Materials Research Express

PAPER

Microstructure and wear resistance of the laser-cladded Al$_{0.8}$CrFeCoNiCu$_{0.5}$B$_x$ high-entropy alloy coating on aluminum

Yanzhou Li$^{1,3}$ and Yan Shi$^{1,5}$

1 College of Electromechanical Engineering, Changchun University of Science and Technology, Changchun, People’s Republic of China
2 College of Electromechanical and Intellectual Technology, Jilin Vocational College of Industry and Technology, People’s Republic of China
3 National Base of International Science and Technology Cooperation in Optics, Changchun, People’s Republic of China

E-mail: shiyan@cust.edu.cn

Keywords: laser technology, aluminum alloy, wear resistance, Al$_{0.8}$CrFeCoNiCu$_{0.5}$B$_x$ high-entropy alloy

Abstract

Coatings with excellent mechanical properties are difficult to prepare on the aluminum alloy surfaces by laser surface engineering because of the low melting point and active chemical properties of aluminum (Al). Based on the unique entropy effect of a high-entropy alloy, we suppress the cracks in the cladding layer caused by the dilution ratio of the substrate, obtaining coatings exhibiting excellent wear resistance. The Al$_{0.8}$CrFeCoNiCu$_{0.5}$B$_x$ coating exhibited a BCC1 + BCC2 + FCC phase when the $x \leq 0.1$. When $x \geq 0.2$, boride was formed in the Al$_{0.8}$CrFeCoNiCu$_{0.5}$B$_x$ coatings, and it became the main phase of the Al$_{0.8}$CrFeCoNiCu$_{0.5}$B$_{0.3}$ and Al$_{0.8}$CrFeCoNiCu$_{0.4}$ coatings; however, no Al-rich intermetallic compound with a complex phase structure was formed. When $0 \leq x \leq 0.3$, the bonding strengths of the Al$_{0.8}$CrFeCoNiCu$_{0.5}$B$_x$ coatings were 70.6–176.2 MPa. An increase in the boron content increased the hardness of all the coatings, except the Al$_{0.8}$CrFeCoNiCu$_{0.5}$B$_{0.3}$ coating. The hardness was 479–705 HV (6–9 times that of the substrate). The wear rate of the coating ranged from $1.50 \times 10^{-7}$ to $1.19 \times 10^{-5}$ mm$^3$/Nm, which was only 0.01%–5.43% that of the substrate. The Al$_{0.8}$CrFeCoNiCu$_{0.5}$B$_{0.2}$ coating exhibited the highest resistance to wearing, and its wear mechanism was identified as abrasive wear.

1. Introduction

Because of its high specific strength, good weldability, and other advantages, the aluminum (Al) alloy has become a popular choice for manufacturing lightweight equipment [1, 2]. However, the low hardness and poor wear resistance of the Al alloy surface limit its applicability in high-end manufacturing industries exhibiting high reliability requirements. Currently, the Al alloy surfaces are modified using various technologies, including electroplating, thermal spraying, and laser cladding [3–5]. The laser cladding method offers unique advantages such as low pollution, high efficiency, and thick coating. As is well known, the laser cladding materials, such as iron–based, nickel–based, and cobalt–based powders and ceramics, exhibiting good mechanical properties usually have a high melting point. To fully melt these powders, the heat input of the laser must be increased considerably beyond the melting point of the Al alloy. Therefore, the Al in the substrate will inevitably float on the coating during the laser cladding process. Because Al is highly electronegative, it readily reacts with the coating powder to form hard and brittle intermetallic compounds, increasing the cracking tendency of the coating. Therefore, laser cladding coating has always been difficult to prepare on the Al alloy surfaces.

