

Study of tribological properties of high-entropy alloy matrix composites

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Abstract

Eutectic high entropy alloys (EHEAs) show promise for high-temperature tribological applications due to their good mechanical properties and high temperature stability. Fe₂₂Co₂₆Cr₂₀Ni₂₂Ta₁₀-(BaF₂/CaF₂)_x (x=3–20, wt%) composites were made by spark plasma sintering (SPS) with solid lubricant made of BaF₂/CaF₂ eutectic powder in order to investigate the high temperature lubrication behavior. Both room temperature and high temperature studies were conducted on the mechanical properties and lubrication behavior. The eutectic powder content of BaF₂/CaF₂ increases with a corresponding decrease in the composites' wear rates and friction coefficients at 600 and 800 °C. Because of the good mechanical properties of the EHEA matrix, the lubricating effect of the BaF₂/CaF₂ phase, and the oxides formed on the worn surface, the composites with eutectic powder content of 15 and 20 weight percent exhibit the best lubricating performance at 600°C, with low friction coefficients and wear rates.

1. Introduction

In industries including petrochemical, automotive, mining, aerospace, and others, self-lubricating materials are crucial. Nonetheless, under extreme operating conditions, operating temperatures can occasionally rise to the point where

traditional lubricating systems are unable to function [1,2]. Thus, the behavior of self-lubricating materials at high temperatures is very important [3-5].

Metal-based powder metallurgical self-lubricating composites were created in the 1930s [6], usually consisting of a metallic matrix and solid-lubricating phases made of ceramic or mineral [7]. Sufficient mechanical properties and resistance to oxidation at high temperatures can be obtained from the matrix phase. Superalloys based on nickel and cobalt are the most often utilized matrix for high temperature self-lubricating composites. Inorganic fluorides, metal oxides, and other ternary compounds are examples of the lubricating phases. Nevertheless, solid lubricants and metals have very different chemical properties, and adding solid lubricants will lessen the composites' ability to sinter as well as their mechanical qualities [8,9]. Thus, when designing self-lubricating composites, it's critical to strike a balance between the mechanical and tribological properties.

In metallic materials, high-entropy alloys (HEAs) are becoming more and more significant [10–13]. HEAs have good properties and a simple structure, even though they typically have four or more principal elements [14–16]. Eutectic high entropy alloys (EHEAs), a novel class of HEAs, were recently proposed by LU et al.

[17]. EHEAs have a number of characteristics, including high hardness, stable microstructures, and good resistance to creep at high temperatures [18]. Consequently, EHEAs show promise as self-lubricating composites at high temperatures. Studies on EHAs or EHEAs with self-lubrication phases are scarce, though. Fe-16.4Mn- 4.8Ni-9.9Al-xC (wt.%) composites were prepared by HAN et al. [19] using spark plasma sintering (SPS), and the self-lubricating effect of graphite was found to significantly improve tribological performance. Compared to pure HEAs, ZHANG et al.'s [20, 21] CoCrFeNi matrix and various solid lubricants, including Ag, Cu, and fluorides, demonstrated superior wear resistance and lubrication performance.

FeCoCrNiTa EHEA demonstrated outstanding mechanical characteristics and high-temperature stability in our earlier study. It can be a good option for engineering applications at high temperatures because it is composed of face-centered-cubic (FCC) and Laves phases [22, 23]. Fe₂₂Co₂₆Cr₂₀Ni₂₂Ta₁₀ EHEA matrix composites were made in this work using SPS. BaF₂/CaF₂ eutectic was chosen as a solid lubricant due to its superior lubricating capabilities and elevated temperature stability. The EHEA composites' lubricating qualities and microstructural changes were examined.

2. Experimental Procedure

Gas-atomized Fe₂₂Co₂₆Cr₂₀Ni₂₂Ta₁₀ powder and BaF₂/CaF₂ eutectic powder were mixed and filled in a graphite die with a diameter of 28 mm. The preparation method of BaF₂/CaF₂ eutectic powder was reported in Refs. [24,25]. The powder was sintered at 1373 K in the SPS Equipment

(HPD25/3), and held for 15 min at 30 MPa, followed by furnace cooling.

