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Achieving a Combination of Higher Strength and Higher Ductility for Enhanced Wear Resistance of AlCrFeNiTi0.5 High-Entropy Alloy by Mo Addition

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Abstract: AlCrFeNiTi0.5Mo. (x = 0, 0.1, 0.2, 0.3 and 0.4) high-entropy alloys (HEAs) were prepared by arc melting and investigated in terms of microstructure, mechanical properties, and wear resistance. All the as-cast HEAs are composed of one disordered BCC phase (BCC) and one ordered BCC (B2) phase. The added Mo acted as a solid solute in the BCC phase. When Mo molar ratio was more than 0.3, a new type or modified BCC phase formed at the grain boundary, which was enriched with both Mo and Ti. Strength, hardness, and ductility of AlCrFeNiTi0.5 were markedly increased with the Mo addition. The increase in hardness was caused by Mo-solute strengthened disordered BCC phase and precipitation-strengthening by precipitation of hard (Mo, Ti)-rich BCC phase at grain boundaries. The improved ductility was largely attributed to reduced interfacial lattice mismatch between the BCC and B2 phase. The Mo-free AlCrFeNiTi0.5 showed the highest wear loss, about 2.5 times as large as that of AlCrFeNiTi0.5Mo0.4 alloy, which possessed the highest hardness, yield strength, maximum strength, and ductility.

Keywords: AlCrFeNiTi0.5 HEA; Mo addition; microstructure; mechanical behavior; wear

1. Introduction

High-entropy alloys (HEAs) have received considerable attention due to their distinctive microstructure and attractive properties. HEA was initially defined as an alloy containing at least five principal elements in equiatomic or near-equatomic concentrations [1–4]. Due to its high entropy, this multi-principal element alloy tends to form a simple solid solution with face-centered cubic (FCC) structure, body-centered cubic (BCC) structure, or hexagonal closed-packed (HCP) structure [5]. The solid-solution hardening caused by multi-elements with large lattice distortion in a simple solid-solution structure makes it possible to obtain high strength/hardness and desired toughness [6–12]. In addition to the high entropy and lattice distortion effects, there are two other beneficial core effects for HEA, called sluggish diffusion effect and cocktail effect [13]. Due to these unique effects, HEAs also possess other wished-for capabilities, such as excellent high-temperature strength, corrosion resistance, wear resistance, irradiation resistance, high toughness, and thermal stability, etc. [14–21].

Many studied HEAs are based on the FeCoNiCr alloy systems with a single FCC structure [7,18,22–24]. For example, FeCoNiCrMn with a single FCC structure is one of the earliest and most-studied HEAs, named the “Cantor alloy” [25,26]. Like most FCC structured alloys, the Cantor alloy exhibits high ductility (about 50%) but low yield strength, usually below 400 MPa at room temperature [27,28]. The BCC or B2 (ordered BCC) structure is generally found to have higher hardness and strength than the FCC phase, due to its larger energy barrier to dislocation generation and movement, at the expense of ductility [29,30]. Tian et al. [31] showed that AlCrFeCoNi had a threefold in-

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Citation: Wu, M.; Yuan, J.; Diao, G.; Li, D. Achieving a Combination of Higher Strength and Higher Ductility for Enhanced Wear Resistance of AlCrFeNiTi0.5 High-Entropy Alloy by Mo Addition. Metals 2022, 12, 1910. https://doi.org/10.3390/met12111910

Academic Editor: Sergey Konovalov
Received: 1 October 2022
Accepted: 4 November 2022
Published: 8 November 2022

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crease in hardiness when the alloy changed its FCC structure (at $x = 0.3$) to a BCC + B2 structure (at $x = 1$). Here, BCC phase is a disordered BCC phase, whereas B2 is an ordered BCC phase as indicated earlier. Properties of HEA are relatively easy to be tuned by changing its combination of multi-elements. It has been noticed that Co-free AlCrFeNi alloy, which consists of BCC phase and B2 phase, exhibits relatively high yield strength (1075 MPa) with a fairly high fracture strain (43.8%) [32]. titanium is another element that shows distinct effects on mechanical properties of the HEA. Due to its large atomic radius, titanium has a strong solid-solution strengthening effect on the ordered B2 phase in AlCrFe(Co)Ni alloy, considerably increasing hardness, strength and wear resistance of the alloy [33–36]. However, if Ti content is sufficiently high (molar ratio $x > 5$), the formation of intermetallic phases make the HEA brittle, which is detrimental to the fracture toughness and wear resistance of the alloy [37,38].