Recently, the research on alloys based on multi-principle component design has gradually increased. An alloy that contains five or more elements in equal or approximately equal atomic ratios can easily form a solid solution. Such alloys are called high-entropy alloys (HEAs) [6]. When the elements and their ratios are appropriately selected, the high-entropy and cocktail effects result in HEAs with high strength, good corrosion resistance, high temperature oxidation resistance, and other excellent properties [7, 8]. Fan et al studied the microstructure and mechanical properties of the as-cast (FeCrNiCo)Al$_{x}$Cu$_{y}$ ($0.5 \leq x \leq 1, 0 \leq y \leq 1$) HEAs
Table 1. Chemical composition of the 5083 aluminum alloy (wt%).

| Element | Si   | Cu   | Mg   | Zn   | Mn   | Ti   | Cr   | Fe   | Al   |
|---------|------|------|------|------|------|------|------|------|------|
| wt%     | ≤0.4 | ≤0.1 | 4.0 – 4.9 | ≤0.25 | 0.4 – 1 | ≤0.15 | 0.05 – 0.25 | 0 – 0.4 | al. |

[9]. As the aluminum content increased from x = 0.5 to 1, the microstructure of the alloy system changed from a single face-centered cubic (FCC) structure to an FCC + body-centered cubic (BCC) structure and finally to a single BCC structure. The addition of Al considerably improved the Young’s modulus, hardness, and yield strength of the alloy. Among the investigated compositions, the (FeCrNiCo)Alx_0.75Cu0.5 HEA exhibited the optimal comprehensive mechanical properties, with a fracture strength of 2270 MPa and a plastic strain of 42.70%. Aliyu et al prepared a composite coating of AlCrFeCoNiCu-graphene oxide composite on a steel surface via electrochemical deposition [10]. Their coating exhibited an FCC + BCC phase structure with no complex-phase intermetallic compounds. Further, increasing the graphene oxide content improved the corrosion resistance of the coating, mainly by improving the composition segregation of the HEA. Crooper et al prepared an AlCrFeCoNiCu HEA film via pulsed laser deposition [11]. This film comprised BCC and FCC phases, with a larger crystal size of the BCC phase when compared with that of the FCC phase. Chang et al detected boride in the as-cladded FeCoNiBcCr HEA deposited on the AlSi1045 steel [12]. When x = 5, the volume fraction of the boride was maximized in coatings, and the hardness reached 860 HV. Thus, HEAs with good mechanical properties can be applied as coating materials in laser-surface modification engineering. Furthermore, Al exhibits a wide range of solid solubility in HEA systems containing Fe, Co, Ni, Cr, and Cu. This property is underlain by the high-entropy effect. Therefore, this HEA system can reduce the probability of cracks in the cladding layer when applied as a coating on aluminum. As explained above, cracks develop when a large number of intermetallic compounds with complex phase structures are formed after the aluminum in the substrate reacts with the added powders.

However, the preparation of HEA coatings on aluminum has received little attention, and the high-efficiency cladding technology with coaxial powder feeding and the wear resistance of the coating have been rarely explored. Moreover, although the addition of B certainly improves the mechanical properties of some HEA system coatings, its effect on the remaining HEA system coatings deposited on different substrates should be further analyzed. Furthermore, the substrate–coating bonding performance is usually qualitatively analyzed by microstructural observation because the thickness of the coatings prepared by laser cladding rarely meets the requirements of the tensile test samples. A quantitative evaluation would provide detailed support with respect to the practical application of a project; however, this evaluation has not yet been achieved. To fill this void, this study prepares Al0.8CrFeCoNiCu0.5Bx coatings on aluminum via coaxial laser cladding and investigates the phase structure as well as wear resistance of the resulting alloy. Further, the bonding property between the coating and substrate is quantitatively analyzed.

2. Materials and methods

The composition of the experimental substrate (5083 aluminum alloy) is presented in table 1. The substrate was formed into test blocks with sizes of 30 mm × 30 mm × 10 mm. The oxide layer on the surface of the test block was initially removed by sandpapering and was subsequently removed by ultrasonic cleaning with absolute ethanol. The experimental powders were Co, Fe, Ni, Cr, Cu, Al, and B (purity > 99.9%, particle size 200–325 mesh). Most powders (except the B powder) were spherical to ensure their fluidity in the powder-feeding tube. Their morphologies are presented in figure 1. The powder ratio and the coating abbreviations are presented in table 2.

Experiments were conducted using the DC050 CO2 laser supplied by the Rofin company. The processing parameters were determined using a large number of preliminary tests. The spot diameter was 1.2 mm, the laser power was 1850 W, the powder feed rate was 5.6 g min⁻¹, the scanning speed was 120 mm min⁻¹, the duty cycle was 70%, the pulse frequency was 50 Hz, the overlap rate was 30%, and the carrier gas flow rate was 5 l min⁻¹. The processing equipment and the experimental diagram are presented in figure 2.

