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Effect of deep cryogenic treatment on the microstructure and mechanical properties of AlCrFe$_2$Ni$_2$ High-entropy alloy

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Abstract

The influence of deep cryogenic treatment on the microstructure and properties of AlCrFe$_2$Ni$_2$ high-entropy alloy were studied by examining its phase composition, microstructure, and properties after cryogenic treatment. The results showed that as the cryogenic treatment increased, the alloy was composed of face-centered cubic (FCC) and body-centered cubic (BCC) phases. As the treatment time increased, the grain orientation of the BCC phase and B2 phase changed and transformed into each other, and the band FCC phase structures became shorter and more disordered. Deep cryogenic treatment effectively improved the hardness, yield strength, and wear resistance of the alloy. The alloy displayed the best performance with a holding time of 4 h, and the Vickers hardness (338 HV) was 11.6% higher than the as-cast alloy, and the yield strength (920 MPa) was 22.7% higher. The friction coefficient was 0.643, and the wear resistance was also significantly improved.

1. Introduction

High-entropy alloys (HEAs) were introduced in the 1990s [1, 2] and overcame the limitations of traditional alloys and became popular due to their simple phase structure [3–9] and excellent mechanical properties [10–16]. Heat treatment of traditional as-cast alloys can eliminate internal structural defects and stresses and improve their properties [17–22]. Deep cryogenic treatment is a type of heat treatment that is widely used to study traditional alloys. Previous research [23] used cryogenic treatment before the aging of FSW 2198 aluminum alloy to obtain a relatively fine crystal structure and strength and toughness improvements. The strengthening mechanism of the deep cryogenic treatment of Al-Zn-Mg-Cu was shown to mainly be fine-grain strengthening [24]. Deep cryogenic treatment was shown to improve the wear resistance by 2%–21% in a series of Al-Si alloys [25]. Other research [26–29] has shown that deep cryogenic treatment causes the grain size to decrease, (e.g., the size of plate martensite [30]), phase transitions (e.g., the transformation of residual austenite into martensite [31]), increased the diffusion of precipitated carbide, and improve the hardness and wear resistance of alloys. The deep cryogenic treatment of magnesium alloys has been shown to refine the microstructures, dissolve the brittle phase, and improve the properties [32–34].

It can be seen that deep cryogenic treatment can improve the performance of traditional alloys; however, previous research has mainly focused on traditional alloys, and no investigation on the effects of deep cryogenic treatment of high-entropy alloys has been proposed. In order to understand whether cryogenic treatment has a similar effect on the performance of HEAs, AlCrFe$_2$Ni$_2$ was subjected to deep cryogenic treatment for different times, and the phase composition, microstructure, and properties of the alloy after treatment were studied.

2. Experimental procedures

AlCrFe$_2$Ni$_2$ samples were melted in a vacuum arc melting furnace with argon gas protection. The purity of the metals was more than 99.9 wt%. About 60 g of the alloy ingot was smelted at least 5 times in a water-cooled copper mold to ensure a uniform chemical composition. 8 × 8 × 4 mm samples were prepared by wire
electrical discharge machining and soaked in liquid nitrogen for 4, 8, 12, 24, and 48 h and then allowed to cool to room temperature. After grinding and burnishing, electro-polishing was carried out in a mixture of 90% acetic acid and 10% perchloric acid. X-ray diffraction (XRD, Shimadzu XRD-7000) was used to measure the phase structure of alloys, and the microstructure and elemental distribution were analyzed by scanning electron microscopy (SEM, Zeiss Gemini). Compression tests were carried out on \(4 \times 6\) mm samples using a universal electronic laboratory machine (MTS-E45) with a strain rate of 5 mm/min. Hardness measurements were carried out using a universal hardness tester (UH250) with a load of 49 N and a dwell time of 5 s. Reciprocating friction and wear experiments (using zirconia as the friction pair) were carried out using a friction and wear testing machine (MFT4000) using a load of 10 N, a speed of 80 mm/min, time of 30 min, and length of 5 mm. Parameters, including the wear morphologies and the wear depth, were determined using a 3D laser confocal microscope (OLS4100).