In this study, we modified AlCrFeNiTi0.5 alloy that consisted of a disordered BCC phase (denoted as BCC) and ordered BCC phase (B2) by using an additional element, Mo. Mo is considered to be an element for the pursuit of a combination of high strength and acceptable toughness [39–43]. It has been reported that the Mo addition in FCC-structured CoCrFeNi [41], CoCrFeMnNi [42], and Al5CoCrFeNi [43] alloys increases hardness via substitutional solute strengthening and reduces the wear rate. Mo promotes precipitation of hard and brittle (Cr, Mo)-rich $\sigma$ and (Mo, Cr)-rich $\mu$ phases in the FCC solid solution [41,42,44]. Properly controlling the Mo content could further strengthen the alloy without losing much ductility or keeping reasonable toughness. However, previous studies on the effect of Mo addition on mechanical properties and wear were mainly conducted for FCC HEAs. There are very limited studies on the effect of Mo addition on FCC HEAs. In addition, Mo is more likely to be enriched in the FeCr-rich phase of FCC-structured HEA. For FCC-structured AlCrFeNiTi0.5 alloy, where Mo stays and how or whether or not it influences properties of the alloy are unclear. This study was designed to investigate the effect of Mo addition on microstructure, mechanical properties, and wear resistance of AlCrFeNiTiMo HEAs (where $x$ was in a range of 0–0.4). As shown in this study, with Mo addition, AlCrFeNiTi0.5 exhibited increased strength with elevated ductility simultaneously. The wear resistance was considerably improved. In this article, underlying mechanisms are elucidated.

2. Materials and Methods

Ingots of high-entropy alloys under study with nominal compositions of AlCrFeNiTi0.5, AlCrFeNiTi0.5Mo0.1, AlCrFeNiTi0.5Mo0.2, AlCrFeNiTi0.5Mo0.3, and AlCrFeNiTi0.5Mo0.4 (named T5, T5M1, T5M2, T5M3 and T5M4, hereafter) were produced by arc melting raw metal powders (purity ≥ 99.5 at. %) with a water-cooled copper crucible in argon atmosphere. The ingots were flipped and remelted at least four times to minimize compositional inhomogeneity. Samples with dimensions of 15 mm × 15 mm × 3 mm were cut from the alloy ingots by using an electrical discharge wire-cutter, which were subsequently ground with SiC papers up to 1200 grits, and finally polished by using a 0.1 μm alumina suspension.

X-ray diffraction analysis was conducted for the samples by using a Bruker D8 Discover instrument (Bruker Ltd., Coventry, UK) with Cu Ka radiation ($\lambda = 0.15418$ nm) having $2\theta$ ranging from 20° to 90° and a step size of 4°/min. Microstructure and compositions of the samples were examined by using a scanning electron microscope (SEM, Sigma 300 VP-FESEM, Zeiss, Oberkochen, German) equipped with an energy-dispersive spectrometer (EDS). Nanoindentation tests were performed in selected surface regions of polished AlCrFeNiTiMo HEA samples by using a NHT3 (Anton Paar, Saint-Laurent, QC, Canada) nanoindenter with a diamond pyramid-shaped Berkovich-type indenter tip. Variations in the applied load versus the indentation depth, dwell, and uploading process were recorded and plotted. A maximum load of 300 mN was set for all tests, and the loading-unloading rate was 3 mN/s. At least six indentations were performed for each sample to obtain an average value. The spacing between each two neighboring in-
dentation points was at least 10 μm. Compressive stress–strain curves of the cylindrical specimens (ϕ 4 × 7.5 mm) cut from the HEA ingots were determined by using a 313 Electromechanical Universal Test Machine (TES-TRESOURCES, Shakopee, MN, USA) at a strain rate of 0.3 mm/min.

Wear resistance of the samples under a normal load of 10 N were evaluated at room temperature by using a pin-on-disc wear testing machine (CSEM Tribometer, Peseux, Switzerland). The counterpart was Si3N4 ball (pin) of 3 mm in diameter. The circular path was 2.4 mm in diameter. The sliding speed and distance were 2 cm/s and 45 m, respectively. Volume losses of the samples were determined based on the dimensions of wear tracks using a 3D optical profilometer (ZeGage, Zygo, Middlefield, OH, USA). Each reported value of volume loss is an average of results from three repeated tests. Morphologies of wear surface and composition of wear debris were further analyzed by using SEM equipped with EDS.

3. Results

3.1. Phase Characterization

Figure 1 presents XRD patterns of as-cast AlCrFeNiTi0.5Mo, HEAs. The distinct diffraction peaks of two BCC phases are observed for AlCrFeNiTi0.5 alloy. By analyzing the JCPDS cards combined with the constituent elements, as mentioned earlier, the two BCC domains are characterized as FeCr-rich disordered BCC phase and NiAl-rich ordered BCC phase (B2), respectively. The diffraction peaks reveal three identical (110), (200), and (211) crystal planes for the two phases while a unique (100) crystal plane, which is around 31.5° for the B2 phase. Previous studies have shown the diffraction peaks of the three crystal planes for BCC and B2 phases coincided with each other in AlCrFeCoNi and AlCrFeNi alloys due to their similar lattice constants [32,45]. With the addition of Ti element in AlCrFeNi alloy, the peaks of B2 phase shift to lower 2θ due to the lattice expansion resulting from the enrichment of Ti have a larger atomic size in the NiAl-rich B2 phase [34,37,45], causing separation of the BCC and B2 peaks. Extrapolating the calculations of diffraction peaks by Bragg’s law, we can conclude that the B2 phase (2.933 Å) has a larger lattice constant than BCC phase (2.886 Å) in AlCrFeNiTi0.5.