After the laser cladding experiment was conducted, the coating was cut into metallographic samples along the test block perpendicular to the scanning speed and then polished. The coating was corroded with a mixed solution of hydrofluoric acid and nitric acid–hydrochloric acid (aqua regia, volume ratio 3:1) to observe microstructure of the heat-affected zone and cladding. The microstructure of the corroded sample was observed using a scanning electron microscope (SEM, JSM-6510). The phase of the coating was analyzed by an x-ray diffractometer (XRD, Empyrean). The hardness of the coating was measured using a microhardness tester (MH-60), where the input load was 200 g and the loading time was 10 s.
The bonding performances between the coatings and substrates were quantitatively analyzed via the shear strength tests. The shear force was determined using the DNS100 universal tensile tester. The bonding quality, which is a measure of shear stress (or bonding shear strength), was calculated as \[ \text{bonding shear strength} \]

Figure 1. SEM diagrams of powders: (a) Al; (b) Cr; (c) Fe; (d) Co; (e) Ni; (f) Cu; and (g) B.

Table 2. Nominal components and abbreviation of Al\textsubscript{0.8}Cr\textsubscript{0.2}Fe\textsubscript{0.2}Co\textsubscript{0.2}Ni\textsubscript{0.2}Cu\textsubscript{0.2}B\textsubscript{x} (at%).

| Sample Abbreviation | Al   | Cr   | Fe   | Co   | Ni   | Cu   | B   |
|--------------------|------|------|------|------|------|------|-----|
| Al\textsubscript{0.8}Cr\textsubscript{0.2}Fe\textsubscript{0.2}Co\textsubscript{0.2}Ni\textsubscript{0.2}Cu\textsubscript{0.2}B\textsubscript{0} | 15.09 | 18.86 | 18.86 | 18.86 | 18.86 | 9.43 | 0   |
| Al\textsubscript{0.8}Cr\textsubscript{0.2}Fe\textsubscript{0.2}Co\textsubscript{0.2}Ni\textsubscript{0.2}Cu\textsubscript{0.2}B\textsubscript{0.1} | 14.81 | 18.51 | 18.51 | 18.51 | 18.51 | 9.25 | 1.85 |
| Al\textsubscript{0.8}Cr\textsubscript{0.2}Fe\textsubscript{0.2}Co\textsubscript{0.2}Ni\textsubscript{0.2}Cu\textsubscript{0.2}B\textsubscript{0.2} | 14.54 | 18.18 | 18.18 | 18.18 | 18.18 | 9.09 | 3.63 |
| Al\textsubscript{0.8}Cr\textsubscript{0.2}Fe\textsubscript{0.2}Co\textsubscript{0.2}Ni\textsubscript{0.2}Cu\textsubscript{0.2}B\textsubscript{0.3} | 14.28 | 17.85 | 17.85 | 17.85 | 17.85 | 8.92 | 5.35 |
| Al\textsubscript{0.8}Cr\textsubscript{0.2}Fe\textsubscript{0.2}Co\textsubscript{0.2}Ni\textsubscript{0.2}Cu\textsubscript{0.2}B\textsubscript{0.4} | 14.03 | 17.54 | 17.54 | 17.54 | 17.54 | 8.77 | 7.01 |

Figure 2. The schematic of coaxial laser cladding.

The bonding performances between the coatings and substrates were quantitatively analyzed via the shear strength tests. The shear force was determined using the DNS100 universal tensile tester. The bonding quality, which is a measure of shear stress (or bonding shear strength), was calculated as \[ [13] \]
where $F_{\text{max}}$ is the maximum shear load, $S$ is the shear area, $D$ is the diameter of the test specimen, and $h$ is the coating width. The related schematic is shown in figure 3.

The dry-sliding friction and wear properties of the test samples were verified using the MM200 friction and wear tester under a load of 98 N. The rotating speed and test time were 400 $\text{r/min}$ and 30 min, respectively. The friction pair was a GCr15 steel ring with a hardness of 61 HRC, a diameter of 50 mm, and a thickness of 10 mm. The sample size was $7 \times 14 \times 10 \text{mm}^3$. The wear diagram is presented in figure 4.

