Smart Manufacturing and Material Processing (SMMP)

DOI: http://doi.org/10.26480/smmp.01.2023.37.40

RESEARCH ARTICLE

EFFECT OF W CONTENT ON WEAR RESISTANCE OF COCRFENIMNWX HIGH ENTROPY ALLOY

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ARTICLE DETAILS

Article History:

Received 20 January 2024
Revised 18 February 2024
Accepted 11 March 2024
Available online 13 March 2024

ABSTRACT

High entropy alloys show excellent properties that traditional metals do not have in many aspects, but their high preparation cost and unstable properties make it difficult to scale production. In this paper, $CoCrFeNiMnW_x$ high entropy alloy was prepared by low-cost mature process powder metallurgy, and the effects of W content on the composition, structure, hardness and rub proofness of the alloy were studied. It was found that the alloy could form FCC phase CoCrFeNiMn solid solution without the addition of W, and Fe_7W_6 phase would be formed with the addition of W. This phase can significantly improve the hardness and wear resistance of the material. With the further increase of W content, the precipitation of W element further increases the hardness of the material, but its wear resistance decreases, because the wear form changes from abrasive wear to oxidative wear with the formation of Fe_7W_6 phase, and the wear form changes to fatigue wear with the precipitation of W element.

KEYWORDS

CoCrFeNiMnW, high entropy alloy, wear resistance, wear pattern

1. INTRODUCTION

The earliest research on high entropy alloys dates back to the late 18th century, when the German scientist Franz Karl Achard mixed five to seven different metals together to create alloys, although there was no concept of high entropy alloys at the time. In 1993, Cantor falsified the chaos principle and created the concept of multi-principal component alloy (Cantor et al., 2002). Until 2004, Professor Ye Junwei of Taiwan Province of China proposed the concept of high entropy alloy for the first time in a public paper, its content is expressed as: by five or more elements, mixed at a near equal molar ratio, the content of each element (atomic ratio) is greater than 5% and less than 35% of the alloy (Yeh et al., 2004). This concept subverts the design concept of traditional materials, forms an additional huge alloy system, opens a new research field, and is expected to break through the limits of mechanical properties of traditional materials. Lim's article, published on the cover of nature in 2016, discusses the vast field opened by high entropy alloys, which provides a new idea for the research and development of new metal materials with special properties under extreme conditions (Lim, 2016). Due to its cocktail effect, tribological studies of high entropy alloys can break through the performance limits of traditional anti-wear and lubrication alloys by taking advantage of their broad composition space and unique structural characteristics (George et al., 2019). Especially to solve the traditional alloy cannot meet the extreme conditions of stable lubrication anti-wear, to ensure the function of the function (corrosion resistance, radiation resistance, low temperature, catalysis, superconductivity, soft magnetic, etc.) to achieve the bottleneck problem of anti-wear.

Powder metallurgy (P/M) is a metallurgical method of alloying component elements in a solid state (Halil et al., 2019). It usually includes the preparation of pre-alloyed powder, such as mechanical alloying, atomization, etc., and the subsequent sintering process, or the alloying and curing process of the element powder is achieved directly by the sintering process (Vaidya et al., 2019; Ge et al., 2017; Fang et al., 2015; Zhu et al., 2000). Among them, the combination of mechanical alloying and vacuum discharge plasma sintering is the most commonly used. In the mechanical alloying process, the long-term violent impact between the metal powder and the grinding ball makes the metal powder constantly broken and cold welded, so as to achieve the mutual diffusion of the atoms in the metal powder, and the most alloyed metal powder. Vacuum discharge plasma sintering technology is a sintering technology that realizes solidification of metal powder in a short time by using the Joule heat effect generated by pulsed current as a heat source. Because the powder metallurgy method avoids the melting and solidification process of the metal, the powder metallurgy alloy usually has a fine grain size (even sub-micron and nano-sized grains), as well as a uniform distribution of component elements, and shows very high room temperature strength, hardness and good plasticity. Based on the excellent properties of powder metallurgy alloys, researchers have gradually carried out research on powder metallurgy refractory high entropy alloys in recent years (Mucsi, 2019; Han et al., 2020; Kang et al., 2019).

