WEAR

Wear 211 (1997) 9–14

Physical and chemical effects of CeF_3 compact in sliding against Hastelloy C in temperatures to 700 °C

Qunji Xue, Jinjun Lu *

Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

Received 27 June 1996; accepted 11 March 1997

Abstract

The dependence of friction coefficient vs. temperature of Hastelloy C/CeF_3 compact was studied in the paper. The wear debris was studied by using X-ray diffraction (XRD) and scanning electron microscopy (SEM). Findings indicated that CeF_3 had physical and chemical effects in sliding at elevated temperatures. The physical effects were known as preferential orientation, degree of crystallization and plastic deformation. The preferential orientation of plane (002) had a positive effect on friction reduction. The friction coefficients were low as the degrees of crystallization were high. The chemical effect was known as oxidation. The difference between static and sliding oxidation was that the starting temperature of the former was higher than that of the latter. The reason was the temperature difference between the sliding surface and environment caused by frictional heat. The oxidation of CeF_3 compact had a negative effect on its lubricity below 700°C since CeO_2 showed poor lubricity within the range of these temperatures. At 700°C, CeO_2 exhibited good friction-reducing, transferring and film-forming properties, which means the oxidation above 700°C may have a beneficial effect on friction reduction. © 1997 Elsevier Science S.A.

Keywords: Friction; Preferential orientation; Degree of crystallization; Plastic deformation; Oxidation; CeF_3 compact

1. Introduction

Oxides, fluorides and graphite are among candidate solid lubricants for uses above 300 °C [1–3]. Rare earth fluorides have been considered as high temperature solid lubricants, up to at least 1000 °C, due to their good film-forming, plastic deformation and transferring properties [3]. Unfortunately however, the correlation between the crystal structure and the lubricity of rare earth fluorides has not yet been studied. Furthermore it is interesting that CeF_3 turned from white to yellow during sliding at high temperatures according to reference [4]. It is well known that CeO_2 is yellow. So it may be deduced that the oxidation of CeF_3 might be involved in sliding. Apparently, these two effects are very important to help to understand the lubricating mechanism of CeF_3 at high temperatures. The authors' previous survey on the tribological characteristics of CeF_3 compact at temperatures to 700 °C showed that the friction coefficient was 0.16~0.38 [5]. X-ray diffraction (XRD) results revealed that the crystal plane (002), (113) of wear debris showed preferential orientations and the content of CeO_2 increased compared to the compact, which suggested that physical and chemical effects may occur during sliding. As indicated in reference [5], the most interesting parts of the tribological characteristics of CeF_3 are stage II (300 to 400 °C) and III (400 to 500 °C). It is likely that these effects have influences on the friction-reducing property of CeF_3 at these temperatures. To have further knowledge on these effects, the dependence of the effects with temperatures 300 to 500 °C was studied in the paper. Comparisons on these effects at static and sliding conditions were made.

2. Experimental details

2.1. *Materials*

CeF_3 powder was obtained from Gansu Rare Earth Company China. The nominal purity is 99.5%.

Hastelloy C is prepared by using the hot-pressing method in an intermediate-frequency furnace. The chemical composition and some mechanical strengths of Hastelloy C are shown in Table 1.

2.2. *Preparation of CeF_3 compact*

CeF_3 compact is prepared by using the hot-pressing method on a substrate of Hastelloy C. Details on making the CeF_3 compact are given in Ref. [5].

---

* Corresponding author.