During the friction and wear test, the friction moment was measured after every 5 min, and the friction-coefficient wear rate of the sample was calculated as follows:

$$\mu = \frac{M}{(P \times R)}$$

Here, $\mu$ is the friction coefficient, $M$ is the friction moment (Nm), $P$ is the load (N), and $R$ is the radius of the steel ring (mm). The wear resistance of the sample was calculated based on the wear rate as follows:

$$\omega = \frac{V_{\text{loss}}}{L \times N},$$

$$L = 2\pi R v t$$

and

$$V_{\text{loss}} = B \left[ \frac{\pi R^2}{180} \arcsin \left( \frac{b}{2R} \right) - \frac{b}{2} \sqrt{R^2 - \frac{b^2}{4}} \right].$$
where \( \omega \) is the wear rate, \( V_{\text{loss}} \) is the wear volume (mm\(^3\)), \( B \) and \( b \) are the length and width of the wear mark, respectively (both in mm), \( v \) is the wheel speed (r/min), and \( L \) is the total length of the grinding block sliding on the sample surface (mm).

3. Result and discussion

3.1. XRD analysis

Figure 5 shows the XRD pattern of the Al\(_{0.8}\)CrFeCoNiCu\(_{0.5}\)B\(_x\) coating. The B0 and B0.1 coatings comprised the FCC, BCC1, and BCC2 phases. The BCC1 phase was a disordered BCC solid solution with diffraction peaks near \( 2\theta = 44.5^\circ, 65.0^\circ, \) and \( 82.0^\circ \), similar to the \( \alpha-(\text{Fe, Cr}) \) (PDF\#52-0513 for Fe and PDF\#19-0323 for Cr). As observed based on the peaks near \( 2\theta = 31.0^\circ \), the BCC2 phase was an ordered BCC structure approximately similar to the AlNi phase (PDF\#65-3199) \([14]\). The diffraction peaks near \( 2\theta = 40.0^\circ, 51.5^\circ, \) and \( 74.5^\circ \) were identified as the FCC phase, similar to \( \alpha-\text{Cu} \) (PDF\#65-9026). The B0.2 coating exhibited a Cr2B phase (PDF\#38-1399), suggesting that the solubility of the solid solution increased with the further addition of B. The Fe2B (PDF\#39-1314) phase was detected when the B contents exceeded 0.2. In addition, increasing the B content in the Al\(_{0.8}\)CrFeCoNiCu\(_{0.5}\)B\(_x\) coatings reduced the intensities of the BCC and FCC peaks, mainly because a large amount of M2B (M = Cr or Fe) formation results in the consumption of the Fe and Cr elements comprising the BCC and FCC phases \([15]\).

3.2. Microstructure

Figure 6(a) shows the surfaces and cross sections of the Al\(_{0.8}\)CrFeCoNiCu\(_{0.5}\) coatings. The coatings exhibited no obvious defects, including pores and cracks, indicating the appropriateness of the experimental powder ratio and process parameters. The coating thickness was 662 ± 74 \( \mu \)m. After hydrofluoric acid corrosion, the heat-affected zone (HAZ) could be observed at the interface near the substrate, as shown in figure 6(b). The microstructure of HEA coatings can be observed by aqua regia corrosion. Figure 7 denotes the microstructure of the middle part of the Al\(_{0.8}\)CrFeCoNiCu\(_{0.5}\)B\(_x\) HEA coating. B0 and B0.1 presented typical interdendritic and dendritic structures (figures 7(a)–(d)). When the B content increased to 0.2, a worm-shaped second phase was observed, whereas B0.2 presented a similar overall morphology to that exhibited by B0.1 (figures 7(e) and 7(f)). In figures 7(g) and (h), a lamellar precipitated phase can be observed at the grain boundaries of the B0.3. This precipitated phase is partially connected with a network. When B reached 0.4, a long strip-like precipitate with directional growth could be observed. The B content significantly changed the microstructure of the Al\(_{0.8}\)CrFeCoNiCu\(_{0.5}\)B\(_x\) HEA coatings. The addition of B caused strong lattice distortion because the atomic radius of B largely differs from those of the remaining elements in the powder. According to Gibbs free energy theory, as the alloy solidifies, the B atoms are discharged from the crystal interior to reduce the lattice distortion energy of the alloy \([16]\). Although rapid cooling reduces the diffusion time of the solute, the small-sized B tended to be enriched at the grain boundary, causing constitutional undercooling at the grain boundary and promoting the growth of primary and even secondary dendrite arms \([16]\). In addition,
increasing the amount of excessive B in the crystallization process impels the discharge of Cr in the BCC phase into the liquid phase, achieving the composition requirements of boride with a topologically close-packed phase. The solidification mode of the FCC and BCC phases is similar to the AF solidification mode of the duplex stainless steel and austenitic stainless steel welding, resulting in strip-like structures without directional growth [17]. When \( x > 0.2 \), the peak of the boride of \( \text{Al}_{0.89}\text{CrFeCoNiCu}_{0.5}\text{B}_x \) becomes the main peak, and a large number of needle-like second phases can be observed, indicating that the aforementioned coatings are no longer HEAs. This is mainly because B exhibits a more negative mixing enthalpy, as shown in table 3. The increase in the amount of B increases the mixing enthalpy of the alloy system, which makes the alloy more inclined to form high-enthalpy intermetallics [18].