![Figure 1. X-ray diffraction patterns of AlCrFeNiTi0.5, AlCrFeNiTi0.5Mo0.1, AlCrFeNiTi0.5Mo0.2, AlCrFeNiTi0.5Mo0.3, and AlCrFeNiTi0.5Mo0.4 HEAs.](image)
The Mo addition doesn’t affect the phase constituents in AlCrFeNiTi_{0.5} alloy, but changes the lattice constant of BCC phase (Figure 1). As shown, with increasing the Mo content, the diffraction peaks of BCC phase gradually shift to lower 2θ whereas those of B2 phase remain nearly unchanged, making the three main characteristic peaks from (110), (200), and (211) crystal planes of the two phases gradually overlapped. This change indicates increases in lattice constant of the BCC phase in AlCrFeNiTi_{0.5}Mo_{x} alloy, which are estimated to be 2.902 Å (x = 0.1), 2.922 Å (x = 0.2), 2.932 Å (x = 0.3), and 2.936 Å (x = 0.4), respectively, whereas lattice constant of the B2 phase (2.935 Å) was not affected. It is logical to infer that the added Mo element most likely stays in the BCC phase. Because the atomic radius of Mo (1.90 Å) is larger than that of Fe (1.56 Å) and Cr (1.66 Å), the enrichment of Mo in this FeCr-rich BCC phase induces the lattice expansion of the phase, thus reducing the lattice mismatch at the BCC/B2 interphase boundary, which may help reduce interfacial stress and thus benefit the toughness of the alloy as discussed later.

3.2. Microstructure

Figure 2 presents SEM backscattering micrographs of AlCrFeNiTi_{0.5}, AlCrFeNiTi_{0.5}Mo_{0.1}, AlCrFeNiTi_{0.5}Mo_{0.2} alloys. Magnified images are shown in Figure 2b,d,e. Chemical compositions of different regions in AlCrFeNiTi_{0.5}Mo_{x} are summarized in Table 1. The SEM images of AlCrFeNiTi_{0.5} and AlCrFeNiTi_{0.5}Mo_{0.1} alloys show a flower-like morphology, which has alternating bright and dark phases (Figure 2a–d). According to Table 1, the bright domain is Fe-Cr enriched, which is the disordered BCC phase. The dark domain is Ni-Al-Ti enriched, which is thus the ordered B2 phase. The added Mo is mainly incorporated in the bright BCC phase. The findings are in agreement with the XRD results, which confirm the enrichment of Mo in the BCC phase and Ti in B2 phase. When the Mo molar ratio increased to 0.2, the SEM images (Figure 2e,f) show an additional bright block region with a size range of 8–12 μm. In combination with elemental maps (Figure 2g) and the EDS results (Table 1), the bright block region and the bright domain in the flower-like regions show identical composition with enriched Fe, Cr, and Mo, indicating they are the disordered BCC phase. The dark domain is rich in Ni, Al, and Ti and depleted in Mo element, indicating that Mo does not stay inside the ordered B2 phase.

![Figure 2](image_url)

**Figure 2.** SEM backscattering electron micrographs of (a,b) AlCrFeNiTi_{0.5}, (c,d) AlCrFeNiTi_{0.5}Mo_{0.1}, (e,f) AlCrFeNiTi_{0.5}Mo_{0.2} HEAs. (b,d,f) High-magnification images of areas marked by yellow squares in image (a,c,e,g). EDS elemental maps of various elements in AlCrFeNiTi_{0.5}Mo_{0.2} HEA, whose SEM image is shown in (f).
Table 1. Compositions (at. %) of different regions in AlCrFeNiTi0.5Mox alloys.

| Alloys            | Areas | Al   | Cr   | Fe   | Ni   | Ti   | Mo |
|-------------------|-------|------|------|------|------|------|----|
| AlCrFeNiTi0.5     | 1     | 26.0 | 6.1  | 17.1 | 28.6 | 22.2 | /  |
|                   | 2     | 9.6  | 39.9 | 37.5 | 5.9  | 7.1  | /  |
| AlCrFeNiTi0.5Mo0.1| 3     | 24.6 | 5.4  | 17.0 | 29.5 | 22.9 | 0.5|
|                   | 4     | 5.9  | 40.8 | 41.9 | 2.3  | 4.8  | 4.3|
| AlCrFeNiTi0.5Mo0.2| 5     | 28.8 | 10.8 | 17.6 | 27.5 | 13.6 | 1.7|
|                   | 6     | 11.0 | 41.0 | 29.0 | 6.2  | 4.4  | 10.4|
| AlCrFeNiTi0.5Mo0.3| 7     | 24.8 | 4.9  | 14.9 | 33.2 | 21.2 | 1.1|
|                   | 8     | 11.2 | 36.1 | 26.5 | 6.6  | 6.7  | 12.7|
|                   | 9     | 5.9  | 26.8 | 39.2 | 6.9  | 12.7 | 8.4|
| AlCrFeNiTi0.5Mo0.4| 10    | 25.1 | 4.1  | 14.1 | 33.9 | 21.9 | 0.9|
|                   | 11    | 13.4 | 31.3 | 24.0 | 10.3 | 7.0  | 13.9|
|                   | 12    | 6.3  | 21.6 | 36.1 | 9.1  | 15.9 | 11.1|

