodynamic parameters of FeCrNiMnAl$_x$ alloys. It is obvious that the VEC value of five FeCrNiMnAl$_x$ HEAs is between 6.80 and 7.75. It seems more Al content favors the forming of the BCC phase. The lattice parameters of the FCC, BCC and B2 phases were 0.364, 0.291, 0.411nm, respectively. When $x = 0.5$ or above, the FCC phase disappears and B2 + BCC coexists in the HEAs with higher Al. This is consistent with the case of Al$_x$CrFeMnNi ($x = 0.5$–0.8) high-entropy alloys (HEAs) studied by Zhang et al [13] and (Fe$_{40}$Mn$_{32}$Cr$_{28}$Ni$_{15}$)$_{100-x}$Al$_x$ Studied by Stepanov et al [14].

Table 1. Calculated thermodynamic parameters of FeCrNiMnAl$_x$ alloys.

| Alloy       | $\Delta H_{\text{mix}}$(KJ/mol) | $\Delta S_{\text{mix}}$(J·K$^{-1}$·mol$^{-1}$) | $T_m$(K) | $\Omega$ | $\delta$(%) | VEC  |
|-------------|----------------------------------|-----------------------------------------------|----------|----------|-------------|------|
| FeCrNiMn   | -4.00                            | 11.52                                         | 1809.5   | 5.21     | 3.57        | 7.75 |
| FeCrNiMnAl$_{0.3}$ | -7.51                           | 12.82                                         | 1418.5   | 2.42     | 4.66        | 7.42 |
| FeCrNiMnAl$_{0.5}$ | -9.28                           | 13.15                                         | 1400.8   | 1.98     | 4.25        | 7.22 |
| FeCrNiMnAl$_{0.8}$ | -11.39                          | 13.35                                         | 1378.6   | 1.61     | 4.95        | 6.96 |
| FeCrNiMnAl$_{1.0}$ | -12.48                          | 13.37                                         | 1361.8   | 1.46     | 5.82        | 6.80 |

Table 2. EDS analysis of ID and DR phases of FeCrNiMnAl$_x$ alloys.

| Elements | Al$_{0.0}$ (at%) | Al$_{0.3}$ (at%) | Al$_{0.5}$ (at%) | Al$_{0.8}$ (at%) | Al$_{1.0}$ (at%) |
|----------|------------------|------------------|------------------|------------------|------------------|
| Fe       | 24.88            | 14.50            | 23.32            | 8.92             | 30.69            | 7.82            | 13.23            | 5.82             | 10.28            |
| Cr       | 23.94            | 17.80            | 20.37            | 6.40             | 29.46            | 5.71             | 13.31            | 2.07             | 7.69             |
| Ni       | 25.21            | 31.24            | 24.67            | 38.36            | 10.85            | 33.64            | 32.11            | 42.32            | 33.88            |
| Mn       | 25.97            | 21.57            | 24.55            | 22.23            | 22.53            | 14.11            | 14.69            | 12.75            | 14.14            |
| Al       | 0                | 14.88            | 7.09             | 7.09             | 7.09             | 7.09             | 7.09             | 7.09             | 7.09             |

Figure 3. SEM images of FeCrNiMnAl$_x$ alloys: (a) for $x = 0$, (b), (b') for $x = 0.3$, (c), (c') for $x = 0.5$, (d) for $x = 0.8$, (e), (e') for $x = 1.0$. (f) Volume fractions variation of ID and DR regions with Al content variation.
Table 3. Shows the melting point ($T_m$), shear modulus ($\mu$), atomic radius ($r_i$) and valence electron concentration (VEC) of the elements, and the mixing enthalpy (kJ/mol) of different atom pairs.

| Elements ($T_m$, $\mu$, $r_i$, VEC) | Al   | Cr   | Fe   | Mn   | Ni   |
|-----------------------------------|------|------|------|------|------|
| Al (660.3 °C, 26GPa, 143 pm, 3)   | —    | 10   | 11   | 19   | 22   |
| Cr (1907 °C, 115.1GPa, 128 pm, 6) | —    |      | 1    | 2    | —    |
| Fe (1538 °C, 81.4GPa, 126 pm, 8)  | —    |      |      | 0    | 2    |
| Mn (1246 °C, 39GPa, 127 pm, 7)    | —    |      |      |      | 8    |
| Ni (1455 °C, 80GPa, 124 pm, 10)   | —    |      |      |      |      |

Figure 4. (a) Microhardness of FeCrNiMnAl$_x$ alloys; (b) Microhardness of the ID and DR respectively in FeCrNiMnAl$_{0.3}$ and FeCrNiMnAl$_{1.0}$; (c) Engineering stress and strain curves of FeCrNiMnAl$_x$ alloys under compression.