The X-ray diffractometer (XRD, Rigaku D/MAX-2250, Japan) using a Cu K α radiation was used to analyze the phase compositions. Scanning electron microscope (SEM, Quanta FEG 250) equipped with an energy dispersive X-ray spectroscopy (EDS) analyzer was used to observe the microstructures of the self-lubricating composites. To further identify the chemical compositions of phases, electron probe micro- analyses (EPMA) was used. The Archimedes method was used to measure the density of the composites. The Vicker's hardness instrument with a load of 0.5 N was used to measure the micro- hardness.

The dry wear tests at room temperature, 600 °C and 800 °C were carried out on a rotational ball-on-disk high temperature tribometer in air. The ball used was Si₃N₄ with a size of 6 mm. The self-lubricating composites were cut in the form of disks with a size of d28 mm × 5 mm. The rotation diameter, sliding speed, loads and sliding time of tests were 4 mm, 0.28 m/s, 20 N and 30 min, respectively. Each sample was tested three times, with each time of 30 min. After testing, the worn surfaces were observed by using SEM. A 3D surface profilometer (NT9100, Veeco) was used to measure the worn volume of composites. A micro- beam XRD diffractometer (Rigaku Rapid IIR) was used to analyze the phase compositions of the worn surface.

3. Results and discussions

3.1. Material Characterization

Figure 1 shows the typical morphologies of the EHEA powder and the fluorides

powder. The EHEA powder is spherical, with a particle size less than 50 μm .

Figure 2 shows the XRD patterns of self-lubricating composites. The FCC phase, Laves phase, fluorides phase (BaF_2 and CaF_2) can be obviously observed. With the Figure 3 demonstrates the microstructures of the composites, and Fig. 4 shows the compositional profiles. The grey phase is rich in Co, Cr, Fe and Ni, the white phase rich in Ta, and the dark phase rich in Ba, Ca and F. This indicates that the grey phase is FCC phase, the

increase of the content of $\text{BaF}_2/\text{CaF}_2$ eutectic powder, there are stronger peaks corresponding to BaF_2 and CaF_2 phases in the XRD patterns. This result suggests that the $\text{BaF}_2/\text{CaF}_2$ eutectic powder does not react heavily with the matrix during SPS.

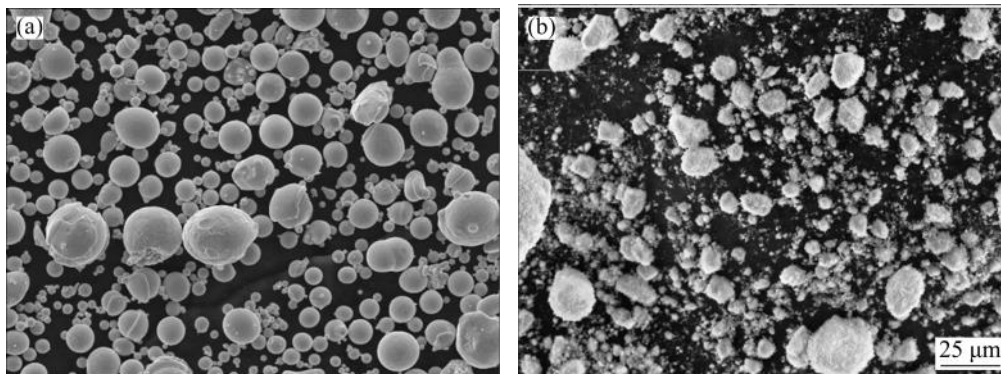


Fig. 1 Morphologies of EHEA powder (a) and $\text{BaF}_2/\text{CaF}_2$ eutectic powder (b)