When Mo molar ratio was further increased to 0.3 and 0.4 (as shown in Figure 3a–d, there are three distinctive regions, which are alternating BCC + B2 region, bright block region (coarsen BCC phase), and the brightest precipitate at the grain boundary. With increasing the Mo addition, the fraction of coarsened BCC phase becomes larger and larger with its Mo content reaching 12.7 at. % and 13.9 at. % in samples T5M3 and T5M4, respectively. The brightest precipitate along the grain boundaries is also the disordered BCC phase but its solubilized elements are somewhat different. Results of EDS line scan analysis across the brightest BCC phase to the normal BCC region are shown in Figure 3e. The composition gradient near the interface is obvious for Mo and Ti. According to the results of EDS points’ analysis shown in Table 1, the brightest BCC domains are enriched with both Mo and Ti. It is known that Ti is mainly incorporated in the NiAl-rich B2 phase, due to large negative mixing enthalpy for Ti, Ni, and Al, whereas Mo is mainly in the disordered Fe-Cr-rich BCC phase. However, the BCC precipitates at grain boundaries are different, in which both Mo and Ti simultaneously enriched. This could be related to the fact that the grain boundary has higher strain energy, making it more attractive and able to accommodate impurity atoms and phases.
Figure 3. SEM backscattering electron micrographs of (a,b) AlCrFeNiTi0.5Mo0.3, (c,d) AlCrFeNiTi0.5Mo0.4 HEAs. (b,d) Magnified images of the regions marked by yellow squares in images (a,c). (e) Line scans analysis of the interface between brightest precipitate and adjacent BCC phase in AlCrFeNiTi0.5Mo0.4 HEA shown in (d).

3.3. Mechanical Properties

Nano-indentation tests were performed in specific regions to investigate the effect of Mo on local hardness related to microstructure features. Typical indentation tests on block BCC, (Mo,Ti)-rich BCC, and the region with alternating BCC & B2 in AlCrFeNiTi0.5Mo0.4 are shown in Figure 4. Values of micro-hardness and overall hardness are given in Table 2. As shown in Figure 4a,b, relatively homogeneous microstructure can be seen in AlCrFeNiTi0.5 and AlCrFeNiTi0.5Mo0.3 alloys, in which the alternated BCC and B2 phases form a compact network structure. The indenter covered the BCC + B2 domain, so that hardness of individual phase could not be measured. However, comparison between micro-hardness of grain and that of grain boundary can be made. As shown in Table 2, the Mo addition markedly increase the micro-hardness and overall hardness of AlCrFeNiTi0.5. Because the added Mo was mainly incorporated in the BCC phase, which strengthened the BCC phase by solution hardening and consequently contributed to the overall hardness of the AlCrFeNiTi0.5Mo0.3 alloy. With increasing the Mo molar ratio, the hardness was further increased. Comparing micro-hardness of the alternating BCC + B2 with that of block BCC, the former is 8571.8 MPa whereas the latter is 8831.8 MPa, indicating that the BCC phase in the Mo-added alloy, AlCrFeNiTi0.5Mo0.2, is slightly harder than the B2 phase.
With further increasing Mo content, the (Mo, Ti)-rich BCC phase at grain boundaries shows great superiority in hardness (Figure 4d,e). In addition, the multi-element phase
could be fine in size due to the sluggish diffusion of atoms in the multi-element lattice [3,46]. On the whole, the bulk hardness of HEAs gradually increased from 752.5 to 989.7 HV0.3 as Mo molar ratio was increased from 0 to 0.4. For more information about the effect of Mo addition on mechanical properties of the alloy, compressive tests were performed. Results of the compressive tests are illustrated in Figure 5.

![Figure 5](image)

**Figure 5.** (a) Engineering stress–strain curves and (b) true stress–strain curves of compression tests for the HEA samples.

