Research on High Temperature Friction and Wear Characteristics of H13-Cr$_2$C$_3$-CaF$_2$ Self-lubricating Materials

Runyin Rao$^1$, Huajun Wang$^{1*}$, Menglu Li$^1$, Zhenhua Yao$^1$, Qingyang Liu$^1$ and Songshan Yan$^2$

$^1$ School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070 China
$^2$ School of Mechanical and Electronic Engineering, Wuhan University of Technology, Wuhan 430070 China
Email of the corresponding author: * wanghuajunhb@163.com

Abstract. Based on the service environment and requirements of hot working die, we proposed a H13-Cr$_2$C$_3$-CaF$_2$ self-lubricating material formula system and powder metallurgy process parameters, and prepared the high temperature composite materials. The phase composition and distribution of H13-Cr$_2$C$_3$-CaF$_2$ samples were analyzed by energy dispersive spectrometer. The friction coefficient, wear rate, wear morphology and spectrum of samples with different contents of CaF$_2$ were tested and compared by ball-on-disc high temperature tribometer under the conditions of test temperature 600 °C, disk rotation speed 200 r/min and friction for 15 min, and the mechanism of high temperature friction and wear was described. It will support the green manufacturing and sustainable development of forging industry.

1. Introduction

Die is an important process equipment in the parts forming manufacturing industry, which directly affects the product's qualification rate and production cost. Friction and wear are the key factors affecting the life of the die, and lubrication is the most effective measure to reduce friction and improve die life [1]. Lubricating oil or grease is usually used to reduce friction and wear. The working temperature of lubricating oil and grease is generally lower than 180 °C, and the working temperature of high-temperature grease is not more than 300 °C [2].

The solid lubricant has good stability and lubrication property under high temperature and pressure [3]. Based on the low temperature utilization of liquid lubricants, researchers have proposed a solution for solid lubricants [4]. Self-lubricating materials are one of the important methods of solid lubrication. Solid self-lubricating materials have been applied in aerospace industry in the United States [5], [6]. In order to protect the natural environment and sustainable social development, the preparation and application of self-lubricating hot work die materials are proposed [7]. Using powder metallurgy technology, the pure metal or alloy is used as the matrix phase and solid lubricating material is added to make the compound antifriction material, so as to achieve the purpose of reducing the friction of the lubrication under the condition of high temperature and high pressure [8].

In this paper, H13 steel metal powder is used as the material matrix, CaF$_2$ is used as the lubricating phase, and Cr$_2$C$_3$ is used as the hard phase to prepare the high temperature self-lubricating material. As a commonly used hot work die material, H13 steel has good comprehensive mechanical properties [9]. CaF$_2$ has good thermal stability and can lubricate at 900 °C [10]. Cr$_2$C$_3$ has strong oxidation resistance and wear resistance [11].
The friction coefficient, wear rate, wear surface morphology and surface composition of H13-Cr2C3-CaF2 materials were tested. The wear mechanism of H13-Cr2C3-CaF2 composites was analyzed. The effect of CaF2 on the high temperature wear properties of H13-Cr2C3-CaF2 was studied.

2. Experimental Materials and Methods
The test materials were H13 steel spheroidized powder, CaF2 solid lubricant, Cr2C3 ceramic powder, zinc stearate, and the particle size was -200+500 mesh. The content of Cr2C3 is 10 wt%, and the addition amount of CaF2 is 0%, 5 wt%, 7.5 wt%, 10 wt%, 12.5 wt%, and content of zinc stearate is 2 wt% of the total mass of the powder. The powder was dry-mixed by ball milling in a pure argon atmosphere. After mixing for 6-8 hours, it was sieved through a 200-mesh sieve, and 22 g of the powder was weighed and compressed at 600 MPa for 1 min. After demolding, the sample was sintered at 1250 °C for 2h.

The high-temperature wear characteristics of the composite were tested by a ball-on-disc tester for high temperature friction and wear. The selected abrasive material was 45 steel with a diameter of 3.5 mm, friction and wear environment temperature was 600 °C, the friction time was 15 min, and the disc speed was 200r/min and the friction radius is 2mm. The friction coefficient, wear rate, wear surface morphology and surface composition of H13-Cr2C3-CaF2 materials were tested.

![Figure 1. Ball-on-disc tribometer for high temperature friction and wear](image1)

3. Results and Discussions

3.1. Composition Distribution
Figure 2 is micrograph of a sintered sample adding 7.5 wt% CaF2. By analyzing the EDS data by the dot analysis, it can be judged that the large-area circular shape is the H13 matrix, and a small amount of Cr2C3 and CaF2 exist in the area, more Cr2C3 and CaF2 exist in the pores between round particles.

![Figure 2. Micrograph of sample adding 7.5 wt% CaF2](image2)
3.2. Coefficient Of friction

Figure 3 is a graph of time versus friction coefficient for samples with different CaF$_2$ contents. In Figure 3, the average friction coefficient of H13-Cr$_2$C$_3$ composite material is 0.5479, which is the highest in the samples. The friction coefficient increases with time. For samples adding 5wt% and 7wt% CaF$_2$, the average friction coefficients were 0.4411 and 0.4194, respectively. The friction coefficient is low in the early stage of the experiment, the medium-term coefficient fluctuates greatly, and it remains stable after a certain increase in the later stage. The composite adding 10wt% CaF$_2$ has the lowest average friction coefficient of 0.3907 in the samples, which is relatively stable throughout the experiment. The friction coefficient of the composite adding 12.5wt% CaF$_2$ is low in the early stage, and it rises steadily in the later stage, and the average friction coefficient is 0.4088.