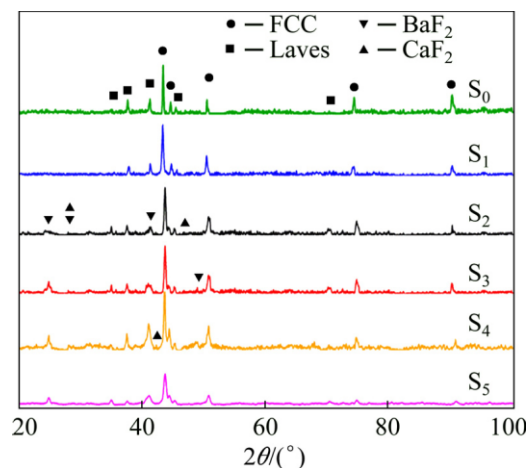


Fig. 2 XRD patterns of different composites

white phase is Laves phase, and the dark phase is of fluorides. From the results of XRD and microstructure of Sample S3, the fluorides uniformly distribute and have chemical stability in the matrix.

3.2. Mechanical properties

The density of the S1 to S4 composites is in the range of 9.11–7.31 g/cm^3 , above 99% theoretical value of all composites. When the content of $\text{BaF}_2/\text{CaF}_2$ eutectic powder

is increased to 20 wt.% (Sample S5), the relative density decreases.

The hardness of the composites gradually decreases with the increasing content of $\text{BaF}_2/\text{CaF}_2$ from 545 HV to 399 HV. The microhardness values of the FCC matrix phase and the Laves phase are higher than those of fluorides phase.