Figure 5 illustrates engineering compressive stress–strain curves of AlCrFeNiTi0.5Mo0.1 (x = 0–0.4) HEAs. Corresponding values of the compressive yield strength, maximum or fracture strength and fracture strain are summarized in Table 3. As shown, with the Mo addition, the yield strength increased from 1709 up to 1969 MPa, and the fracture strength increased from 2275 up to 2751 MPa. It is of particular interest to note that the Mo addition not only increased the strengths but also increased the fracture strain from 21.8% to 24.1%. Figure 6 shows the mechanical properties of the AlCrFeNiTi0.5Mo0.1 alloy in comparison with those of other as-cast HEAs reported in the literature [32,43,44,47–50]. One may see that almost all the strengthened alloy systems by solid-solution strengthening or precipitate hardening are always accompanied with obviously reduced ductility. In other words, the Mo addition helped achieve increases in both strength and ductility, but other as cast HEAs cannot achieve. The mechanism for the simultaneously increased strength and ductility of the Mo-added HEA, AlCrFeNiTi0.5Mo0.1 (x = 0–0.4), is discussed in Section 4.

**Table 3.** Effect of Mo on the mechanical properties for the AlCrFeNiTi0.5 HEA.

| Types     | Alloys          | T5   | T5M1 | T5M2 | T5M3 | T5M4 |
|-----------|-----------------|------|------|------|------|------|
| Engineering  | Yield strength (MPa) | 1709.3 | 1763.2 | 1810.9 | 1873.3 | 1968.5 |
|           | Fracture strength (MPa) | 2274.7 | 2236.1 | 2342.5 | 2504.4 | 2750.9 |
| Fracture strain (%) | 21.8 | 20.7 | 21.9 | 22.4 | 24.1 |
| True       | Yield strength (MPa) | 1486.7 | 1557.2 | 1612.6 | 1662.1 | 1731.6 |
|           | Fracture strength (MPa) | 1773.2 | 1780.9 | 1836.6 | 1948.6 | 2088.4 |
| Plastic strain (%) | 12.5 | 11.3 | 12.6 | 13.1 | 15.1 |
3.4. Wear Resistance

The resistance of AlCrFeNiTi₀.₅Moₓ HEAs to sliding wear against Si₃N₄ ball was evaluated by using a pin-on-disc tester. Figure 7a illustrates volume losses of AlCrFeNiTi₀.₅Moₓ with different Mo contents caused by wear over a sliding distance of 45 m. As shown, the volume loss is markedly reduced by the Mo addition. The Mo-free AlCrFeNiTi₀.₅ (7.05 × 10⁶ μm³) has its volume loss about 2.5 times as large as that of AlCrFeNiTi₀.₅Mo₀.₄ (2.85 × 10⁶ μm³). Worn surfaces of AlCrFeNiTi₀.₅Moₓ samples are illustrated in Figure 7b–f. For AlCrFeNiTi₀.₅ (Figure 7b), the worn surface is locally grooved without much ductile deformation. Patches are observed on the worn surface of AlCrFeNiTi₀.₅ alloy, some of which have been cracked or flaked off. There is a high amount of oxygen in the patches, indicating that oxidation occurred during the wear test with the formation of an oxide scale (Table 4). When the molar fraction of Mo is increased to 0.1 and 0.2, oxide debris rather than oxide patches are detected on the wear tracks (Figure 7c,d). There are still grooves formed by micro-plowing on the worn surface. For AlCrFeNiTi₀.₅Mo₀.₃ and AlCrFeNiTi₀.₅Mo₀.₄ alloys, little oxide debris is observed on the wear track and the grooves are considerably reduced with the addition of Mo.
Figure 7. (a) Wear volume loss of AlCrFeNiTi0.5Mo0.4 over a sliding distance of 45 m, and corresponding SEM micrographs of worn surfaces. (b) AlCrFeNiTi0.5, (c) AlCrFeNiTi0.5Mo0.1, (d) AlCrFeNiTi0.5Mo0.2, (e) AlCrFeNiTi0.5Mo0.3, and (f) AlCrFeNiTi0.5Mo0.4, respectively.

Table 4. Chemical compositions (at. %) of different regions in worn surfaces of AlCrFeNiTi0.5, AlCrFeNiTi0.5Mo0.1, and AlCrFeNiTi0.5Mo0.2 alloys shown in Figure 7.

| Alloys                | Symbols | O  | Si  | Al  | Cr  | Fe  | Ni  | Ti  | Mo |
|-----------------------|---------|----|-----|-----|-----|-----|-----|-----|----|
| AlCrFeNiTi0.5         | 1       | 62.1| 2.7 | 10.7| 7.0 | 6.2 | 6.8 | 4.5 | -  |
|                       | 2       | 44.2| 2.8 | 12.0| 13.3| 11.1| 10.3| 6.2 | -  |
| AlCrFeNiTi0.5Mo0.1    | 3       | 36.7| 2.1 | 14.2| 12.8| 12.4| 13.9| 6.9 | 1  |
| AlCrFeNiTi0.5Mo0.2    | 4       | 32.3| 2.4 | 15.3| 12.7| 13.6| 14.2| 7.7 | 1.8|

To better understand the wear behavior of the HEAs, three-dimensional morphologies and cross-section profiles of wear scars are displayed in Figure 8. The color in the figure represents the depth of wear track as illustrated in Figure 8a–e. AlCrFeNiTi0.5 alloy shows grooves on the wear track (Figure 8a), which has a maximum depth of 7.9 μm and a maximum width of 295.6 μm (Figure 8f). With an increase in the Mo content, both the depth and width of wear track decrease. AlCrFeNiTi0.5Mo0.4 alloy has the smallest depth
(3.2 μm) and width (259.7 μm) among all samples, demonstrating the highest wear resistance.