![Figure 3. Friction coefficient curves of samples with different CaF$_2$ contents](image)

At the beginning of the test, the contact area of the friction pair is small, and the contact point has a stress concentration phenomenon, convex portion of surface is deformed, and the friction coefficient increases rapidly. When the content of CaF$_2$ is low, the precipitation of the lubricant during the high-temperature friction is insufficient to form a complete lubricating film, and the abrasive grains generated by the friction increase the friction coefficient of the material. With CaF$_2$ contents increasing, sample precipitates more lubricant during the friction process, forming a continuous lubricating film on the friction surface, which reduces the friction coefficient and wear rate. When the content of CaF$_2$ exceeds a certain range, the bonding force of the sintered sample matrix and the hardness is reduced, the hard phase in the composite material is stripped, the lubricating film is destroyed and the friction coefficient is increased.

3.3. Sample Wear Rate

Figure 4 shows the variation of the wear rate of the samples with different CaF$_2$ contents. The H13-Cr$_2$C$_3$ composite material with no lubricating phase has a high friction coefficient. The wear rate of the H13-Cr$_2$C$_3$-CaF$_2$ composite decreased first and then increased with the increase of CaF$_2$ content. As the content of CaF$_2$ increases, the area of the lubricating film increases, and the friction coefficient of the sample decreases, so that the wear rate decreases. When the content of CaF$_2$ exceeds 10wt%, the compactness of the sample is decreased and the pores are increased, the crack generated by the friction is rapidly expanded, and the hard phase and the lubricating phase of the sample are peeled off and rubbed against the friction surface, so that the wear rate increases again.
Figure 4. Wear rate histogram of samples with different CaF$_2$ contents

3.4. Wear Mechanism

Figure 5 is topography of the high temperature friction and wear electron probe of the sample with different CaF$_2$ contents. Figure 5a is 200-fold backscattered electron image of the high-temperature friction and wear profile of a sample containing no CaF$_2$. Figures 5b~5e are high temperature friction and wear morphology of samples with CaF$_2$ addition of 5wt%, 7.5wt%, 10wt%, and 12.5wt%, respectively. Due to adhesive wear, the material on the wear area is partially peeled off, and a large amount of abrasive grains are produced, and a bright white peeling area appears (In Figure 5a). The main wear form of H13-Cr$_2$C$_3$ composites is oxidative wear, followed by abrasive wear and adhesive wear. H13-Cr$_2$C$_3$ composite material will promote the formation of a large number of oxides under the high temperature environment of 600 °C. Some of these oxides form an oxide film during the rubbing process, which protects the grinding surface; some oxides form hard abrasive grains, so the oxide film and the matrix material on the surface are plastically deformed by the abrasive grains and then fall off [12].

In Figure 5b~5e, there is ploughing phenomenon in the wear area. The main wear forms of the composite are slight oxidative wear and abrasive wear. Under the environment of high temperature and frictional stress, the lubricating phase CaF$_2$ with lower hardness is separated from the composite material and precipitates out of the friction surface. When the content of the lubricating phase CaF$_2$ is increased, the hardness of the material decreases, and the hard phase Cr$_2$C$_3$ is worn out to the surface. In Figure 5b~5c, the lubricating phase CaF$_2$ content is low, the lubricating film formed on the friction surface is discontinuous. When the lubricating phase CaF$_2$ content is increased, a relatively continuous lubricating film can be formed, and the friction coefficient can be further reduced. When the content of CaF$_2$ exceeds a certain range, it will decrease the bonding force of the matrix particles, which leads to the decrease of mechanical properties and bearing capacity of the composite material [13].
Figure 5. The surface morphology of samples with (a) 0% (b) 5wt% (c) 7.5wt% (d) 10wt% (e) 12.5wt% CaF$_2$ content after high temperature friction

4. Conclusions
(1) This paper proposed H13-CaF$_2$-Cr$_2$C$_3$ self-lubricating material formula system and preparation process.

(2) In the microstructure of H13-Cr$_2$C$_3$-CaF$_2$ self-lubricating material, there is mainly H13 matrix and a small amount of Cr$_2$C$_3$ and CaF$_2$ in the large-area circular shape. In the pores between circular shape particles, there are Cr$_2$C$_3$ and CaF$_2$.

(3) The friction coefficient and wear rate decrease first and then increase with the increase of CaF$_2$ content. When the CaF$_2$ content is 10wt%, friction coefficient and wears rate reach the minimum value.

(4) In the high temperature friction and wear test, the main wear form of H13-Cr$_2$C$_3$ composite is oxidative wear, accompanied by abrasive wear and adhesive wear. The main wear forms of H13-Cr$_2$C$_3$-CaF$_2$ composite are slight oxidative wear and abrasive wear when load is small. When load is large, the dominant wear mechanism of H13-Cr$_2$C$_3$-CaF$_2$ composite is oxidative and adhesive wear.

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