Figure 3 shows the microstructure of five FeCrNiMnAl$_x$ HEAs ($x = 0, 0.3, 0.5, 0.8, 1.0$). While the FeCrNiMn alloy presents FCC grain microstructure, Al-adding alloys display a dendritic (DR) interdendritic (ID) microstructure. Combined with XRD results, it can be inferred that the bright ID region corresponds to single FCC phase, and the dark DR region is the BCC + B2 structure with a uniform honeycomb-like dispersion of spherical particles in FeCrNiMnAl$_{0.3}$ HEA. The region ID area is reduced and in which some coarse rectangular particles appeared when $x$ is 0.5. When $x$ is above 0.5, long strip particles appeared in the region ID. And the long strip presented uniform distribution when $x = 0.8, 1.0$. While in the DR region, it was found that a large number of approximate spherical precipitates with the size of 0.1−0.5 μm were embedded in the substrate, which was densely distributed and uniform. Furthermore, the image with higher magnification clearly shows that the coarse bulk microstructure is decomposed to flake and rod microstructure with the increase of Al content.

Table 2 shows the EDS analysis of ID and DR phases of FeCrNiMnAl$_x$ alloys. According to EDS results, the honeycomb-like spherical (DR region) precipitates are enriched in Al and Ni. The matrix phase in HEAs and the single FCC phase (ID region) in FeCrNiMnAl$_{0.3}$ HEA are enriched in Cr and Fe. The Mn content is not much different in the DR and ID region. The special BCC + B2 structure morphologies could attribute to the spinodal decomposition, which is found in some Al-containing HEAs [6, 17]. In that research, two BCC phases with (Al, Ni)-enriched (B2) and (Co, Fe, Cr)-enriched (BCC) were observed. The case was also observed in the study of Zhang et al. [13] table 3 shows the mixing enthalpy (kJ/mol) different atom pairs [18], when the mixing enthalpy of a multi-principal component alloy is less than 0, the bonding force between alloy elements is strong and it is easy to form ordered phase or intermetallic compound. And the more negative enthalpy of mixing, the more obvious effect will become. The mixing enthalpy of Ni-Al is much negative (with $\Delta H_{\text{mix}} = -22$KJ/mol), thus with more addition of Al element, the fraction of BCC phase increases, more Al and Ni atoms dissolved into the BCC phase tend to form Ni-Al-rich precipitation phase. Further detailed analysis in figure 3(f) reveals that Volume fractions variation of ID and DR regions with different Al content. And the higher magnification images clearly show that the coarse grains change from massive to flake with the increase of Al. By adjusting the Al content in the alloy system, the proportion of ID and DR regions shows a great change. In contrast, when Al content is $x = 0.5$, the area proportion of ID region is smaller than that of ID region when Al content is $x = 1.0$. With the increase of Al content from $x = 0.5$ to $x = 1.0$, the area proportion of ID area increased continuously, whereas that of DR area decreased continuously, indicating that the increase of Al content has an important influence on the regulation of tissue distribution.

