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The Microstructure and Mechanical Properties of High Entropy Alloy CoCrFeNiMn Matrix with Cr_3C_2 Reinforcement and Ag, BaF_2/CaF_2 Solid Lubrication

Zhiming Guo *, Jingdan Li and Xiaoyan Ren

Department of Mechanical Engineering, Taiyuan Institute of Technology, Taiyuan 030008, China; lijingdan9@163.com (J.L.); renxiaoyan03@126.com (X.R.)
* Correspondence: guozhiming0602@163.com; Tel./Fax: +86-35-1356-6033

Abstract: A series of CoCrFeNiMn high-entropy alloy matrix self-lubricating composites were prepared by spark plasma sintering. The composites are composed of an FCC phase, Cr_7C_3, Ag, and eutectic fluoride BaF_2/CaF_2 phases. The microstructure of the composites is uniform. The additional phases distribute along the boundary of equiaxed grains of the FCC phase. The compressive yield strength and fracture toughness decrease with the increase of eutectic fluoride BaF_2/CaF_2. The composites are susceptible to brittle cleavage fracture.

Keywords: high-entropy alloy; composite; self-lubricating; microstructure; mechanical properties

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1. Introduction

Self-lubricating materials have attracted serious attention due to their extensive applications in areas like gas turbine engines and aerospace under extreme conditions, such as vacuum environments, extreme loading conditions, high speeds, and broad temperature ranges [1–3]. Self-lubricating composites are composed of a matrix phase, hard reinforced wear-resistant phases, and solid-lubricant phases [4,5]. Metallic oxides or carbide ceramics are good candidates for hard reinforced phases due to their high strength and hardness, which can greatly improve the wear-resistant properties of the composites. Solid lubrication is the only viable alternative to reduce friction at a certain temperature. Various solid-lubricating materials have been developed to meet different applications, such as graphite, MoS_2, hBN, Ag, PbO, $SrSO_4$, Ag_2MoO_4, Ag_2MoO_7, $BaMoO_4$, CeF_3, CaF_2/BaF_2, and so on. Also it is hard for a single kind of lubricant to provide effective lubrication through a broad range of ambient conditions. With regard to the matrix phase, choice of materials is a key factor. Over the past decades, traditional Ni-based alloys and Co-based alloys have been widely applied as matrix materials due to their good mechanical and high-temperature-withstanding properties. However, high-entropy alloys (HEA) as potential materials are yet to be explored [6–9]. High-entropy alloys are rarely investigated in self-lubricating composites as matrix materials [10]. Recently Zhang A.J. et al. have prepared high-entropy alloy CoCrFeNi matrix self-lubricating composites through spark plasma sintering (SPS); they exhibit a low friction coefficient and good wear resistance due to the excellent mechanical properties and high temperature stability of the HEAs [11,12].

In this study, CoCrFeNiMn HEA, possessing excellent strength resistance and ductility, was selected as the matrix material. For very demanding applications, Cr_3C_2 carbide ceramic was added to obtain even higher strength and wear resistance through dispersion strengthening, working hardening, and grain boundary reinforcement [13]. With regard to the choice of solid lubricant, Ag was used to decrease the friction coefficient at low and mid-temperatures [14], and CaF_2/BaF_2 was added to reduce friction and minimize wear at high temperatures. The effect of the solid lubrication addition on the microstructure and mechanical properties was investigated in this paper.

2. Materials and Methods

The raw powder was a mixture of pre-alloyed CoCrFeNiMn HEA powder, Cr_3C_2 powder, Ag powder, and CaF_2/BaF_2 powder used to prepare the self-lubricating composites (CoCrFeNiMn-Cr_3C_2-Ag-CaF_2/BaF_2). The raw powders were sintered via a spark plasma sintering (SPS) experiment in a vacuum environment. Table 1 lists the detailed composition of raw powders and the mass fraction. The composites' names are HEA-5F and HEA-15F, respectively. In the sinter process, the heating rate was 50 °C/min from room temperature (RT) to 1100 °C with heating pressure of 30 MPa; heat was preserved for 20 min at 1100 °C, followed by furnace cooling.