3. Results and discussion

3.1. Crystal structure

Figure 1(a) shows the XRD pattern of AlCrFe2Ni2 in the as-cast condition and after different deep cryogenic treatment times. The as-cast alloy was composed of FCC and BCC phases. As the deep cryogenic treatment time increased, the crystal structure of the alloy did not change. After deep cryogenic treatment, the diffraction peak intensity of the FCC phase did not significantly change, and the diffraction peak of the BCC phase in crystal planes \((110)\) and \((200)\) significantly changed. By comparing the XRD patterns of the sample treated for 4 h with the as-cast alloy, it can be seen that the diffraction peak intensity of each crystal surface of the alloy increased after deep cryogenic treatment. As shown in figures 1(b) and (c), when the deep cryogenic treatment time increased from 4 h to 8 h, the BCC diffraction peak intensity of crystal plane \((110)\) increased, while that of crystal plane \((200)\) decreased. When the deep cryogenic treatment time increased from 8 h to 12 h, the BCC diffraction peak intensity of the \((110)\) crystal plane decreased while that of the \((200)\) crystal plane increased. The results show that deep cryogenic treatment did not change the crystal structure of AlCrFe2Ni2, but as the deep cryogenic treatment time increased, the diffraction peak intensities of the \((110)\) BCC and \((200)\) BCC phases showed an inverse relationship.

3.2. Microstructures and elemental distribution

Figure 2 shows the SEM of AlCrFe2Ni2 after different cryogenic processing times. Among them, (a), (c), (e), (g), (i) and k are low-power tissue photos, and (b), (d), (f), (h), (j) and (l) are the marked areas of A, B, C, D, E and F which correspond to high-resolution images, to facilitate observations of the changes in the BCC phase after treatment. Figure 2(a) shows that the as-cast structure of the alloy was composed of striated FCC and BCC phases, in which the BCC phase included BCC and B2 (figure 2(b)) [35]. A structure, which was composed of...
Figure 2. SEM images of AlCrFe$_2$Ni$_2$ after different deep cryogenic treatment times ($t = 4, 8, 12, 24, 48$ h), in which a, c, e, g, i, and k are low-resolution images, while b, d, f, h, j, and l are high-resolution images.
BCC and B2 structures, formed due to spinodal decomposition [35]. Longer deep cryogenic treatment times caused the organization of the alloy to change, band FCC structures to break, become shorter, and more disordered (figures 2(c), (e), (g), (i) and (k)). The content of BCC and B2 structures increased or decreased inversely, as shown in figures 2(d), (f), (h), (j) and (l). The organization of the BCC and B2 phases changed, as indicated by the peak strength of the (110) and (200) crystal planes in the XRD patterns (figure 1). When the deep cryogenic treatment time was 4 h, the B2 structure increased beyond its original value in the as-cast condition. Then, as the deep cryogenic treatment time continued to increase, the BCC and B2 phases were transformed into one another, and the B2 phase increased again at 24 h. This inverse change is consistent with changes observed in the (110) and (200) crystal faces in figures 1(b) and (c).

Figure 3 shows the EDS surface elemental maps of AlCrFe$_2$Ni$_2$. Figure 3(a) shows that the BCC phase was enriched with Al and Ni, while the FCC phase was enriched with Fe and Cr. During the cooling process of the alloy, FCC phase is first produced, and then the Al and Ni elements are segregated into the boundary to form a BCC phase rich in Al and Ni [35]. It can be seen from figure 3(b) that there was no significant change in the type and distribution of elements in the BCC and FCC phases before and after deep cryogenic treatment.

### 3.3. Mechanical properties

The button ingot prepared by vacuum arc furnace was not large enough for tensile tests. Figures 4(a) and (b) respectively show the compression stress-strain curves and Vickers hardness of AlCrFe$_2$Ni$_2$ after different deep cryogenic treatment times. None of the compression samples were fractured after treatment, so it can be inferred that no significant brittle transformation occurred in the alloy. Figure 4(a) shows that the yield strength of the treated alloy first increased and then decreased, reaching a maximum at 4 h. The yield strength increased by 22.7% from 750 MPa to 920 MPa. Long FCC phase fractures in the alloy became shorter after deep cryogenic treatment, and the distribution became more disordered and more energy was stored in grains. This meant that deformations in the alloy required higher energy, resulting in a higher yield strength (figures 2(c), (e), (g), (i), (k)).