3.2. Mechanical properties

Figure 4(a) shows the hardness of the five FeCrNiMnAl$_x$ HEAs ($x = 0, 0.3, 0.5, 0.8, 1.0$) with a loading force of 200 GF for a dwell time of 15 s. It is observed that the hardness increased from 195 HV$_{0.2}$ to 483 HV$_{0.2}$ as the aluminum content increases and FeCrNiMnAl$_{1.0}$ alloy has 2.5 times microhardness as much as FeCrNiMn alloy.
When measured with a less load of 10 GF, the microhardness of the ID and DR alone can be measured. Figure 4(b) shows the FeCrNiMnAl0.3 HEA has microhardness of 188 HV0.01 in the ID region (FCC phase) and 453 HV0.01 in the DR region (BCC + B2). FeCrNiMnAl0.8 HEA has microhardness of 395 HV0.01 in the ID region (BCC + B2) and 623 HV0.01 in the DR region (BCC + B2). The microhardness depends on the lattice types and microstructures. At higher Al contents, the value of BCC hardness becomes higher, the microstructure of the spinodal decomposition structure introduces obvious precipitation strengthening and grain boundary strengthening effects, the hardness of BCC and B2 phases are much higher than that of FCC phase. In comparison with the microstructural evolution indicated in figure 3, it can be seen that the hardness value rise is coincident with the large increase of the volume fraction of BCC and B2 phases.

Figure 5(c) and table 4 show presents stress-strain curves obtained during compression testing at room temperature. The yield strength of the FeCrNiMnAlx alloys increases from 297 MPa to 1269 MPa with the increase of Al content in the range of x = 0 to x = 0.8. It is noted that FeCrNiMnAl0.3 with FCC + BCC + B2 phase structure exhibit superior compressive mechanical properties and it is dramatically that HEAs are exceptionally brittle with x = 1.0. With the increase of Al content, the large radius atom (Al) in BCC can hinder the movement of atoms in FeCrNiMnAlx HEAs and can trigger solid solution strengthening effect, and the B2 phase with high hardness shows good second phase strengthening effect. But the stress concentration can happen in the coarse BCC + B2 area, and cracking is apt to generate during the compression, thus the HEAs with excess Al content when x = 1.0 will turn fragile.

### 3.3. Wear behavior

Figure 5(a) shows the coefficient of friction (COF) of FeCrNiMnAlx high entropy alloys at room temperature under a 5N applied load in dry conditions. In the beginning, the COF had an initial rapid increase and then tended to be stable and flat. Later, the COF of the FeCrNiMnAlx HEAs (x = 0, 0.3, 0.5) fluctuated in the range of 0.717 to 0.756, 0.596 to 0.735, 0.485 to 0.539. Al addition has a positive effect on reducing friction coefficient of the FeCrNiMnAlx HEAs significantly, the COF of Al0.8 and Al1.0 were relatively small and more stable among the five samples. However, the COF of Al0.3 fluctuated obviously in the friction process, and fluctuations of the COF of Al0.8 and Al1.0 are relatively smooth, increased from 0.523 to 0.616 and 0.544 to 0.617.

Figure 5(b) gives the volume losses and wear rate of the samples measured and calculated by a 3D surface profiler. The wear volume was 1.213, 1.108, 0.497, 0.416, 0.535 mm³ for the FeCrNiMnAlx HEAs (x = 0, 0.3, 0.5, 0.8, 1.0). The average wear volume loss decreased with the increase of Al content in the range of Al = 0–0.8 but had a rebound Al = 1.0 HEA respectively. The specific wear rate of five HEA was 202.209 × 10⁻⁶, 184.615 × 10⁻⁶.

| Alloys            | Yield stress [MPa] | Maximum stress [MPa] | Compressive strain to fracture [%] |
|-------------------|-------------------|----------------------|-----------------------------------|
| FeCrNiMn         | 297               | 2321                 | 55                                |
| FeCrNiMnAl0.3     | 538               | 2799                 | 55                                |
| FeCrNiMnAl0.5     | 1065              | 2576                 | 39                                |
| FeCrNiMnAl0.8     | 1269              | 2235                 | 24                                |
| FeCrNiMnAl1.0     | 971               | 1064                 | 5                                 |

![Figure 5](image-url)
$82.829 \times 10^{-6}, 69.256 \times 10^{-6}, 89.171 \times 10^{-6}$ mm$^3$/N.m, respectively. Al addition caused a significant improvement in the wear resistance of HEAs. The best wear resistance of HEAs was corresponding to the excellent microhardness and toughness.