The preparation of high entropy alloys with remarkable properties requires the selection of appropriate elements. Co, Cr, Fe, Ni, Mn elements are often selected as elements for the preparation of high entropy alloys because of their excellent mechanical properties and relatively low prices. Cheng prepared FCC phase CoCrFeMnNi high entropy alloy and found that it has the characteristics of high toughness and low strength (Cheng et al., 2019). By using Nb doping on the alloy, the strength of the material is greatly improved while high toughness is retained. Yongming sprayed Al_2O_3 on the surface of FeCoNiCrMn high entropy alloy, and studied the microstructure, mechanical properties and tribological properties of the composite coating and found that Al_2O_3 could improve the mechanical properties of the high entropy alloy to a greater extent, and the wear

Quick Response Code	Access this article online	
	Website: Website: www.topicsonchemeng.org.my	**DOI:** 10.26480/smmp.01.2023.37.40

Cite The Article: Wenjie Zhu, Yuzuo Liu, Charan Kumar Gatenda (2023). Effect of W Content on Wear Resistance of Cocrfenimnwx High Entropy Alloy. *Topics In Chemical & Material Engineering, 2(1): 37-40.*

amount of the material was reduced by 50% under the same wear conditions (Yongming et al., 2022). Al_2O_3 can greatly improve the rub proofness of the material. Hao sprayed CoCrFeNiWx high entropy alloy on the surface of the metal material and tested its microhardness and wear resistance, finding that with the increasing content of W in the alloy, the hardness and rub proofness of the layer were significantly improved (Hao et al., 2022). Based on the above situation, this paper attempts to use the theory of powder metallurgy to prepare CoCrFeMnNiWx high entropy alloy, and explore the influence of W content on its hardness and rub proofness. The wear-resistant mechanism was investigated by observing the microstructure.

2. Experiment

The article adopts the method of powder metallurgy process preparation CoCrFeMnNiWx high entropy alloys (x = 0,0.15, 0.3, 0.45, 0.6, 0.75, 0.9). The purity of the powder raw materials is above 99.9%, and the particle size is 30-50um. The powder is mixed in the argon environment according to the following mass ratio (Table 1).

The metal powder is mechanically alloyed by the planetary ball mill. The speed of the ball mill is 400r/min, the ball mill time is 48h, and the ball mill mode is one-way ball mill for 30 minutes and the machine stops for 15 minutes. The obtained metal powder was loaded into a prototype mold with a diameter of 25mm, held at 300°C for 1h under argon and pressed at a pressure of 300MPa. The pressed green billet was put into a vacuum furnace for self-propagating sintering. The sintering temperature was set at 1200°C and the sintering time was set at 2h.

Table 1: CoCrFeMnNiWx High entropy alloy powder preparation table

Element	Fe(g)	Co(g)	Ni(g)	Cr(g)	Mn(g)	W(g)
Mass distribution(100g)	19.92	21.02	20.93	18.54	19.59	0
	18.13	19.14	19.06	16.88	17.84	8.9537
	16.64	17.56	17.49	15.50	16.37	16.436
	15.38	16.23	16.16	14.32	15.13	22.782
	14.29	15.08	15.02	13.31	14.06	28.232
	13.35	14.09	14.03	12.43	13.13	32.963
	12.53	13.22	13.16	11.66	12.32	37.109

3. Results and Discussion

3.1 Phase Analysis

Figure 1 shows the XRD patterns of different W content. It can be seen from the figure that when the alloy doesn't contain W, a solid solution single phase of FCC structure is formed. When W is added to the alloy, a μ phase of Fe_7W_6 is formed, and the μ phase particles are large, which can generally significantly improve the hardness and wear resistance of the material (Lei et al., 2020). At the same time, it is accompanied by the precipitation of W elemental. With the increase of W added, the Fe_7W_6 phase and W element are also increased. It should be noted that although the XRD test results show that the hard phase of Fe7W6 is precipitated after the addition of W element, the hard phase precipitated is very likely to be the mixed phase of Co_7W_6 and Fe_7W_6 due to the similar properties of Co_7W_6 and Fe_7W_6, and the pattern is also similar.c