Table 1. The detailed composition of raw powders.

Sample	CoCrFeNiMn	Cr_3C_2	Ag	BaF_2/CaF_2
HEA-5F	70	10	15	5
HEA-15F	60	10	15	15

The phase composition of the composites was analyzed using X-ray diffraction (XRD, D/MAX-2400). The microstructure and elemental analysis of the composites were characterized with a scanning electron microscope (SEM, JSM-5600LV, JEOL Co., Akishima, Japan) equipped with energy-dispersive spectroscopy (EDS, Oxford Instrument, Abington, UK). The density of the composite was measured using Archimedes' method, and the hardness was measured using a HV-1000 type Vicker's hardness instrument. The compressive test was measured with a materials testing machine (CMT5202, Shenzhen Sans Material Test Instrument Co., Shenzhen, China). The compressive specimens were Φ 5 mm × 10 mm in dimension. The RT fracture toughness K_{Ic} of the composite was measured using a three-point bending test with single edge notch binding (SENB) specimens through ASTM E399-12. The dimension of the SENB specimens were 24 mm × 5 mm × 2.5 mm, and a straight notch of about 2.5 mm depth was prepared at the mid-length of the specimens. The nominal cross-head speed was 0.1 mm/min, and the span was 20 mm. Both the compressive tests and fracture toughness tests were executed at least three times and the average values were calculated.

3. Results and Discussion

3.1. Phase Composition

The XRD patterns of the mixed composite powder are shown in Figure 1a. The composites are composed of a face-centered cubic (FCC) phase, Cr_7C_3, Ag, and BaF_2/CaF_2 without impurity, which exhibit the physical mixture of different powders. The raw powders of Cr_3C_2 decarburize, forming Cr_7C_3 with the rapid sintering of the SPS technique. The Ag and BaF_2/CaF_2 phases exhibit the physical mixture of powders. When the content of fluoride eutectic increases to 15%, the intensity of BaF_2 and CaF_2 improves obviously, but the peaks of Cr_7C_3, Ag, and FCC weaken. Figure 1b presents the XRD spectra of the SPSed composites. The HEA-5F composite just exhibits two phases, the Ag and FCC phase, which is due to the content of fluoride eutectic being too little to clarify. The SPSed HEA-15F is composed of BaF_2/CaF_2, Ag, and FCC phases from the spectra, and the peaks of BaF_2/CaF_2 are clearly distinguishable. Compared to the intensity of different phases in the SPSed composites, that of the FCC phase is significantly higher than other phases, which suggests that the CoCrFeNiMn HEA's FCC phase is the dominant role, and other phases have a synergetic effect on the properties of the composites. The FCC phase is the solid solution of Co, Cr, Fe, Ni, and Mn elements.

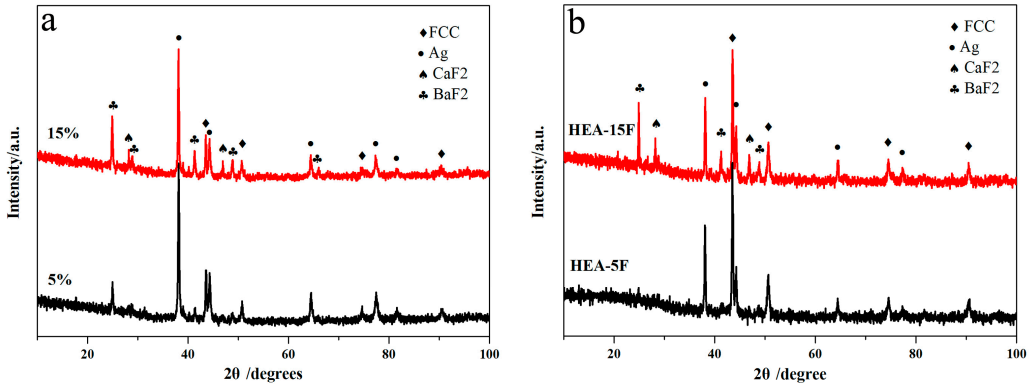

Figure 1. The XRD patterns of the mixed raw powders and the SPSed composites: (**a**) the mixed raw powders and (**b**) the SPSed composites.