Figure 4(b) shows that the hardness of the treated alloy first increased and then decreased, reaching a maximum at 4 h, while the hardness increased 11.6% from 303 HV to 338 HV. The alloy hardness increased due to fracture and configurational changes in the FCC phase in the alloy after treatment. Its strengthening mechanism was similar to the fine-grain strengthening during deep cryogenic treatment often observed in traditional alloys [23, 30, 36]. After deep cryogenic treatment, the microstructure of the alloy produced fine crystal strengthening, which improved its deformation resistance and increased its hardness.

When the deep cryogenic treatment time was longer than 4 h, the yield strength and hardness of the alloys decreased. This may have occurred due to the reduction in the amount of B2 in the tissue (figures 2(d), (f), (h), (j), (l)) or the fact that the deep cryogenic treatment changed the orientation of BCC phase. Some of the B2 phase was converted into BCC phase (the inverse change of the diffraction peak intensity of the B2 and BCC phases in...
Figure 1). Figure 4(b) shows that when the deep cryogenic treatment time was 24 h, the yield strength and hardness of the alloy increased, which may have been because more B2 phase was present in the BCC phase after 24 h of deep cryogenic treatment.

Figure 5 shows the 3D wear surface morphologies of AlCrFe2Ni2 after different deep cryogenic treatment times. There was less wear deformation in the alloy after treatment than in the as-cast alloy after friction and wear tests (figure 5(a)), indicating that deep cryogenic treatment improved the wear resistance of the as-cast alloy. After 4 h deep cryogenic treatment, the alloy had the smallest wear and deformation (figure 5(b)), i.e., the optimal wear resistance.

Table 1 shows the friction coefficient, scratch depth, and roughness of the alloy after different deep cryogenic treatment times. All three parameters decreased first and then increased, indicating that the wear resistance of the alloy increased first and then decreased as the deep cryogenic treatment time increased.

The wear resistance was higher because the band FCC phase broke and was shortened (figures 2(c), (e), (g), (i), (k)) after deep cryogenic treatment. This made the alloy deformation require more energy, and the abrasion resistance declined due to an orientation changed in the BCC and B2 phases after deep cryogenic treatment (figure 1 and figures 2(d), (f), (h), (j), (l)). According to table 1, deep cryogenic treatment improved the wear resistance of the alloy because the friction coefficient, grinding mark depth, and roughness of the as-cast alloy were larger. The best wear resistance was obtained at a deep cryogenic treatment time of 4 h.
4. Conclusions

The effect of deep cryogenic treatment on the phase composition, microstructure, and properties of AlCrFe$_2$Ni$_2$ high-entropy alloy was studied, and the following conclusions were drawn:

1. After different cryogenic treatment times, AlCrFe$_2$Ni$_2$ was composed of BCC and FCC phases. The phase type in the alloy did not change after deep cryogenic treatment, but the orientation of the BCC and B2 phases changed. After deep cryogenic treatment, the long strip FCC phase in the alloy structure decomposed and became shorter and more disordered. BCC and B2 phases transformed into each other during deep cryogenic treatment.

2. As the cryogenic treatment time increased, the alloy did not undergo an obvious brittle transition, and the yield strength and hardness tended to increase first and then decrease, and both were superior to the as-cast alloy. The optimal mechanical properties of the alloy were obtained at a treatment time of 4 h, and an 11.6% higher Vickers hardness of 338 HV and a 22.7% higher yield strength of 920 MPa were obtained.

3. As the cryogenic treatment time increased, the wear resistance of the alloy first increased and then decreased, but all treatment times produced alloys with superior properties to the as-cast alloy. The wear resistance of the alloy was the best when the treatment time was 4 h, and the friction coefficient was 0.643.

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| Time of treatment (h) | Friction coefficient | Wear scar depth (μm) | Roughness |
|----------------------|----------------------|----------------------|-----------|
| As-cast              | 1.442                | 14.308               | 1.717     |
| 4                    | 0.643                | 6.339                | 0.731     |
| 8                    | 1.118                | 10.864               | 1.439     |
| 12                   | 1.243                | 12.159               | 1.504     |
| 24                   | 0.923                | 9.878                | 1.011     |
| 48                   | 1.432                | 13.826               | 1.571     |
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