Figure 8. Three-dimensional images of wear scars on five samples after wear tests over a sliding distance of 45 m. (a) AlCrFeNiTi0.5, (b) AlCrFeNiTi0.5Mo0.1, (c) AlCrFeNiTi0.5Mo0.2, (d) AlCrFeNiTi0.5Mo0.3, and (e) AlCrFeNiTi0.5Mo0.4 alloys. (f) Cross-sectional profiles of wear tracks on the five samples.

4. Discussion

4.1. Mo Distribution and Phase Prediction

In previous studies, the coexistence of Fe-Cr-rich disordering BCC phase (BCC) and NiAl-rich ordered BCC phase (B2) was observed in Co-free AlCrFeNi HEA. The Ti element increased the yield strength and hardness of the AlCrFeNi alloy due to the fact that Ti stayed in the Ni-Al rich ordered B2 phase, leading to the locally distorted lattice with enhanced capability to pin dislocations [32,34,37]. The mixing enthalpy of binary atom pairs [51] reveals considerably larger negative mixing enthalpy among Ni, Al, and Ti, which facilitates the formation of strengthened Ni-Al-Ti rich B2 phase. However, when Ti content exceeds a certain level (x > 0.5), a brittle Laves phase forms, which lowers the toughness and wear resistance of the alloy [37,38]. To mitigate the loss of toughness, in this study on AlCrFeNiTi0.5 alloy, we considered the addition of appropriate elements for the following possibilities: (1) they retain the high-strength BCC + B2 structure, (2) they do not interfere with the strengthening effect of Ti, (3) they reduce the interfacial mismatch between the disordered BCC phase and the ordered B2 phase, which helps reduce interfacial stress concentration and thus the probability of cracking.

As shown earlier, Mo preferentially stays in the disordered BCC phase. Thus, adding this element with a larger atomic size (atomic radius of Mo: 190 pm) may increase the lattice constant of the disordered BCC phase, bringing it closer to that of B2 phase. As a matter of fact, the lattice constants of the disordered BCC and ordered BCC (B2) phases are indeed closer as Mo is added (see XRD pattern shown in Figure 1). As demonstrated
by the compressive tests, the Mo addition does improve the ductility with higher strength.

The simple duplex-BCC phase structure and the preferential incorporation of Mo in the disordered BCC phase could be explained or expected. Several parameters are used in reported studies to predict the stability of phases in HEAs [52–56]. For a multi-component HEA, \( \Delta H_{mix} \) (the element mixing enthalpy) and \( \delta \) describe the chemical bond’s energy among different elements and the difference in atomic size between different elements, respectively. The two parameters are usually used to determine the formation of solid solutions [54,55]. Guo et al. [56] showed that the valence electron concentration, \( VEC \), was also a good indicator of the stability of BCC and FCC phases. These parameters are expressed as

\[
\Delta H_{mix} = \sum_{i=1,i \neq j}^{n} 4\Delta H_{AB}^{mix} c_i c_j \\
\delta = \sqrt{\sum_{i=1}^{n} c_i (1 - \frac{r_i}{r})^2} \\
r = \sum_{i=1}^{n} c_i r_i \\
VEC = \sum_{i=1}^{n} c_i (VEC)_i
\]

where \( \Delta H_{mix} \) and \( \delta \) are the mixing enthalpy and the atomic size difference for atomic pairs in multi-components HEAs, respectively, \( \Delta H_{AB}^{mix} \) stands for the mixing enthalpy of elements A and B, \( c_i \) and \( r_i \) are the atomic percentage and radius of the \( i \)th element, respectively, and \( r \) is the average atomic radius. Table 5 lists the enthalpy of mixing for atomic pairs, atomic radius and \( VEC \) of elements in Al-Cr-Fe-Ni-Ti-Mo system. The calculated \( \Delta H_{mix} \), \( \delta \) and \( VEC \) are shown in Table 6.

**Table 5.** The mixing enthalpy of atomic pairs and physiochemical parameters of constituent elements.

| Elements | Al | Cr | Fe | Ni | Ti | Mo | VEC | Atomic Radius (pm) |
|----------|----|----|----|----|----|----|------|-------------------|
| Al       | 0  | -10| -11| -22| -30| -5 | 3    | 118               |
| Cr       | -10| 0  | -11| -22| -30| 0  | 6    | 166               |
| Fe       | -11| -1 | 0  | 8  | 4  | 6  | 8    | 156               |
| Ni       | -22| -7 | 0  | 10 | 0  | 6  | 10   | 149               |
| Ti       | -30| -7 | -17| -35| 4  | 0  | 1    | 176               |
| Mo       | -5 | 0  | -2 | -7 | -4 | 0  | 6    | 190               |