To understand the different tribological performance, the morphology and roughness of worn surface were investigated. Figure 6 shows the 3D worn morphologies, roughness and cross-section curves of wear scars of five samples with different Al content. The wear scars depth of the FeCrNiMnAl$_x$ ($x = 0, 0.3, 0.5, 0.8, 1.0$) samples is 100.4 µm, 82.9 µm, 44.2 µm, 22.4 µm, 22.9 µm, respectively, which decreases gradually with the Al content until Al content is high at $x = 1.0$. This also respond the changing trend of the wear volume and wear rate. The FeCrNiMn and FeCrNiMnAl$_{0.3}$ HEA show deeper and wider wear scar, and FeCrNiMnAl$_{0.8}$ HEA has the smallest depth and width of wear scar compared with the samples of the other four components. It is concluded that the alloy material with small Al content has poor wear resistance. The FeCrNiMnAl$_{0.8}$ HEA has the best wear resistance. As shown in the figure 6(a), the roughness of wear trace in HEA samples change with Al content variation. FeCrNiMn HEA sample after sliding has the biggest roughness with measured values of $Ra = 0.565$ µm, and FeCrNiMnAl$_{0.8}$ HEA has the smallest roughness with $Ra = 0.257$ µm. In the process of friction, the microstructure of the lowest hardness sample surface is apt to damage and the wear debris is generated. In the final sliding, the random stacking of wear debris led to high roughness, which means adhesive wear [19] can be the important type of wear in FeCrNiMn HEA. The decreasing roughness in other HEAs indicating other wear mechanism occur in the sliding process. To further analyze the wear mechanisms, SEM and EDS are conducted to investigate the worn surfaces and debris of FeCrNiMnAl$_x$ HEAs. As is seen in figure 7, the worn surface of FeCrNiMn and FeCrNiMnAl$_{0.3}$ HEAs had more peeling or rips generated due to plastic deformation [20], long and deep continuous grooves due to abrasive wear, the big and a large amount of debris with less oxides by EDS showing evidence of adhesive wear. With the increase of Al content, the plastic deformation was relatively small and the deformation rips alleviated on the worn surfaces of FeCrNiMnAl$_{0.5}$ HEA and almost invisible in FeCrNiMnAl$_{0.8}$ and FeCrNiMnAl$_{1.0}$ samples, on which plowing grooves still existed but become less and shallower indicating that the wear mechanism turn to be the typical abrasive wear. There is several flaking several small oxide particles appeared on the worn surface of the Al$_{1.0}$ sample. With the increase of Al content, the wear debris become finer, which is particle-like and, around 10 µm in size when x is above 0.8. As the EDS result of the

Figure 6. 3D worn morphologies and roughness of the worn surface: (a) FeCrNiMn, (b) FeCrNiMnAl$_{0.3}$, (c) FeCrNiMnAl$_{0.5}$, (d) FeCrNiMnAl$_{0.8}$, (e) FeCrNiMnAl$_{1.0}$ and (f) the measured cross-section curves of wear scars.
debris is displayed in table 5, it is obvious that lower oxygen content existed in the debris of FeCrNiMn and FeCrNiMnAl0.3 HEAs and the oxygen concentration increase with the increase of Al content in FeCrNiMnAlx HEAs, which indicated some oxidation wear could occur in the surface during the wear test.

It is well known that the wear resistance of metallic materials is highly dependent on their microstructure, phase composition and phase distribution. In FeCrNiMnAlx, with the increase of Al content, the fraction of FCC phase lessened and the fraction of BCC + B2 phases increased and even FCC phase disappeared when x is beyond 0.5, and with more addition of Al element, more Al and Ni atoms dissolved into the BCC phase tend to form Ni-Al-rich B2 precipitation phase [21]. BCC phase is stronger than FCC due to the difference in the number of available slip systems. The precipitation of fine scale B2 precipitates increases the hardness of the alloy and the BCC + B2 phases mixture is much harder than FCC phase. During the wear test, the soft FCC and ductile phase will suffer plastic deformation and damage accumulation below the contact surface and some particles are detached from the surface. The BCC + B2 phases area can effectively prevent plastic deformation and the plow cutting from proceeding and interrupt the groove at any time. Wearing resistance is improved with the increase of Al content. Although there are always weak oxidative wear particles, their number tend to increase but size tend to decrease. Debris left on the worn surface may cause grooves and scratches to appear, which indicates the wear mechanism turn to mainly abrasive wear with only a small amount of oxidative wear. However, when x is 1.0, the hard long strip Ni-Al-rich B2 phase in ID region get more and coarse than spherical debris is displayed in table 5, it is obvious that lower oxygen content existed in the debris of FeCrNiMn and FeCrNiMnAl0.3 HEAs and the oxygen concentration increase with the increase of Al content in FeCrNiMnAlx HEAs, which indicated some oxidation wear could occur in the surface during the wear test.