3.3. Hardness

Figure 8 denotes the average hardness of the \( \text{Al}_{0.89}\text{CrFeCoNiCu}_{0.5}\text{B}_x \) HEA coating. An increase in the B content increased the hardness of the coating, except for B0.3. The average hardness of the \( \text{Al}_{0.89}\text{CrFeCoNiCu}_{0.5}\text{B}_x \) coatings increased from 479 HV \(_{0.2}\) to 705 HV \(_{0.2}\). The hardness of B0.2 was improved by B addition, mainly because the boride dispersed in the coating hindered the dislocation movement. Meanwhile, the hardness of B0.3 slightly decreased. On the one hand, the continuous addition of B consumed the main constituent elements (Fe and Cr) of the BCC phase because the mixing of Fe, Cr, and B is a negative enthalpy process (table 3). The hardness of the coating reduced as the volume fraction of the BCC phase decreased. On the other hand, the addition of B increased the hard phase and the hardness of the coating. The combination of the two factors makes the hardness of B0.3 lower than that of B0.2. When the B content reached 0.4, the average hardness of the coating increased to 705 HV \(_{0.2}\). Although the volume fraction of the BCC phase continued to decrease with increasing B content, the boride in the alloy played a leading role in the overall hardness of the material, enhancing the hardness of B0.4.

3.4. Bonding quality

Table 4 presents the calculated shear strengths of each sample. The shear strengths of B0 and B0.1 were similar (176.2 and 168.2 MPa, respectively). In contrast, the shear strength of B0.4 was only 37.5 MPa, which was only 21.2% of that of B0. The shear fracture was observed via SEM to understand the fracture mechanism of samples. Figure 9 depicts the shear fracture morphologies of the \( \text{Al}_{0.89}\text{CrFeCoNiCu}_{0.5}\text{B}_x \) coatings. Figures 9(a) and 9(b) present low- and high-power images of the fractures on the B0 surface, respectively. The slip band along the shear direction and the dimple along the shear direction are forms of ductile fracture. The fracture morphologies of B0.1 and B0.2 resembled that of B0 (figures 9(c)–(e)). Figures 9(f) and 9(g) display lower- and higher-magnification images of the B0.3 fracture, respectively. Further, tearing edges and tearing dimples are observed. A second crack appears in the second dimple phase. On the B0.4 fracture surface (figure 9(h)), large cleavage surfaces and dense second-phase particles can be observed, indicating that the cleavage surface was stripped under the action of the shear load on secondary particles. Thus, the included particles reduced the shear strength of the coating.

3.5. Wear resistance

Figure 10 plots the relations between the wear time and the friction coefficient of the \( \text{Al}_{0.89}\text{CrFeCoNiCu}_{0.5}\text{B}_x \) HEA coating and its substrate. When the friction coefficient stabilized (at 20 min), the friction coefficient of the HEA coating ranged from 0.538 to 0.589, which was significantly lower than that of the substrate (0.655). As the
Figure 7. The typical microstructure of the middle part of the $\text{Al}_0\text{CrFeCoNiCu}_0\text{B}_x$ HEA coatings. (a) $x = 0$. (b) Enlarged image of that in figure 7(a). (c) $x = 0.1$. (d) Enlarged image of that in figure 7(c). (e) $x = 0.2$. (f) Enlarged image of that in figure 7(e). (g) $x = 0.3$. (h) Enlarged image of that in figure 7(g). (i) $x = 0.4$. (j) Enlarged image of that in figure 7(i).
B content increased, the friction coefficient of the Al$_{0.8}$CrFeCoNiCu$_{0.5}$B$_x$ coating decreased and subsequently increased; further, it was smallest in B$_{0.2}$. The wear resistance of B$_{0.4}$ was not investigated because the applicability of B$_{0.4}$ is limited by the low bonding strength between the coating and the substrate.