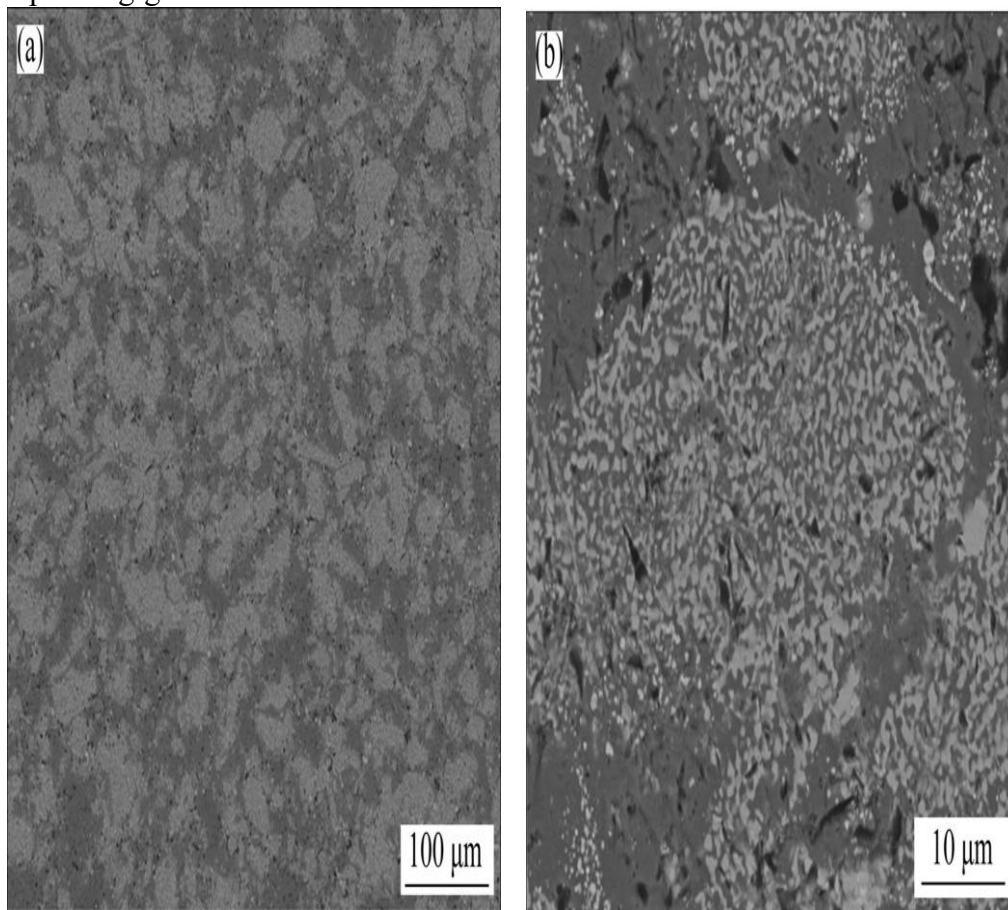
3.3. Friction and wear behavior

The coefficient of frictions (COFs) with the testing time is shown in Fig. 5. Compared to Samples S1 and S2, the high-temperature COFs of Samples S3, S4 and S5 decrease obviously. And the COFs of Samples S4 and S5 are more stable.

The wear rates and averaged COFs of composites at different temperatures are shown in Fig. 6. The COFs of composites decrease at high temperature, and the COFs of Samples S3, S4 and S5 decrease. In order to investigate the wear mechanism, the worn surface of the composites was analyzed, and the results are shown in Fig. 7. Some plowing grooves can be observed

dramatically. As the content of BaF₂/CaF₂ increases to 9 wt.%, the averaged COF of Sample S3 decreases to 0.22 at 600 °C, and the wear rate maintains to be 5.9×10^{-5} mm³/(N·m). Further increasing the content of BaF₂/CaF₂, the COF becomes more stable and maintains around 0.22. The wear rates of the composites are in the magnitude of 10^{-5} mm³/(N·m). With temperature increasing, the wear rate decreases.

abrasive wear happens. Adhesive wear also occurs during the wear process, evidenced by the formation of patches and the transfer of materials.



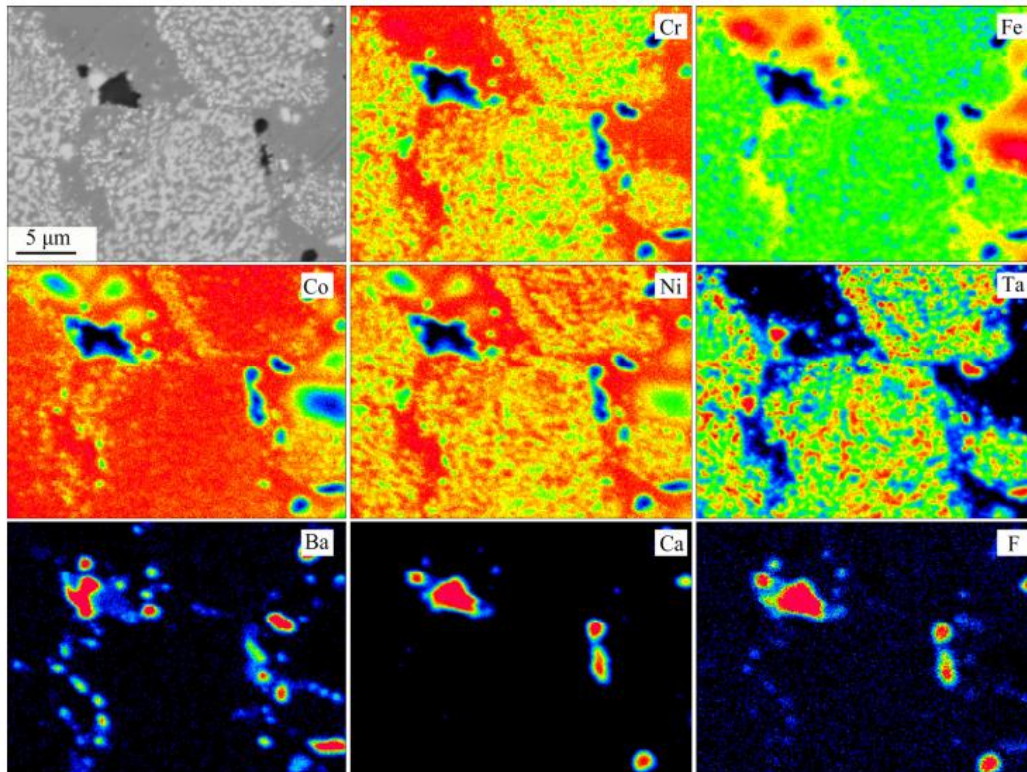
on the worn surfaces, suggesting that slight

Fig. 3 Microstructures of Sample S3 sintered at 1100 °C: (a) Low magnification; (b) High magnification.