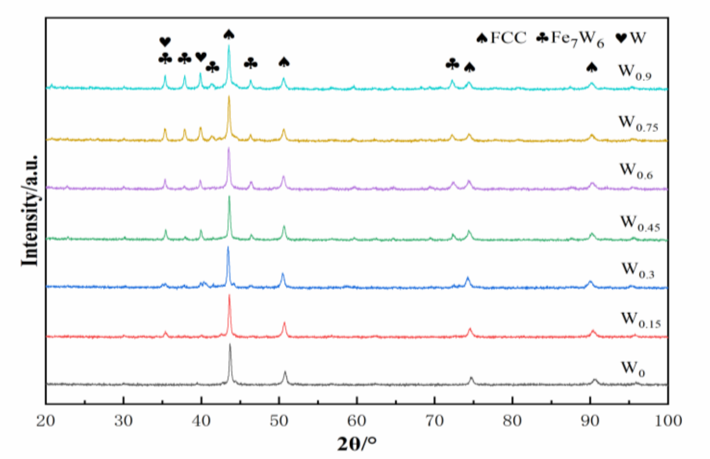

Figure 1: XRD patterns of different W content

3.2 Microstructure Analysis

a) According to the SEM test results, it can be found that Fe, Co, Ni, Cr and Mn can be mixed and dissolved with each other when no W element is added to the high entropy alloy, and the high entropy alloy can form a stable FCC phase (FIG. 2 a). With the addition of W element, FeCoNiCrMnWx high entropy alloy began to form a bis-phase structure. When the content of W was less in the alloying element, it was observed that the FCC solid solution was also inlaid with μ phase Fe7W6 (FIG. 2b). When the content of element W further increases, it can be observed that the microstructure of the high entropy alloy has the characteristics of eutectic structure. As can be seen from FIG. 2c, when the maximum amount of element W is reached, the element W cannot be fused into other elements at all, and the alloy begins to precipitation W single phase, at which time the phase structure of the high entropy alloy is three-phase structure. It can be seen from Figure 2 that the difference of W content will have a great impact on the microstructure of high entropy alloy. With the W content become more, the microstructure of high entropy alloy experiences a transformation from stable FCC single-phase to dual-phase or even three-phase.