3.2. Microstructure

Figure 2 shows typical SEM images of the composites that are etched by aqua regia, and Figure 3 shows the element distribution of HEA-15F composites. Table 2 lists the chemical composition of CoCrFeNiMn-Cr_3C_2-Ag-CaF_2/BaF_2 composites. Combining the XRD results and the corresponding EDS analysis (see Figure 3 and Table 2), the CoCrFeNiMn HEA's FCC phase as a matrix distributes uniformly and exhibits a near-equiaxed shape, which is rich in Cr, Mn, Fe, Co and Ni elements. As shown in Figure 3, solid-lubricating Ag distributes uniformly in the grain boundary of the FCC phase and connects to form a reticulate structure, which can bond the matrix and improve the density and toughness of the composites [14]. In addition, the BaF_2/CaF_2 and Cr_7C_3 scatters in the boundary or matrix of the composites. On the whole, the C elements disperse everywhere in the sample. The C element in the matrix is mainly attributed to the decarburization of Cr_3C_2 in the rapid sintering process, and it also results from the graphite die. The C element in the matrix plays an important role in solid solution strengthening.

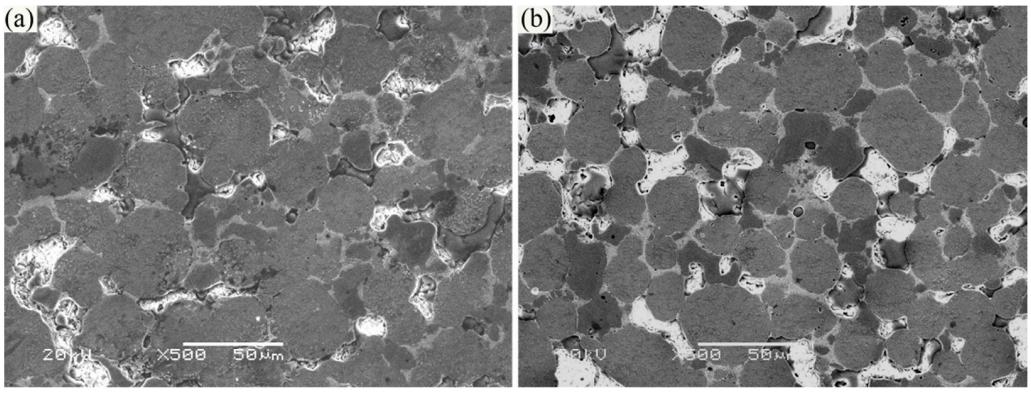

Figure 2. The SEM images of CoCrFeNiMn-Cr_3C_2-Ag-CaF_2/BaF_2 composites: (**a**) CoCrFeNiMn-Cr_3C_2-Ag-5%CaF_2/BaF_2, and (**b**) CoCrFeNiMn-Cr_3C_2-Ag-15%CaF_2/BaF_2.

Table 2. Chemical composition of CoCrFeNiMn-Cr_3C_2-Ag-CaF_2/BaF_2 composites.