Table 5. EDS compositions (in at%) for the debris of different aluminum contents which FeCrNiMnAlx (x = 0, 0.3, 0.5, 0.8, 1.0). The numbers refer to figure 7.

| Elements | Al (at%) | Al (at%) | Al (at%) | Al (at%) | Al (at%) |
|----------|----------|----------|----------|----------|----------|
|          | Point 1  | Point 2  | Point 3  | Point 4  | Point 5  |
| Fe       | 19.98    | 19.74    | 17.22    | 13.17    | 14.13    |
| Cr       | 20.23    | 17.70    | 15.72    | 11.69    | 12.78    |
| Ni       | 15.95    | 18.76    | 16.39    | 12.54    | 13.49    |
| Mn       | 21.18    | 18.94    | 16.80    | 12.58    | 13.68    |
| Al       | 0        | 6.15     | 8.10     | 7.84     | 8.08     |
| O        | 22.66    | 18.71    | 25.78    | 42.19    | 37.83    |

Figure 7. SEM microstructures of worn surface and wear debris of FeCrNiMnAlx alloys with different aluminum contents (x-value): (a)–(a1) x = 0; (b)–(b1) x = 0.3; (c)–(c1) x = 0.5; (d)–(d1) x = 0.8; (e)–(e1) x = 1.0.
B2 particles region DR, which can be highly brittle, stress concentration is liable to occur under repeated shear stress of the abrasive material and cracks or fall off will be generated. Therefore, when the Al content was x less than 0.5, the wear mechanism was mainly adhesive wear, abrasive wear and oxidative wear. When the Al content was x above 0.8, the wear mechanism was mainly abrasive wear and oxidative wear.

4. Conclusion

In this study, the microstructure, mechanical properties, friction and wear properties of the FeCrNiMnAlx (x = 0, 0.3, 0.5, 0.8, 1.0) high entropy alloys were discussed. Based on obtained results and analyses, tentative conclusions can be drawn as follows:

1. The addition of Al changes the microstructure of FeCrNiMnAlx alloys. As the microstructure for FeCrNi alloy was mainly homogeneous structure with FCC phase, two BCC phases with (Al, Ni)-enriched (B2) and (Co, Fe, Cr)-enriched (BCC) were appeared as dendritic microstructure in FeCrNiMnAl0.3 alloy, and the FCC phase disappeared and the mixture BCC + B2 dendritic interdendritic microstructure appeared when the molar ratio of Al is beyond 0.5.

2. The microhardness of FeCrNiMnAlx high-entropy alloy increased continuously and the yield strength first increased and then decreased with the increase of Al content.

3. With the increase in Al content, the average friction coefficient and wear rate of the FeCrNiMnAlx alloys were reduced obviously until x = 0.8. The volume wear rate of the FeCrNiMnAlx (x = 0, 0.3, 0.5, 0.8, 1.0) is 202.2 × 10^-6, 184.6 × 10^-6, 82.8 × 10^-6, 69.2 × 10^-6, 89.1 × 10^-6 mm^3 N^-1 m^-1, respectively. The FeCrNiMnAl0.8 alloy shows the lowest wear rate.

4. The wear mechanism of FeCrNiMn, FeCrNiMnAl0.3 and the FeCrNiMnAl0.5 shows adhesive wear, abrasive wear and oxidation wear. While that of the FeCrNiMnAl0.8 and the FeCrNiMnAl1.0 is abrasive wear and oxidation wear.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

ORCID iDs

Xuewei Xing @ https://orcid.org/0000-0002-7471-5979
Ying Liu @ https://orcid.org/0000-0003-4149-7300

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