Figure 11 shows the microhardness and wear rate curves of the Al$_{0.8}$CrFeCoNiCu$_{0.5}$B$_x$ HEA coating and substrate, and table 5 displays the measured wear results and the calculated wear coefficients. The wear rate of Al$_{0.8}$CrFeCoNiCu$_{0.5}$B$_x$ was significantly lower than that of the substrate. As the B content increased, the wear rate of the coatings initially decreased and subsequently increased. This result, which mirrors the trend of the hardness changes, conforms to Archard’s law [19]. The wear surface was observed via SEM to analyze the wear mechanism of the samples.

Figure 12 shows the wear surfaces of the Al$_{0.8}$CrFeCoNiCu$_{0.5}$B$_x$ coatings and substrates. The wear surfaces of the coatings are more paved and smoother than those of aluminum and show a reduced degree of plastic deformation. The wear surface of the substrate exhibited severe plastic deformation and step faulting (figure 12(a)), indicating that stratified fractures occurred during the wear process. The elongated dimples along the wear direction can be mainly attributed to the large plasticity and ductility of the Al alloy. Spalling, scratches, and abrasive grains appeared on the wear surface of B$_0$ (figure 12(b)), and a plastic deformation region could be observed near the scratches. The wear mechanism was adhesive and abrasive wear. Although grooves and a large number of abrasive particles were observed on the B$_{0.1}$ surface (figure 12(c)), spalling and plastic deformation were absent, indicating a stronger wear resistance than that exhibited by B$_0$. The wear mechanism of B$_{0.1}$ was abrasive wear. The grooves were smaller and shallower on the B$_{0.2}$ surface than those on B$_{0.1}$, and the number of abrasive particles was reduced. The wear resistance of B$_{0.2}$ was further improved (figure 12(d)). As shown in figure 12(e), the B$_{0.3}$ surface was covered with many hard-phase particles that prevented the expansion of

| Table 3. Mixed enthalpy between various elements (kJ mol$^{-1}$). |
|------------------|---|---|---|---|---|---|
| Fe | Cr | Ni | Co | Cu | Al | B |
| Fe |  — | −1 | −2 | −1 | 13 | −11 | −26 |
| Cr | −1 | — | −7 | −4 | 12 | −10 | −31 |
| Ni | −2 | −7 | — | 0 | 4 | −22 | −24 |
| Co | −1 | −4 | 0 | — | 6 | −19 | −24 |
| Cu | 13 | 12 | 4 | 6 | — | −1 | 0 |
| Al | −11 | −10 | −22 | −19 | −1 | — | 0 |
| B  | −26 | −31 | −24 | −24 | 0 | 0 | — |

Figure 8. Average microhardness of the Al$_{0.8}$CrFeCoNiCu$_{0.5}$B$_x$ HEA coatings.

| Table 4. Results of shear strength. |
|-----------------------------------|
| Simple | Maximum shear load ($F_{\text{max}}$/kN) | Shear area ($S$ mm$^{-2}$) | Shear strength ($\sigma_c$/MPa) |
| B0  | 36.3 | 205.9 | 176.2 |
| B0.1 | 35.3 | 209.7 | 168.2 |
| B0.2 | 24.5 | 218.5 | 112.1 |
| B0.3 | 14.1 | 199.7 | 70.6 |
| B0.4 | 8.2 | 218.5 | 37.5 |

B content increased, the friction coefficient of the Al$_{0.8}$CrFeCoNiCu$_{0.5}$B$_x$ coating decreased and subsequently increased; further, it was smallest in B$_{0.2}$. The wear resistance of B$_{0.4}$ was not investigated because the applicability of B$_{0.4}$ is limited by the low bonding strength between the coating and the substrate.