Composites	Phase	Composition (at%)									
		C	F	Ca	Cr	Mn	Fe	Co	Ni	Ag	Ba
5% CaF_2/BaF_2	Grey phase	22.5	-	-	16.4	15.1	15.7	15.5	14.8	-	-
	Dark phase	35.8	-	-	62.8	-	1.4	-	-	-	-
	Bright grey phase	7.9	-	-	1.3	8.1	1.0	0.6	0.5	80.6	-
	Bright phase	-	50.8	1.6	2.7	2.1	1.3	1.5	1.8	1.3	37.0

Table 2. *Cont.*

Composites	Phase	Composition (at%)									
		C	F	Ca	Cr	Mn	Fe	Co	Ni	Ag	Ba
15% CaF_2/BaF_2	Grey phase	16.7	-	-	17.3	17.1	16.4	16.7	16.0	-	-
	Dark phase	41.4	-	-	57.4	-	1.2	-	-	-	-
	Bright grey phase	12.4	-	-	6.6	8.4	1.0	0.7	0.9	70.1	-
	Bright phase	7.6	60.6	3.0	0.8	0.9	1.2	1.0	0.9	-	24.0

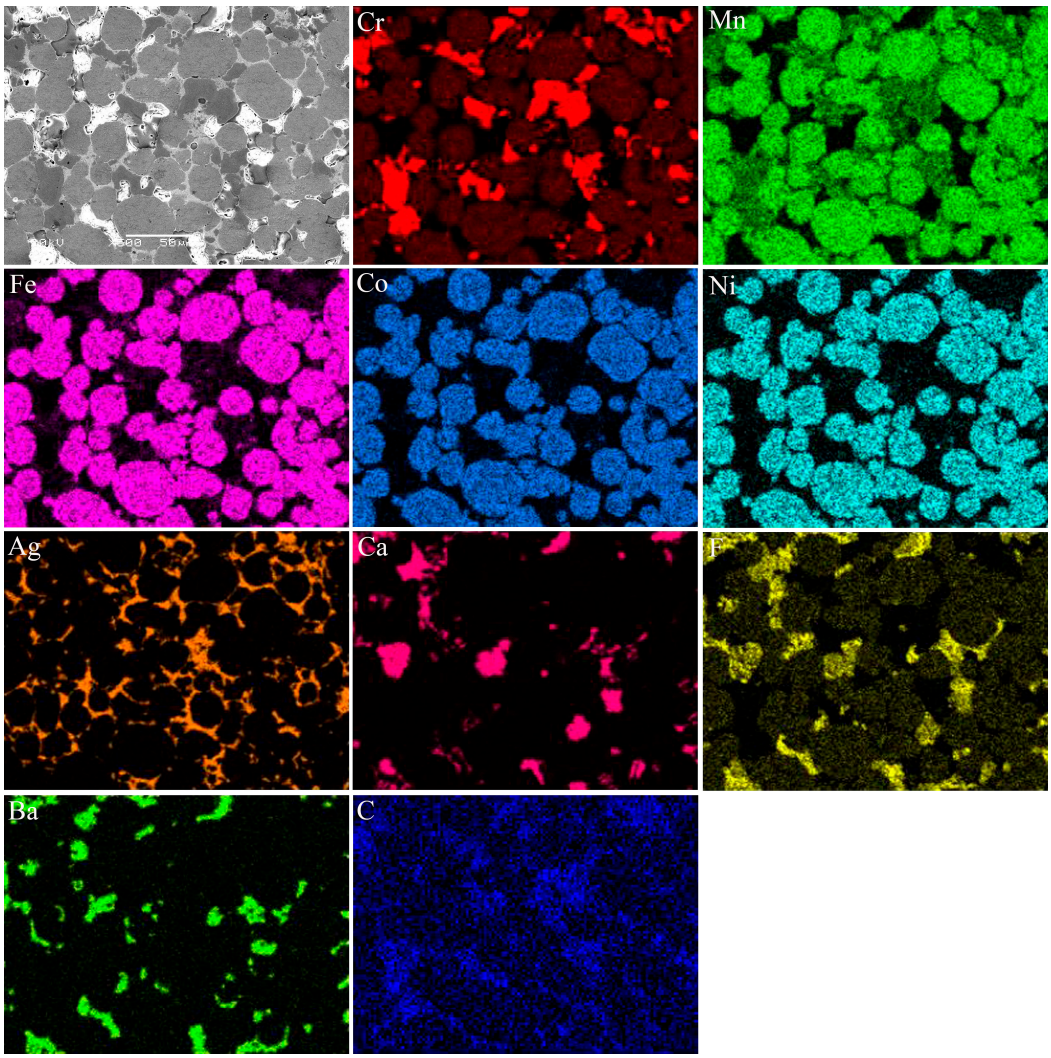

Figure 3. Typical SEM images of the SPSed HEA-15F composites after etching and element distribution.

3.3. Mechanical Properties

The density of the composites with 5% and 15% BaF_2/CaF_2 additions is 6.79 g/cm^3 and 6.95 g/cm^3, respectively. The hardness measurements are 50 HV and 58 HV. Density exhibits a slightly decreasing trend, and hardness appears to exhibit a small uptrend.