According to the change of O content in the EDS result, severe oxidation occurs at high temperatures.

The COF of Sample S2 is about 0.35 at 600 °C, which is the same as that of Sample S1. According to Fig. 7, the wear mechanisms

of S2 are adhesive wear, abrasive wear and oxidation wear. With the increase of BaF₂/CaF₂ content, the worn surface of S2 forms a discontinuous and broken glassy layer, which may lose the self-lubricating ability.



The worn surfaces of Sample S3 tested at RT have similar morphology with Samples S1 and S2, showing adhesive wear and slightly abrasive wear. With temperatures increasing to 600 and 800 °C, the worn surfaces of the composites become smooth, and the continuous glassy layers form on the worn surfaces. According to the EDS results, the Ba, Ca and F contents of the glassy layer (Region 8) are higher than those of the rough surface (Region 9). This result is mainly due to the fact that the glassy layer is rich in fluorides.

With further increasing of BaF₂/CaF₂ content, the whole worn surface of Samples S4 and S5 is similar to those of Sample S3

after testing at RT, 600 °C and 800 °C. The glassy layers form on the worn surface at high temperatures, which are rich in fluorides. In summary, the major wear behavior of Samples S4 and S5 is almost the same with that of Sample S3.

To further study the lubricating behavior of Sample S3 at high temperatures, the cross-sectional microstructure and EDS results of the worn surface at 600 °C are shown in Fig. 8. The Ba, Ca and F contents of the glassy layer (Region A) are higher than those of the composite (Region B). The thickness of the continuous glassy layer is about 7 μm, which is bonded with the composite closely.

Figure 9 shows the micro-beam XRD patterns of Sample S3 after testing at RT, 600 °C and 800 °C. At RT, FCC phase, Laves phase, BaF2 and CaF2 are observed, and no peaks of oxides appear on the worn

surface. At 600 and 800 °C, the glassy layer mainly consists of different metal oxides (Cr2O3, Fe2O3 and other oxides) and BaF2/CaF2 eutectic phase.

4. Discussion

4.1. Microstructures

In this work, the EHEA matrix composites were prepared by SPS with microstructures consisting of FCC phase, Laves phase, BaF2 and CaF2. Fluoride phases distribute