Figure 11 shows the microhardness and wear rate curves of the Al$_{0.8}$CrFeCoNiCu$_{0.5}$B$_x$ HEA coating and substrate, and table 5 displays the measured wear results and the calculated wear coefficients. The wear rate of Al$_{0.8}$CrFeCoNiCu$_{0.5}$B$_x$ was significantly lower than that of the substrate. As the B content increased, the wear rate of the coatings initially decreased and subsequently increased. This result, which mirrors the trend of the hardness changes, conforms to Archard’s law [19]. The wear surface was observed via SEM to analyze the wear mechanism of the samples.

Figure 12 shows the wear surfaces of the Al$_{0.8}$CrFeCoNiCu$_{0.5}$B$_x$ coatings and substrates. The wear surfaces of the coatings are more paved and smoother than those of aluminum and show a reduced degree of plastic deformation. The wear surface of the substrate exhibited severe plastic deformation and step faulting (figure 12(a)), indicating that stratified fractures occurred during the wear process. The elongated dimples along the wear direction can be mainly attributed to the large plasticity and ductility of the Al alloy. Spalling, scratches, and abrasive grains appeared on the wear surface of B$_0$ (figure 12(b)), and a plastic deformation region could be observed near the scratches. The wear mechanism was adhesive and abrasive wear. Although grooves and a large number of abrasive particles were observed on the B$_{0.1}$ surface (figure 12(c)), spalling and plastic deformation were absent, indicating a stronger wear resistance than that exhibited by B$_0$. The wear mechanism of B$_{0.1}$ was abrasive wear. The grooves were smaller and shallower on the B$_{0.2}$ surface than those on B$_{0.1}$, and the number of abrasive particles was reduced. The wear resistance of B$_{0.2}$ was further improved (figure 12(d)). As shown in figure 12(e), the B$_{0.3}$ surface was covered with many hard-phase particles that prevented the expansion of
grooves along the wear direction. However, the hard phases removed from the coating were crushed into fine abrasive particles by the friction pair, causing a large number of scratches near the hard phase. Therefore, the wear rate of B0.3 was not lower than that of B0.2. Generally, because a hard coating can effectively block the micro-cutting and micro-shearing by the micro-convex body of the GGr15 friction pair, the contact area between the coating surface and the friction pair is reduced; accordingly, the wear resistance of the coating is an increasing function of hardness.

4. Conclusions

1. B0 and B0.1 comprised the BCC1, BCC2, and FCC phases. When x exceeded 0.1, boride was detected in the Al0.8CrFeCoNiCu0.5Bx coating. When x ≥ 0.2, boride can be observed in the Al0.8CrFeCoNiCu0.5Bx coating.
A large amount of \((\text{Fe, Cr})_2\text{B}\) phase can be detected and the \(\text{Al}_{0.8}\text{CrFeCoNiCu}_{0.5}\text{B}_{0.3}\) and \(\text{Al}_{0.8}\text{CrFeCoNiCu}_{0.5}\text{B}_{0.4}\) coatings are no longer HEAs.

2. Increasing the B content increased the hardness of the coating, mainly by increasing the degree of lattice distortion and promoting the formation of hard boride. All the coatings were considerably harder than the substrate. When \(0 \leq x \leq 0.3\), the shear strengths of the \(\text{Al}_{0.8}\text{CrFeCoNiCu}_{0.5}\text{B}_x\) coating were \(70.6–176.2\) MPa.

3. The wear rate of the \(\text{Al}_{0.8}\text{CrFeCoNiCu}_{0.5}\text{B}_x\) \((0 \leq x \leq 0.3)\) coating ranged from \(1.50 \times 10^{-7}\) to \(1.19 \times 10^{-5}\) mm³/Nm, which was only 0.01%–5.43% that of the substrate \((3.50 \times 10^{-4}\) mm³ N⁻¹ m⁻¹).
The Al$_{0.8}$CrFeCoNi$_{0.5}$Cu$_x$B$_2$(0 $\leq x \leq 0.3$) HEA is a promising candidate coating for the Al alloy surfaces exhibiting improved mechanical properties.

Acknowledgments

This project was supported by the Equipment pre-research field Foundation of China (Grant No. JZX7Y20190263002101).

Disclosure statement

The authors declare no potential conflicts of interest.

