The effect of different Ag addition on microstructure, mechanical properties and tribological behavior of CoCrFeNiMn-Cr3C2 composite

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Abstract
CoCrFeNiMn high entropy alloy (HEA) matrix composites with Cr3C2 reinforcement (10 wt%) and different mass fraction of Ag lubricant (10, 15 and 20 wt%) were produced by spark plasma sintering. The composites consist of HEA’s FCC phase, Cr7C3 phase and Ag phase, and the microstructures of composites are dense and uniform. The ultimate plasticity strain and fracture toughness improve with the addition of Ag increasing at room temperature. The composites exhibit excellent self-lubricating and wear resistance below 400 °C, and the composite with 20 wt% Ag content has the lower friction coefficient and wear rate. The Ag addition exhibits positive role in improving the wear behavior at medium-low temperatures. The main wear mechanisms of the composites are micro-cutting and abrasive wear at low temperatures. At high temperatures, the oxide tribo-layer generates on the wear surface and deeply torn. Oxide wear and surface deformation are the main wear mechanisms.

1. Introduction

In recent decades, self-lubricating materials have attracted much attention due to their widespread applications especially in gas turbine engines and aerospace at high temperature [1–5]. In self-lubricating composites, the metallic matrix is the key to the composites, which can provide excellent loading capacity, high strength, excellent ductility, good wear properties, high temperature stability, etc [6–8]. For example, PS/PM metal matrix high temperature self-lubricating composites developed by NASA have been applied to high temperature bearing of aeroengines and governing mechanism of steam turbines. These composites usually chose Ni-based alloy and Co-based alloy as matrix material, which have excellent mechanical properties and thermal stability [9–12]. However, high entropy alloy (HEAs) is rarely used as the matrix materials in self-lubricating materials. High entropy alloys contain multiple metal elements, which possess distinguished properties [13–16]. For example, Zhang Aijun et al studied a series of high entropy alloy based self-lubricating composites. CoCrFeNi-Graphite-MoS2 high-entropy alloy based self-lubricating composites were prepared by spark plasma sintering technology [17]. The CoCrFeNi-Graphite-MoS2 composites have good high temperature tribological properties. When Ag and eutectic fluoride BaF2/CaF2 are added to CoCrFeNi high entropy alloy as lubricants, the friction coefficient of the composite is lower than 0.26 at room temperature to 800 °C, and the wear rate is lower than 10−5 mm3/N·m [18]. CoCrFeNiSx self-lubricating composite material is prepared by adding different contents of FeS in CoCrFeNi HEA, and the material has good tribological properties in a wide temperature range [19].

In this work, CoCrFeNiMn HEA is a good candidate for high temperature tribological application. CoCrFeNiMn HEA consists of single FCC phase and has excellent yield strength and fracture toughness.
especially at cryogenic temperatures [20]. Also the CoCrFeNiMn HEA has higher microstructure stability [21]. Therefore, CoCrFeNiMn HEA is selected as matrix material. Cr$_2$C$_2$ (10 wt%) is added as reinforcement to improve the wear resistance [22], which has good oxidation resistance and high temperature strength. To improve the self-lubricating properties of the composites at a wide temperature range, adding solid lubricant is an effective way. In this work, soft metal Ag (10, 15 and 20 wt%) is used as solid lubricant, which has low shear strength and can attach to interacting surfaces to decrease friction and wear. The composites were fabricated by spark plasma sintering (SPS) which can eliminate the aggregation and segregation to synthesize uniform microstructure. The evolution of Ag additions on phase constitution, microstructure, mechanical properties and tribological behavior were discussed and analyzed.

2. Materials and methods

The CoCrFeNiMn-Cr$_2$C$_2$-Ag composites were sintered by SPS (Shanghai Chen Hua Technology Co., China) under vacuum environment with the mixed powders of pre-alloyed CoCrFeNiMn, Cr$_2$C$_2$ and Ag. The shape of pre-alloyed CoCrFeNiMn powder exhibits spherical with an average particle size of 53 μm. The shape of Cr$_2$C$_2$ powder and Ag powder was irregular, and the average size is 25 and 35 μm, respectively. The mixed powder was sintered in vacuum environment at 950°C for 30 min with a pressure of 30 MPa.

The phase constitutions of composites were characterized by x-ray diffraction (XRD, D/MAX-2400) with 40 kV operating voltage and Cu Kα radiation at a scanning rate of 5 deg./min. The microstructures were conducted by scanning electron microscope (SEM, JSM-5600) equipped with energy dispersive spectroscopy (EDS, Oxford instrument). The hardness of the composites was characterized by a HV-1000 type Vicker’s hardness instrument applied a load of 300 N. The compressive experiments at room temperature (RT) were performed on a universal materials tester (CMT5202, Shenzhen Sans Material Test Instrument Co., China). The strain rate of compressive experiment was $1.6 \times 10^{-3}$ s$^{-1}$. The compressive specimens were $\varnothing 3$ mm $\times$ 6 mm in dimension. The dry friction and wear properties of the composites were tested from RT to 800°C with counterface of Si$_3$N$_4$ ball ($\varnothing 6$ mm in diameter) on a high-temperature tribometer (HT-1000, China) for 30 min. The sliding speed and sliding distance were 0.28 m s$^{-1}$ and 504 m, respectively. The worn surfaces were characterized by SEM, EDS and micro-beam XRD (Bruker, XRD).