Zhang et al. [55] showed that solid solutions were stable when \(-20 < \Delta H_{mix} < 5 \text{ kJ/mol} \) and \( \delta \leq 6.6\% \), including disordered and ordered solid solutions. Larger negative mixing enthalpy means that the binding force between elements is larger, more favoring mixing of the elements. However, the positive mixing of enthalpy causes element segregations. For AlCrFeNiTi0.5, values of \( \Delta H_{mix} \) and \( \delta \) are \(-19.22 \text{ kJ/mol} \) and \( 7.11\% \), respectively (Table
6). Clearly, the δ is beyond the range of forming a solid solution. Our previous and present studies have revealed the coexistence of disordered BCC solid solution and ordered BCC (B2) phases in AlCrFeNiTi0.5 alloy. These results are consistent with the study by Zhang et al. [55] which, with a standard $\Delta H_{mix}$, a little increase in δ will deepen the extent of ordering, thus bringing out the precipitation of the ordered phase, except for the dominant solid solution. After adding Mo, values of $\Delta H_{mix}$, δ in AlCrFeNiTi0.5Mo$_x$ ($x = 0.1, 0.2, 0.3$ and $0.4$) are $-18.73 \leq \Delta H_{mix} \leq -17.31$ kJ/mol, and $6.87\% \leq \delta \leq 7.04\%$, where the $\Delta H_{mix}$ is in the range of forming a solid solution and the δ is still a little higher than the standard range ($\delta \leq 6.6\%$) although it is lower than that in AlCrFeNiTi0.5. Therefore, AlCrFeNiTi0.5Mo$_x$ is expected to maintain the microstructure of disordered BCC solid solution plus the ordered B2 phase, similar to that of the AlCrFeNiTi0.5.

Table 6. Calculated parameters for AlCrFeNiTi0.5Mo$_x$ ($x = 0.0, 0.1, 0.2, 0.3$ and $0.4$) HEAs.

| HEAs             | $\Delta H_{mix}$ (kJ/mol) | δ (%) | VEC  |
|------------------|---------------------------|-------|------|
| AlCrFeNiTi0.5    | -19.22                    | 7.11  | 6.4425|
| AlCrFeNiTi0.5Mo0.1| -18.73                  | 7.04  | 6.4348|
| AlCrFeNiTi0.5Mo0.2| -18.24                  | 6.98  | 6.4268|
| AlCrFeNiTi0.5Mo0.3| -17.76                  | 6.93  | 6.4159|
| AlCrFeNiTi0.5Mo0.4| -17.31                  | 6.87  | 6.4056|

For prediction of BCC or FCC phase for HEAs, it is proposed that FCC would be the only phase present for alloys with VEC $\geq 8.0$, and the BCC structure would be the only phase for alloys with VEC $< 6.87$. Intermediate VEC values would include a mixture of the two structures [56]. The values of VEC in AlCrFeNiTi0.5Mo$_x$ ($x = 0, 0.1, 0.2, 0.3$ and $0.4$) are $6.405 \leq VEC \leq 6.443$ (Table 6), which fall into the region of stable BCC phase. The XRD results (Figure 1) have shown that AlCrFeNiTi0.5Mo$_x$ alloys all have the disordered BCC phase (BCC) and ordered BCC phase (B2), indicating that the $\Delta H_{mix}$, δ, and VEC successfully predict the phase formation and structural stability of AlCrFeNiTi0.5 with Mo addition.

The addition of Mo has shown some interesting effects on microstructure, which is also related to the above parameters. Mo mainly acts as a solute in the Fe–Cr disordered BCC with minor influence on the NiAlTi ordered B2 phase. This can be predicted from the mixing enthalpy of binary atom pairs (Table 5). Mo has larger negative mixing enthalpies with NiAlTi ($-7$, $-5$ and $-4$ kJ/mol) than that with FeCr ($-2$ and $0$ kJ/mol), but it mostly dissolves into the latter phase. This unexpected phenomenon could be attributed to the fact that the mixing enthalpy among Ni, Al, and Ti is significantly more negative than that for any other element pairs, thus facilitating the formation of the NiAlTi phase (B2) and blocking the incorporation of Mo into the B2 phase. As a result, Mo preferentially gets into the disordered BCC phase without influencing the B2 phase, hence helping minimize the mismatch of lattice constant between Fe–Cr and NiAlTi phase as illustrated in Figure 1.