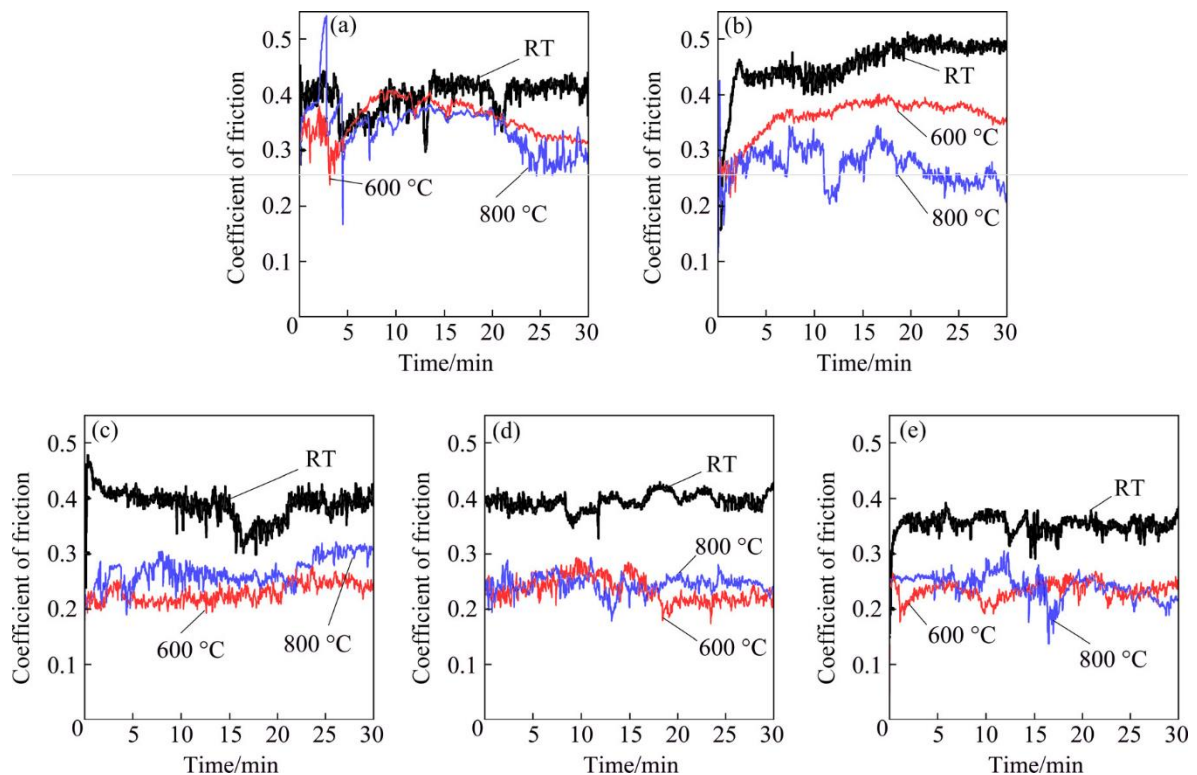


Fig. 5 COFs with sliding time of different composites: (a) Sample S₁; (b) Sample S₂; (c) Sample S₃; (d) Sample S₄; (e) Sample S₅

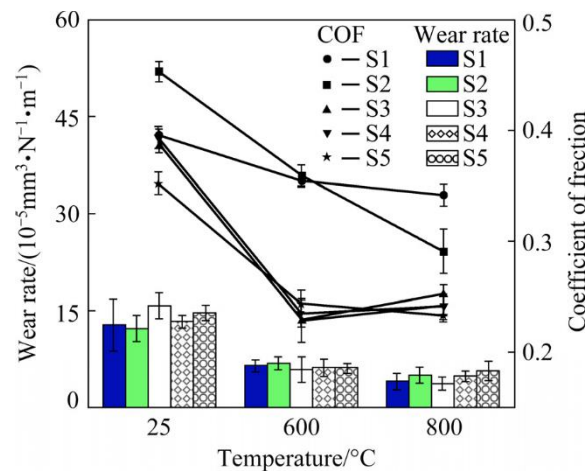


Fig. 6 Wear rates and averaged COFs of different composites with temperature

homogeneously in the EHEA matrix, and have good chemical stability. This distribution makes the microstructure uniform, and also makes it easier to form a complete and continuous lubrication layer during the wear process.

The melting point of BaF₂/CaF₂ eutectic phase is lower than the sintering

4.2. Wear behavior

The smooth and continuous glassy layer formed on the worn surface is the key for decreasing the friction coefficients at high temperatures. When the content of BaF₂/CaF₂ is higher than 9 wt.%, the glassy layers forming on the worn surface can prevent the direct contact between composite disk and SiN₄ ball, which keeps the COF stable and the wear rates low.

temperature, so the fluoride phases mostly distribute in the pores of the matrix. The liquid phase sintering can further improve the density of the composites [26], but excessive liquid phase during the sintering process will have an adverse impact on the mechanical properties of the composites.