3. Results and discussion

The phase constitutions of the composites with 10wt% Cr$_2$C$_2$ and different Ag content are shown in figure 1. The HEA-10% Cr$_2$C$_2$ composite is composed of HEA’s FCC and Cr$_2$C$_3$ phases [22]. The FCC phase was solid solution phase of Co, Cr, Fe, Ni and Mn element. When adding 10wt%, 15wt% and 20wt% Ag content in the composites, the XRD patterns detect a new phase of Ag. Ag possesses positive enthalpy with all other elements.
Thus Ag will not react with other elements and remain as Ag in composites. Because of the rapid sintering of SPS technique, the Cr$_3$C$_2$ decarburizes forming Cr$_7$C$_3$ [23]. Compared to Cr$_3$C$_2$, Cr$_7$C$_3$ has higher thermal stability, strength and wear resistance, which can improve the strength of composites.

Figure 2 shows the typical SEM image of CoCrFeNiMn-Cr$_3$C$_2$-Ag composite after etched by aqua regia, and Table 1 shows the EDS results of CoCrFeNiMn-Cr$_3$C$_2$-Ag composites in different regions. The corresponding EDS elemental mapping of CoCrFeNiMn-Cr$_3$C$_2$-20wt%Ag is shown in Figure 3. The composites have dense and uniform microstructures, and there are three different color contrasts: grey, dark and bright. Combined the XRD and EDS analysis, the grey, dark and bright regions are attributed to FCC, Cr$_7$C$_3$ and Ag phase, respectively. The volume of Cr$_3$C$_2$ phase is the same in the composites with different Ag addition. The Ag phase is uniformly distributed along the FCC boundaries and surrounded the Cr$_7$C$_3$ phase, which can bond the matrix and improve...
the density and toughness of the composites. The Cr$_7$C$_3$ phase dispreads in the interstice of the FCC phase which inhibits the dislocation movement at the interface to strengthen the composites.

The hardness of the composites with 10wt%, 15wt% and 20wt% Ag addition is 116.2, 105.6 and 94.2 HV, respectively. Figure 4 shows the typical compressive strain–stress curves of the composites. The yield strength of

![Figure 4. Typical compressive strain–stress curves of the composites.](image)

![Figure 5. SEM images of fracture surfaces of CoCrFeNiMn-Cr$_3$C$_2$-Ag composites: (a) CoCrFeNiMn-Cr$_3$C$_2$, (b) CoCrFeNiMn-Cr$_3$C$_2$-10wt%Ag, (c) CoCrFeNiMn-Cr$_3$C$_2$-15wt%Ag, (d) CoCrFeNiMn-Cr$_3$C$_2$-20wt%Ag.](image)
HEA-10wt%Cr₃C₂ composite is 578 MPa without fracture. Adding 10wt% and 20wt% Ag in the composites, the yield strength decreases to 432 and 328 MPa, respectively. More addition of Ag results in the soft of composite, which leads to the decrease of strength. However, the fracture strain increases with the increase of Ag addition. It improves significantly from 30.2% to 52.3% as the content of Ag increases from 10wt% to 20wt%. The improvement of the ductility is attributed to the shear formation of more addition of ductile element Ag [24]. Another reason may be that more Ag addition can decrease the grain size of matrix phase. Figure 5 shows the fracture surfaces of composites. The composite with 10wt% Ag content exists lots of planer facets, river-like pattern and some of dimples, while the composite with 20wt% Ag addition appears some dimples and little of tear edges and cleavage steps. The coordination of brittle phase Cr₇C₃ and toughness phases of matrix FCC and Ag is attributed to the fracture toughness of the composites.