PII S0043-1648(97)[illegible]

Table 1
The chemical composition and mechanical strength of Hastelloy C

	Composition (wt.%)	Density (kg m^{-3})	Impact toughness (kJ m^{-2})	Compressive strength (MPa)	
				20 °C	700 °C
Hastelloy C	Cr 16, Mo 16, W 4, Fe 6, Co 2.5, Ni balance	[illegible] × 10^3	[illegible]	[illegible]	[illegible]

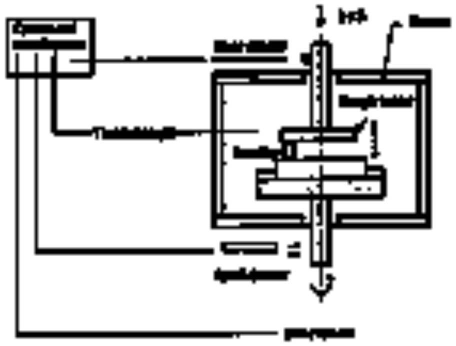

Fig. 1. Schematic of the high temperature tribometer.

2.3. Tribological tests

2.3.1. Apparatus and specimens

The tribological tests were conducted on a pin-on-disk tribometer. The schematic diagram of the tribometer is shown in Fig. 1. The pin is made of Hastelloy C, with size of [illegible] mm. The disk is made of CaF$_2$ compact and is 45 mm in diameter.

2.3.2. Procedures

The tests were conducted by sliding Hastelloy C against CaF$_2$ compact to study the relationship between friction coefficient and sliding distance at 300, 400, 500, 600, and 700 °C. Test conditions were load 39.2 N, velocity 0.3 m s^{-1}. The duration of the tests was [illegible], which is 1.8 km in distance. The friction coefficient was measured at 5 minute intervals (0.09 km in distance).

2.4. Analysis

The physical and chemical effects were studied by using XRD ([illegible]) to detect the composition and orientation of the wear debris after the tribological tests at different temperatures. The plastic deformation of the wear debris and the morphology of the CaF$_2$ compact were studied by using scanning electron microscopy (SEM) ([illegible]). The tribochemical film was studied by using Auger electron spectroscopy (AES) (P.E. PHI-550).

3. Results and discussion

3.1. The dependence of friction coefficient vs. sliding distance at evaluated temperatures

Fig. 2 shows friction coefficient as a function of sliding distance of Hastelloy C/CaF$_2$ couple at evaluated temperatures. At 300 °C, the starting friction coefficient was 0.25, and increased to 0.28–0.30 after sliding 0.45 km. Then the friction coefficient stayed at 0.40 to the distance of 1.2 km. Finally, the friction coefficient dropped to the value of 0.34. The friction coefficient at 300 °C was not low enough to lubricate Hastelloy C. At 400 °C, the friction coefficient was relatively constant as a function of sliding distance. Only within the distance of 0–0.15 km did the friction coefficient increase from 0.15 to 0.19 and then stabilized at [illegible] for the rest of the distance. At 500 °C, the starting friction coefficient was low—0.14, then increased to 0.20 after sliding 0.36 km, finally it reached 0.26 after sliding a distance of 0.83 km. At 600 and 700 °C, the friction coefficient vs. sliding distance was simple. The friction coefficients were within the range of 0.15–0.20.

At 300 °C, the mass loss of Hastelloy C was [illegible] mg and the transfer was be observed. At 400, 500, 600, and 700 °C, Hastelloy C had negative wear losses (0.7–1 mg increment) due to the formation of transferred film on its wear surface. Although the wear loss of the compacts was high (24.7–33.0 mg), it can be concluded that CaF$_2$ compacts [illegible] to be commendably lubricating Hastelloy C by forming transferred film on the wear surface of Hastelloy C at evaluated temperatures.

Fig. 2. Dependence of friction coefficient vs. sliding distance at evaluated temperatures (load 39.2 N, velocity 0.3 m s^{-1}).

3.2. Physical effect

3.2.1. Preferential orientation and degree of crystallization

XRD results reveal that no preferential orientation occurred by simply heating CaF$_2$ compact sample at 700 °C, where the crystal planes (220), (111), and (200) of CaF$_2$ had preferential orientations (see Fig. 3).