Fig. 7 Morphologies of worn surface and marked areas for EDS

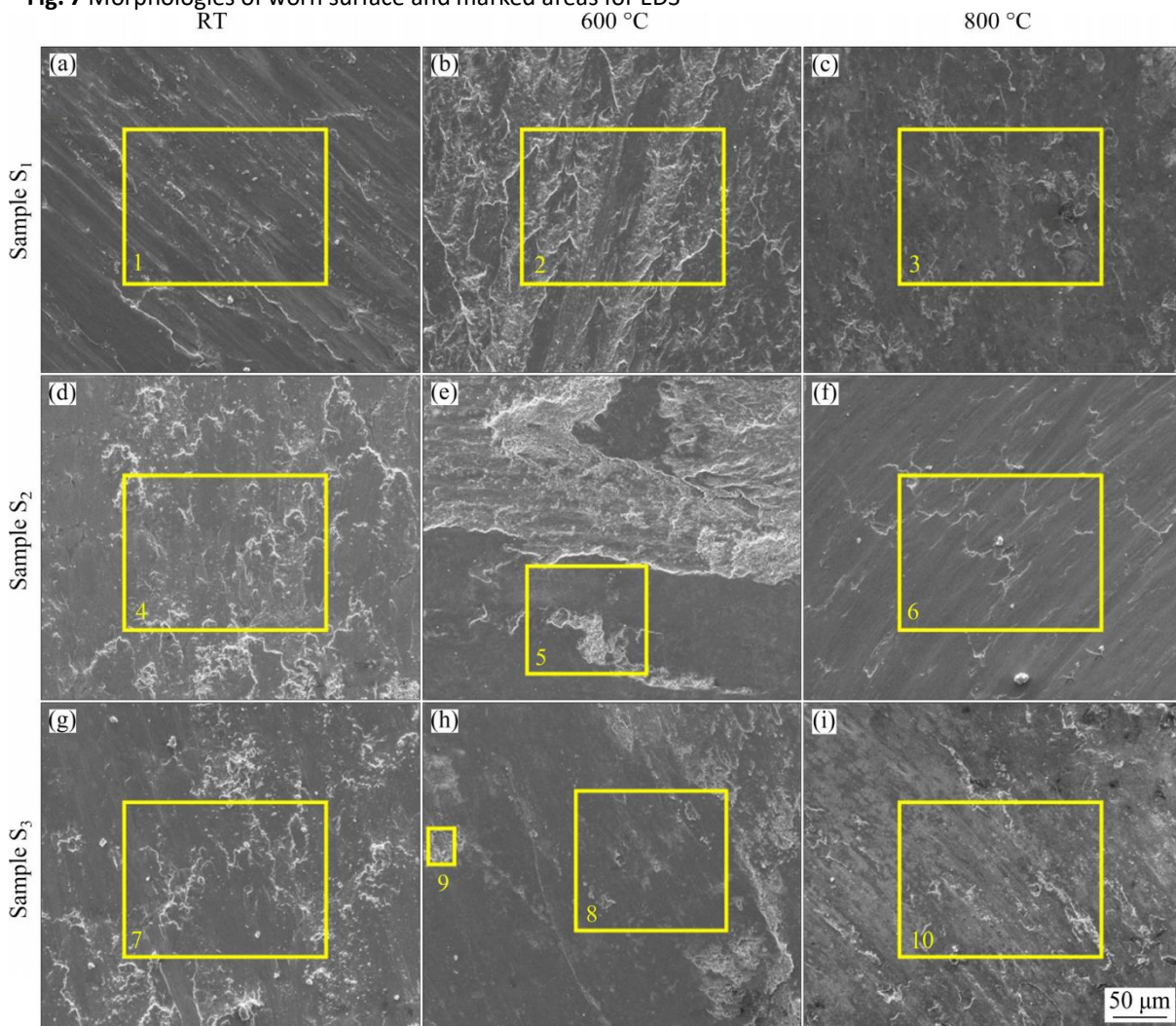


Fig. 7 Morphologies of worn surface and marked areas for EDS

The BaF₂/CaF₂ phase is stable at high temperatures, and it has good lubricating properties because of its lower melting point and shear stress. During the sliding test at high temperatures, the BaF₂/CaF₂ eutectic powder can coat on the worn surface easily. Therefore, sufficient and homogeneously distributed BaF₂/CaF₂ eutectic phase in the matrix is the very important for the self-lubricating effect. In addition, the oxides may soften at high temperatures and easily form a continuous layer with the BaF₂/CaF₂ eutectic phase.