The compressive stress–strain curves of the different BaF_2/CaF_2 composites at room temperature are shown in Figure 4, and the typical compressive mechanical properties are listed in Table 3. The yield strength and the peak stress of HEA-5F composites are 273 MPa and 688 MPa, respectively. When the addition of BaF_2/CaF_2 increases to 15%, the yield strength and peak stress decrease to 236 MPa and 677 MPa. The plastic strain of the HEA-5F composite is 17.4%, and the HEA-15F composite falls to 12.2%, which is mainly attributed to the addition of fluoride eutectic. The fracture toughness of HEA-5F

and HEA-15F composites is 9.3 MPa·$m^{1/2}$ and 8.0 MPa·$m^{1/2}$, respectively. The addition of eutectic fluoride BaF_2/CaF_2 causes a brittle phase at room temperature, and dissevers the matrix phase of the CoCrFeNiMn high-entropy alloy. Therefore, the fracture toughness of the composites decreases with an increasing addition of eutectic fluoride BaF_2/CaF_2.

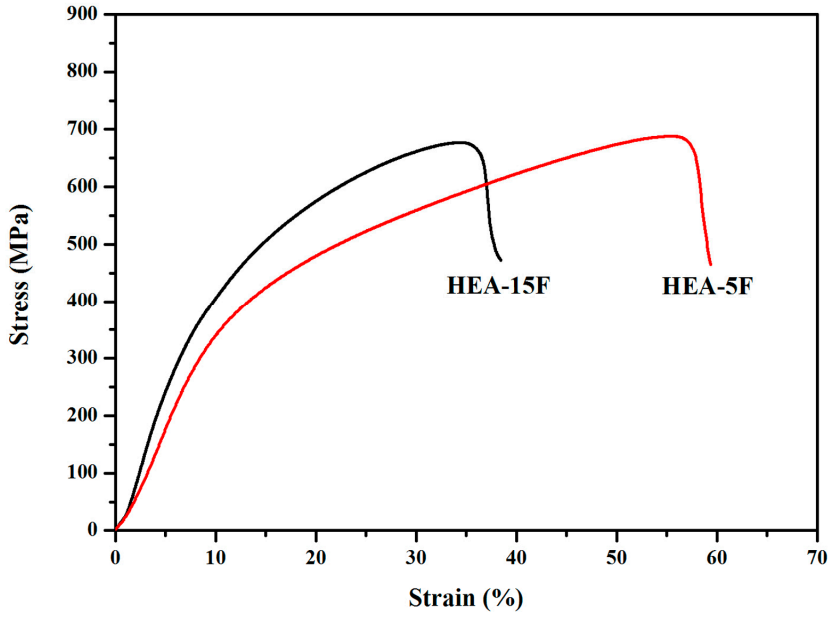

Figure 4. The compressive stress–strain curves of the composites at room temperature.

Table 3. The mechanical properties of CoCrFeNiMn-Cr_3C_2-Ag composites.