4.2. Further Discussion on Mo Effects Mechanical Properties and Wear Resistance

In AlCrFeNiTi0.5 alloy, the lattice distortion caused by Ti in B2 phase leads to solid solution strengthening but enlarges the lattice mismatch between B2 and disordered BCC phase. When adding Mo to this alloy, the preferential incorporation of Mo into the disordered BCC phase increases its lattice cell size, thus (1) reducing the lattice mismatch between the disordered BCC phase and the B2 phase, and (2) strengthening the disordered BCC phase via solid solution-strengthening mechanism. As a result, the strength-
ened disordered BCC phase helps increase the overall hardness of the alloy. In the meanwhile, Mo increases the lattice constant of disordered BCC phase, gradually catching up with the enlarged one of B2 phase caused by Ti [45]. The reduced lattice mismatch consequently makes the interface between the disordered BCC phase and the B2 phase coincident, which reduces the interfacial stress and thus minimizes the probability of interfacial failure caused by excessive dislocation build-up, leading to improved toughness [57] and ductility as illustrated by Figure 5.

With further increasing the Mo addition, in addition to the strengthened disordered BCC phase, the precipitation of a new type or modified BCC phase at the grain boundary also strengthens the alloy, which is a Fe–Cr phase enriched with both Mo and Ti as shown in (Figures 3 and 4). AlCrFeNiTi0.5Mo0.3 and AlCrFeNiTi0.5Mo0.4 alloys are strengthened by Mo-solute strengthening of the disordered BCC phase and the precipitation at grain boundary. The increases in both strength and ductility are largely responsible for the considerably increased wear resistance, as Figure 7 illustrates.

In general, the wear resistance of an alloy depends on its mechanical strength and ductility, both of which determine the alloy’s toughness. However, during wear in ambient environment, the frictional heat-induced oxide scale may also affect the wear resistance. As shown in Figure 7, the oxide can be seen in some areas on the worn surfaces. To obtain the information on the role of the oxide scale in resisting wear, another set of wear tests were conducted with an air flow directed to the contacting area between sample and the counterpart to eliminate the frictional heating effect, thereby minimizing the influence of oxidation on wear. Figure 9 shows volume losses of the samples tested with and without the air flow. As illustrated, the volume loss of AlCrFeNiTi0.5 was slightly increased when air flow was introduced, indicating that the oxide scales resulting from the frictional heat benefit the wear resistance to some extent. The wear mechanism for AlCrFeNiTi0.5 is mainly abrasive wear accompanied with some oxidation. However, for the Mo-containing alloy, there is a mild decrease in volume loss with the air flow cooling. In this case, the oxidation did not much influence the wear performances of the samples, and abrasive wear is the main wear mechanism for AlCrFeNiTi0.5Mo0.4 [58]. The little or minor difference in volume loss between Mo-containing samples tested with or without the air flow indicates that the improvement in the wear resistance by the Mo addition primarily comes from its benefits to the alloy’s strength, ductility, and toughness.
Figure 9. Wear volume loss of AlCrFeNiTi_{0.5}Mo_{x} over a sliding distance of 45 m with and without air flow.

5. Conclusions

Microstructure, mechanical properties, and wear resistance of Mo-containing high-entropy alloy, AlCrFeNiTi_{0.5}Mo_{x} (x = 0.1–0.4), were investigated in comparison with those of Mo-free AlCrFeNiTi_{0.5} alloy. The following conclusions are drawn:

1. The as-cast AlCrFeNiTi_{0.5}Mo_{x} alloys all consisted of a Fe-Cr-rich, disordered BCC phase and a NiAl-rich, ordered BCC phase (B2). The added Mo mainly stayed and acted as a solid solute in the BCC phase, strengthening the phase. When Mo molar ratio was more than 0.3, a modified BCC phase formed at the grain boundary, which was enriched with both Mo and Ti.

2. The Mo addition markedly increased the strength and ductility of AlCrFeNiTi_{0.5} alloy. The increase in strength was mainly caused by Mo-strengthened disordered BCC phase and precipitation-strengthening by hard (Mo, Ti)-rich BCC precipitates at grain boundaries. The improved ductility benefited from the reduced interfacial lattice mismatch between the disordered BCC phase and B2 phase.

3. The Mo-free AlCrFeNiTi_{0.5} showed the largest wear volume loss, which was about 2.5 times as large as that of AlCrFeNiTi_{0.5}Mo_{0.4} due to its lower yield strength, fracture strength, and ductility. The AlCrFeNiTi_{0.5}Mo_{0.4} alloy showed the lowest wear volume loss, which possessed the highest values of all the abovementioned three mechanical properties.

Author Contributions: Conceptualization, M.W. and D.L.; methodology, M.W. and J.Y.; validation, M.W., J.Y., and G.D.; formal analysis, M.W.; investigation, M.W. and J.Y.; resources, M.W. and G.D.; data curation, M.W. and D.L.; writing—original draft preparation, M.W.; writing—review and editing, D.L.; visualization, M.W.; supervision, D.L. All authors have read and agreed to the published version of the manuscript.

Funding: The authors are grateful for financial support from the Natural Science and Engineering Research Council of Canada (ALLRP 567506-21 Li, ALLRP 561172-20 Li), Alberta Innovates (AB Innovates ADVANCE 202102824 Li), Trimay, and Mitacs.

Data Availability Statement: The paper is self-containing. For additional information or data, please contact the corresponding author.
Conflicts of Interest: The authors declare no conflict of interest.

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