ORCID iDs

Yan Shi https://orcid.org/0000-0001-6539-837X

References

[1] Jawad D H, Hosseinzadeh A and Yapici G G 2019 On the mechanical behavior of accumulative roll bonded lightweight composite Mater. Res. Express 6 12
[2] Tazari H and Siadati M H 2019 Nanocomposites of Al5083/SiC$_x$ strength and wear behaviors Mater. Res. Express 6 27
[3] Li Y X, Zhang P F, Bai P K, Zhao Z Y and Liu B 2018 Analysis of geometrical characteristics and properties of laser cladding 85 wt% Ti +15 wt% TiBCN powder on 7075 aluminum alloy substrate Materials 11 1151-75
[4] Wang G, Bian D W, Kou L Y and Zhu X J 2019 Hot deformation behavior and processing map of 6063 aluminum alloy. Mater. Res. Express 6 9
[5] Raj R M and Raj V 2019 Electrosynthesis of Zr-loaded copolymer coatings on Al for defluoridation of water and its corrosion protection ability Prog. Org. Coat. 137 9
[6] Yeh J-W, Chen S-K, Lin S-J, Gan I-Y, Chin T-S, Shun T-T, Tsau C-H and Chang S-Y 2004 Nanostructured high-entropy alloys with multiple principal elements: Novel alloy design concepts and outcomes Adv. Eng. Mater. 6 299–303
[7] Cai Y C, Ao S, Manladan S M, Xue J C and Luo Z 2019 Evolution mechanisms of TiC ceramic particles in FeCoCrNiAl high-entropy alloy laser cladding layers Mater. Res. Express 6 14
[8] Cai Y C, Zhu I S, Cai Y, Geng K P, Manladan S M and Luo Z 2019 High-temperature oxidation behavior of FeCoCrNiAlx high-entropy alloy coatings Mater. Res. Express 6 11
[9] Fan Q C, Li B S and Zhang Y 2014 Influence of Al and Cu elements on the microstructure and properties of (FeCrNiCo)AlxCuy high-entropy alloys J. Alloy Compd. 614 203–10
[10] Aliyu A and Srivastava C 2019 Microstructure-corrosion property correlation in electrodeposited AlCrFeCoNiCu high entropy alloys-graphene oxide composite coatings Thin Solid Films 686 11
[11] Cropper M D 2018 Thin films of AlCrFeCoNiCu high-entropy alloy by pulsed laser deposition Appl. Surf. Sci. 455 153–9
[12] Chang F, Cai B J, Zhang C, Huang B A, Li S and Dai P Q 2019 Thermal stability and oxidation resistance of FeCrxCoNiB high-entropy alloys coatings by laser cladding Surf. Coat. Tech. 359 132–40
[13] Xu S M, Jiang J B, Li B B, Cong W L and Zhang D D 2016 Experimental characterizations of laser cladding of iron- and nickel-based alloy powders on carbon steel 1045 for remanufacturing P. I. MECH. ENG. L. J. MAT. 232 13
[14] Li M, Gaozhe J, Borisieich A, Mishra R and Flores K M 2018 Evaluation of microstructure and mechanical property variations in AlxCoCrFeNi high entropy alloys produced by a high-throughput laser deposition method Intermetallics 95 110–8
[15] Ding J, Inoue A, Han Y, Kong F L, Zhu S L, Wang Z, Shalaan E and Al-Marzouki F 2016 High entropy effect on structure and properties of (Fe,Co,Ni,Cr)-B amorphous alloys J. Alloy Compd. 696 345–352
[16] Hou L L, Hui J T, Yao Y H, Chen J and Liu J N 2019 Effects of boron content on microstructure and mechanical properties of AlFeCoNiBx high entropy alloy prepared by vacuum arc melting Vacuum 164 212–8
[17] Ma J C, Yang Y S, Tong W H, Fang Y, Yu V and Hu Z Microstructural evolution in AlSi304 stainless steel during directional solidification and subsequent solid-state transformation Mater. Sci. Eng. 444 64–8
[18] Miracle D B and Senkov O N 2017 A critical review of high entropy alloys and related concepts Act. Mat. 122 448–511
[19] Ranjith R, Giriwharan P K, Velmurugan C and Chinnusamy C 2019 Formation of lubricated tribo layer, grain boundary precipitates, and white spots on titanium-coated graphite-reinforced hybrid composites J. Aust. Ceram. Soc. 55 645–55