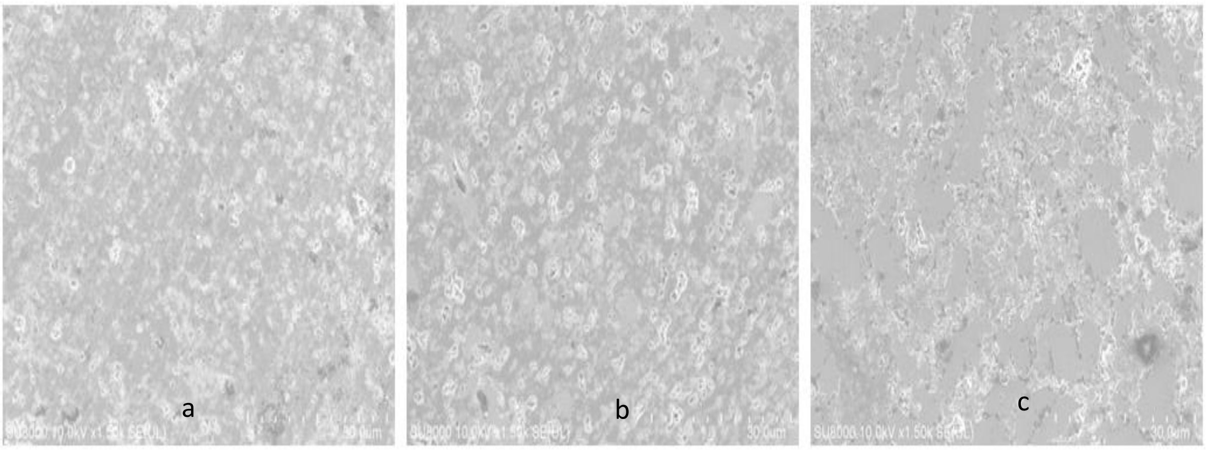

Figure 2: SEM images of Co-Cr-Fe-Ni-Mn-Wx alloy: (a) x=0; (b) x=0.3; (c) x=0.9

3.3 Hardness Test

The Vickers hardness of the sample is tested, and the test results are shown in Figure 3. It is easy to observe that the hardness of the sample is gradually increased with the increase of the content of W. Combined with the previous test results, it is not difficult to find that the hardness of FCC solid solution formed by CoCrFeNiMn without W is low. With the increase of the hardness of the alloy, as the added W continues to increase, a large number of W elements are precipitated, further improving the hardness of the alloy, so with the increase of W content, the hardness of the alloy is more obvious. The maximum hardness can reach 578.36HV. It's not difficult to see from the experimental results that the formation of Fe_7W_6 hard phase has a positive effect on the enhancement of material hardness, and the precipitation of W simple substance can further improve the hardness of the material.

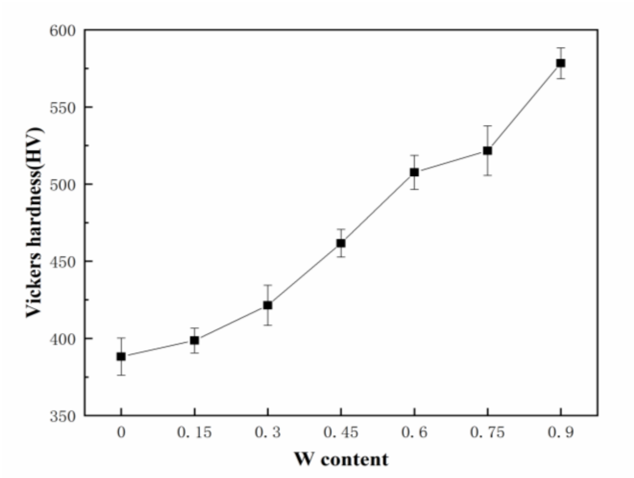

Figure 3: Vickers hardness of samples with different W content

3.4 Wear Resistance Test

The friction test platform selected MFT-3000 friction and wear testing machine of RTEC Instrument company. In the test, the sample was cut into slices of 12×6mm and fixed on the test platform. Si3N4 small balls with a diameter of 6.3mm were selected for the grinding pair, positive pressure was applied at 10N, the grinding speed was 100mm/s, and the test time was 30min. The test results were shown in Figure 4.

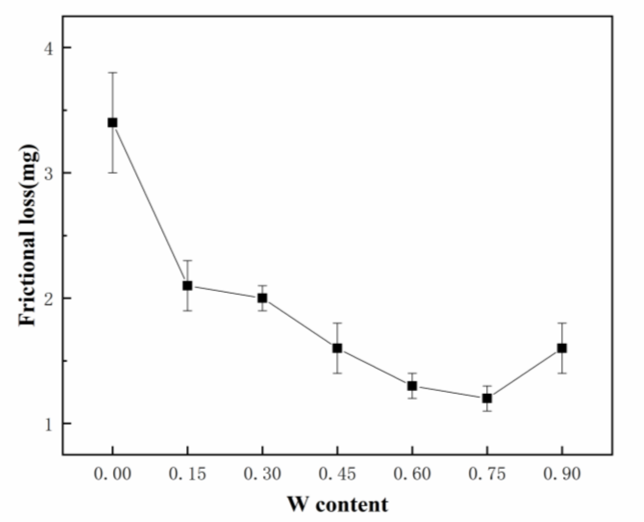

Figure 4: Samples with different W content lose weight by friction

As we can see from the figure, the wear amount of the sample decreased significantly after the addition of metal W, and gradually decreased with the increase of the amount of W, showing improved wear resistance. Interestingly, however, when the atomic content of W increased from 0.75 to 0.9, the wear amount increased instead of decreasing. In order to explore the cause of this phenomenon. In this paper, SEM scanning was performed on the surface morphology of samples with different W contents after wear, as shown in Figure 5.