Figure 6 shows the plots of friction coefficient of composites with different content of Ag at RT, 200, 400, 600 and 800 °C. It is evidently that Ag addition has the lubricating effect at low temperatures. The friction coefficients of HEA-10wt%Cr₃C₂ composite are 0.46, 0.63 and 0.51, respectively, at RT, 200 and 400 °C. As to composite with 10wt% Ag addition, they are 0.49, 0.38 and 0.43, respectively. The 20wt% Ag added composite exhibits excellent self-lubricating properties, and the friction coefficients are 0.26, 0.30, and 0.32, respectively. But at high temperatures, the friction coefficients of the composites with Ag addition increase seriously, which are beyond the HEA-10wt%Cr₃C₂ composite. At 800 °C, the three composites with Ag addition have the approximately same friction coefficient, which is mainly due to the invalidation of Ag lubricant. Compare the 10wt% and 15 wt% Ag added composite, the friction coefficient doesn’t exhibit a trend of increasing or decreasing, which may be due to that the role of addition of Ag is not obvious. Compared the three different composites at the same temperature, the friction coefficient of the 20wt% Ag added composite is lower than the other two composites from RT to 600 °C. More addition of Ag has excellent lubricating effect in the composites. Figure 6(d) shows the variations of the friction coefficient of the composites with different Ag content. At low temperature, the addition of Ag extrudes on the wear surfaces diminishing shear junctions, which contributes to lubricating and decreasing the friction coefficient. When the temperature further rises, the content of Ag excessively diffuse and is oxidized losing its lubricating effect.
and more addition of Ag causes the softening of composites, which result in the increase of friction coefficient. Figure 7 shows variation in wear rates of CoCrFeNiMn-Cr$_3$C$_2$-Ag composites at different temperatures. When 10wt% Ag content is added, the wear rate of the composite gradually increases with the increase of temperature and reaches the maximum at 600 °C. When the temperature continues to increase to 800 °C, the wear rate of the composite decreases sharply and reaches the minimum. When 15wt% Ag was added as solid lubricant, the wear rate of the composite also increases gradually with the increase of temperature, and the wear rate reached the maximum at 400 °C, and then shows a downward trend with the increase of temperature. When 20wt% Ag was added, the wear rate of the composite gradually increases with the increase of temperature, and the wear rate reached the highest at 600 °C and then decline when the temperature increased to 800 °C. The wear rates of composites decrease with the more addition of Ag content at low temperatures. The lubricating of Ag plays an important role in decreasing the wear rate at medium-low temperature. At high temperatures, the oxide tribo-layer generates on the wear surface, and the surface deeply torn. The invalidation of Ag lubricating and rougher surface at high temperature would increase wear rate. By comparing the wear rate of composites with different Ag contents at the same temperature, it can be seen that the wear rate of CoCrFeNiMn-Cr$_3$C$_2$-20wt%Ag composite have good tribological properties at medium-low temperature.

To analyze the wear mechanisms of composites at different temperatures, the typical SEM wear surface morphologies and XRD analysis of the composites with 15wt% Ag content at different temperatures are shown in figures 8 and 9. Table 2 summarizes the EDS analysis of different elements distributions inside and outside the wear surfaces. At low temperatures, abundant wear particles and pits are observed on the wear surfaces, indicating that the wear mechanisms are micro-cutting and abrasive wear. From the EDS analysis, the Ag content in the worn surfaces is higher than the outside, which implies that the Ag exposes on the wear surface to lubricate the surface and reduce the friction. It is also verified by XRD analysis that Ag is covered on the wear surface at RT. In low temperature, silver diffused and spread uniformly on the friction surface, which has a positive effect on lubrication. Therefore, the wear rates of composites decrease with the more addition of Ag content at low temperatures. At high temperatures, the oxide tribo-layer generates on the wear surface and deeply torn as shown in figure 8(h), which indicates that oxide wear and surface deformation are the main wear mechanisms. The rougher surface at high temperature would increase the friction coefficient. Compared the elements distribution inside and outside the wear surfaces, the oxygen content at high temperature is significantly higher than the low temperature. In other side, the oxide layer would protect the composite from the wear, which result in the decrease of the wear rate at high temperature. From XRD analysis of the wear surfaces in figure 9, it confirms that oxides of Ag$_2$O and Fe$_3$O$_4$ are formed at 800 °C, which indicates that the lubricant of Ag loses its effect. At high temperature, Ag became excessively soft and severe oxidized, which result in the high friction coefficient.
Figure 8. SEM images of worn surfaces of CoCrFeNiMn-Cr3C2-15wt%Ag composite at RT (a) and (b), 200 °C (c) and (d), 400 °C (e) and (f), 600 °C (g) and (h) and 800 °C (i) and (j).
4. Conclusion

In this work, CoCrFeNiMn HEA matrix added Cr$_3$C$_2$ and different content of Ag composites were prepared. The composites with Ag addition are comprised of HEA’s FCC phase, Cr$_7$C$_3$ phase and Ag phase. As the addition of Ag increases, the fracture toughness of composites increases. The composites exhibit excellent self-lubricating and wear resistance below 400 °C, and the composite with 20wt% Ag content has the lower friction coefficient and wear rate. The main wear mechanisms translate from micro-cutting and abrasive wear to oxide wear and surface deformation from low temperatures to high temperatures. Combined mechanical properties and friction behavior, the 20wt% Ag added composite possesses good properties to next investigation. In the future, high-temperature solid lubrication will be added to decrease the friction coefficient of composite at high temperatures, which can prepare the composites with excellent tribological properties at wide temperatures range.

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Data availability statement

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

Conflicts of interest

The authors declare no conflict of interest.
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