Compared with other self-lubricating materials of almost the same type of compositions, the composites in this work have lower COFs and wear rates at 600 °C. In summary, the EHEA composites may have potential applications in high temperature service.

Therefore, the metal oxides can also improve lubricating properties at high temperatures.

For metallic solid self-lubricating materials, the lubricating phase can decrease the mechanical properties. It is important to find a balance between lubricating properties and mechanical properties. When the composite has 9–15 wt.% lubricants (Samples S3 and S4), it has the best combination of lubricating and mechanical properties.

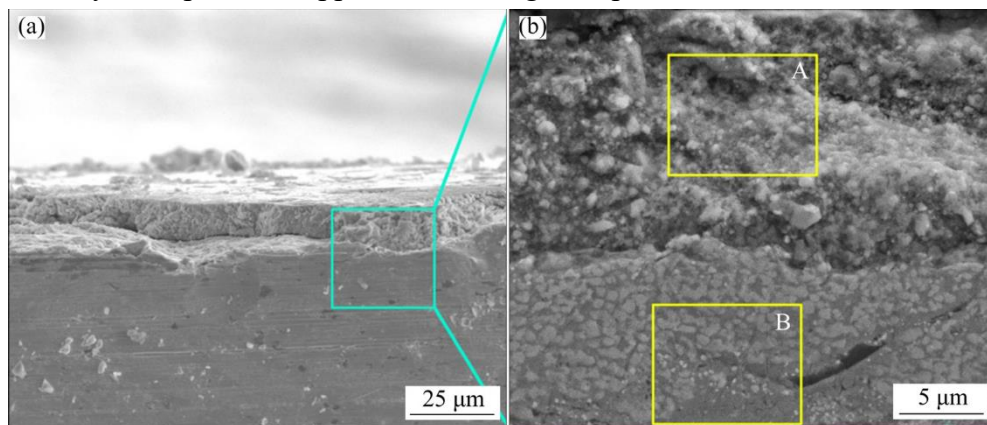


Fig. 8 Microstructures of cross-sections of worn Sample S₃ after testing at 600 °C

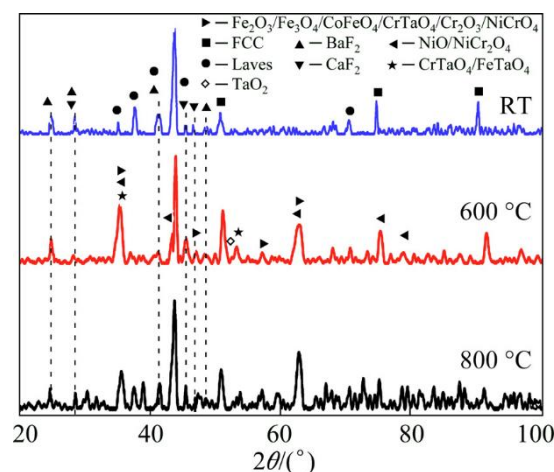


Fig. 9 Micro-beam XRD patterns of Sample S₃ after testing at different temperatures

5. Conclusions

- (i) Fe₂₂Co₂₆Cr₂₀-Ni₂₂Ta₁₀-BaF₂/CaF₂ composites have phase compositions of FCC, Laves phase, BaF₂, and CaF₂. With the EHEA, the BaF₂ and CaF₂ exhibit excellent chemical stability.
- (ii) The Fe₂₂Co₂₆Cr₂₀Ni₂₂Ta₁₀-BaF₂/CaF₂ composite's hardness progressively drops as the amount of BaF₂/CaF₂ eutectic powder increases from HV 545 to HV 399.
- (iii) At high temperatures, the EHEA composites exhibit good lubricating performance. Compared to other FeCoCrNi-based composites, the COF and wear rate at high temperatures are lower when the content of BaF₂/CaF₂ eutectic powder is 9–15 wt%. The formation of complex oxides, the high hardness of the matrix, and the influence of the BaF₂/CaF₂ eutectic phase are responsible for the good lubricating performance.

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