It can be obviously observed in Fig. 5a that a good deal of particles are attached to the surface of the sample after friction, and the wear is in the form of abrasive wear. Particles generated in the wear process make the surface more rough and further aggravate the wear, so the wear loss is the highest when W is not added. When the content of W reaches 0.3 (Fig. 5b), it can be observed that less abrasive particles are produced on the surface of the wear sample, and a film-like substance is produced on the surface, which is the oxide film of metal with high hardness and attached to the friction surface, which can effectively reduce wear. At this time, the wear form is mainly oxidative wear and the abrasive wear is supplemented.

The oxide film greatly reduces the wear degree, which is also reflected in the wear amount described above. When the content of W further increased to 0.75 (Fig. 5c), the wear surface of the sample was very flat, and the entire sample surface was covered by a layer of metal oxide film, which protected the wear surface to prevent further wear, so the wear was further reduced. At this time, the wear was in the form of oxidative wear.

Finally, when the W content reaches the maximum of 0.9 (Fig. 5d), obvious metal oxide film can still be observed, but faults on the wear surface of the sample can also be observed at the same time, which indicates the fatigue strength failure of the material and aggravates the wear of the material. In this case, the wear form is the joint action of oxidative wear and fatigue wear.

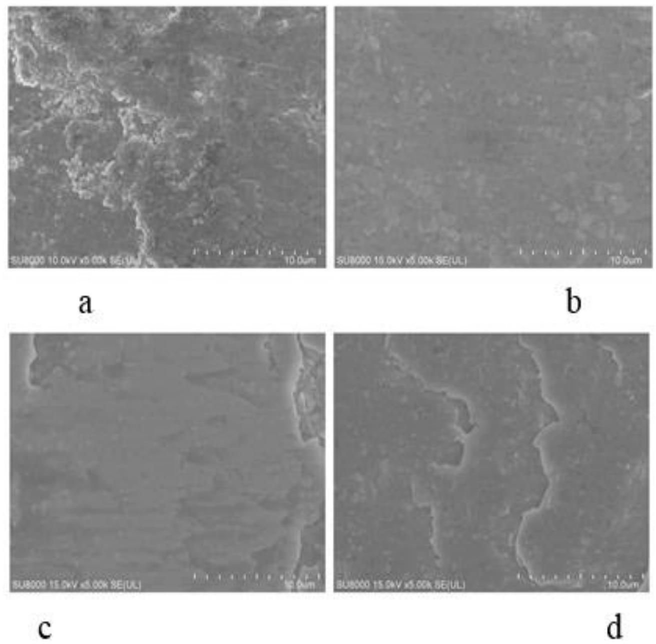

Figure 5: SEM images of Wear surface morphology of samples with different W content: (a) x=0; (b) x=0.3; (c) x=0.75; (d) x=0.9

4. Conclusion

In this paper, CoCrFeNiMnWx high entropy alloy was obtained by vacuum sintering. The composition, microstructure, hardness and wear resistance of the alloy were studied, and it is easy to draw the following conclusions.

When the alloy does not contain W, the CoCrFeNiMn solid solution of FCC phase can be formed. After adding W, a new hard phase Fe7W6 is formed. With the increase of the content of W added, the content of Fe7W6 gradually increases, and the W elemental is precipitated at the same time.

The hardness of CoCrFeNiMnWx high entropy alloy was measured, and it was found that its hardness increased significantly with the increasing content of W in the alloy, because the new phase Fe7W6 produced with the addition of W is a hard phase, which can observably promote the hardness of the alloy. At the same time, with the precipitation of W, the hardness of the material further increased, reaching a maximum of 578.36HV.

The wear resistance of CoCrFeNiMnWx high entropy alloy was tested, and it was found that it showed a trend of first increasing and then decreasing of the wear resistance of CoCrFeNiMnWx when the W content continues to increase. By observing the morphology of the wear surface, it was found that the wear form of the high entropy alloy without W was abrasive wear, and the abrasive particles could significantly reduce its wear resistance. With the increasing content of W in the alloy, the wear surface shows obvious characteristics of oxidative wear. The oxide film can effectively protect the wear surface to prevent further wear, so the wear degree decreases. However, the wear form gradually changes from oxidative wear to fatigue wear due to the precipitation of a large number of W elements, and the wear surface material is stripped off in large quantities, resulting in a significant increase in the wear amount.

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