Composites	HEA-5F	HEA-15F
Density (g/cm^3)	6.79	6.95
Hardness (HV)	50	58
$\sigma_{0.2}$ (MPa)	273	236
σ_p (MPa)	688	677
ε_p (MPa)	17.4	12.2
Fracture toughness (MPa·$m^{1/2}$)	9.3	8.0

SEM images of the fracture surfaces of CoCrFeNiMn-Cr_3C_2-Ag-CaF_2/BaF_2 composites are shown in Figure 5. The dimples and cleavage steps are observed on the fracture surface of the composites. The dimples appear in the matrix phase of the CoCrFeNiMn high-entropy alloy and the Ag phase. Ag is a soft metal that possesses excellent ductility. A large number of cleavage steps and tear edges exist in the brittle phase of eutectic fluoride BaF_2/CaF_2 phase and Cr_7C_3 phase, which is the dominant cause of facture. The phases of eutectic fluoride BaF_2/CaF_2 and Cr_7C_3 are also the main reason for the decrease in ductility.

The tribological properties of CoCrFeNiMn-Cr_3C_2-Ag-CaF_2/BaF_2 composites are improved with the addition of eutectic fluoride BaF_2/CaF_2, especially at high temperatures, which are reported in another article.

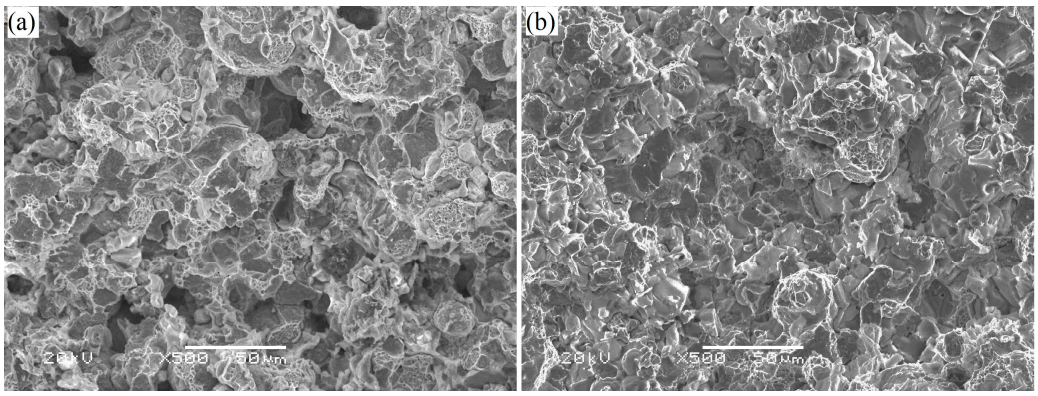

Figure 5. SEM images of fracture surfaces of CoCrFeNiMn-Cr_3C_2-Ag-CaF_2/BaF_2 composites: (**a**) CoCrFeNiMn-Cr_3C_2-Ag-5%CaF_2/BaF_2, and (**b**) CoCrFeNiMn-Cr_3C_2-Ag-15%CaF_2/BaF_2.

4. Conclusions

A series of novel, high-entropy alloy matrix self-lubricating composites were prepared via SPS using a mixture of pre-alloyed CoCrFeNiMn HEA powder, Cr_3C_2 powder, Ag powder and CaF_2/BaF_2 powder. The composites are composed of an FCC phase of CoCrFeNiMn HEA matrix, Ag and eutectic fluorid BaF_2/CaF_2 phases. The microstructure of the composites is densified and uniform. The CoCrFeNiMn HEA's FCC phase as a matrix distributes uniformly and exhibits a near-equiaxed shape. Solid-lubricating Ag distributes uniformly in the grain boundary of the FCC phase, and BaF_2/CaF_2 and Cr_7C_3 scatter in the boundary or matrix of the composites. The fracture mode of the composites is cleavage fracture, which is derived from the brittle phase of the eutectic fluoride BaF_2/CaF_2 phase.

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