Table 2 lists the crystal planes of CaF$_2$ wear debris that had preferential orientations after friction tests at 400, 500, 600, 600, and 700 °C. Crystal plane (002) had preferential orientation except at 700 °C. The crystal structure of CaF_2 is [illegible] and shows the so-called [illegible] structure which approximates a layer lattice. The layers are held together only by weak van der Waals' forces. This type of structure is readily sheared in the direction parallel to layer orientation [3], so the preferential orientation of crystal plane (002) is beneficial to friction reduction of CaF_2. As seen in Fig. 4(b), the intensity of plane (002) exceeded that of plane (111). Combined with the result of friction coefficient–sliding distance at 400 °C, it can be concluded that the preferential orientation of plane (002) was the dominant factor in friction reduction. Planes (112), (004) had preferential orientations at all evaluated temperatures. This may be due to the [illegible] [illegible] surface.

As seen in Fig. 4, the degrees of crystallization of the wear debris at evaluated temperatures were influenced by sliding. At 300 °C, the degree of crystallization was low (see Fig. 4(a)), and as a result the friction coefficient was higher despite the preferential orientation of plane (002). At other temperatures, the degrees of crystallization of wear debris were higher than that at 300 °C to give lower friction.

Considering these observations, it was concluded that the preferential orientation of plane (002) and the degree of crystallization of wear debris were the two underlying physical factors that affect the friction-reducing property of CaF_2 compact. The preferential orientation of plane (002) had a positive effect on the friction-reducing property of CaF_2 and the degree of crystallization had a positive effect on friction-reduction when it was high.

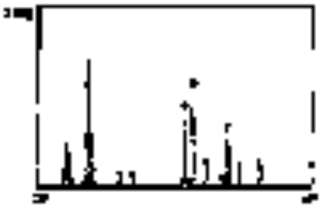

Fig. 3. XRD spectrum of CaF_2 [illegible] after heating at 700 °C in air [illegible] [illegible] [illegible], (112), [illegible].

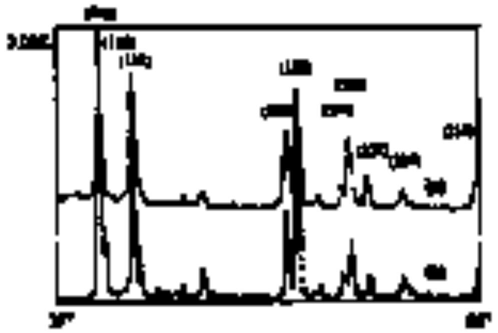

Fig. 4. XRD spectra of CaF_2 wear debris at evaluated temperatures: (a) 300 °C; (b) 400 °C.

3.2.2. Plastic deformation

Fig. 5 shows the morphology of CaF_2 powder as received, CaF_2 compact and wear debris. CaF_2 powder as received was spherical-like, about 1 μm in size. After sintering, the particle size of CaF_2 grew. The wear debris was sheet-shaped, which means plastic deformation occurred in sliding. Plastic deformation contributes to energy release and film-forming on the wear surface. Because CaF_2 has low hardness [3], the deformation can easily occur. However, the compressive strength in the direction of c_0 (direction vertical to plane (002)) is higher than that in the direction of a_0 (direction parallel to plane (002)) while the shear strength is just the opposite. So the plastic deformation occurred in the direction parallel to a_0 and slip followed the direction. This explains the shape of the wear debris.

3.3. Chemical effect

3.3.1. The early oxidation behavior of CaF_2 compact

XRD results show that the CaF_2 compact began to oxidize between 400 and 500 °C, and totally converted to [illegible] at 700 °C after being heated in a furnace for an hour (see

Table 2

Crystal planes of wear debris that had preferential orientations (+) [illegible] at evaluated temperatures

Crystal plane	Temperature				
	300 °C	400 °C	500 °C	600 °C	700 °C
(002)	+	+	+	+	
[illegible]					
[illegible]					
[illegible]					
[illegible]					
[illegible]	+				+
(112)	+	+	+	+	+
(004)	+	+	+	+	+
[illegible]	+				+
[illegible]	+				
[illegible]	+				
[illegible]	+				

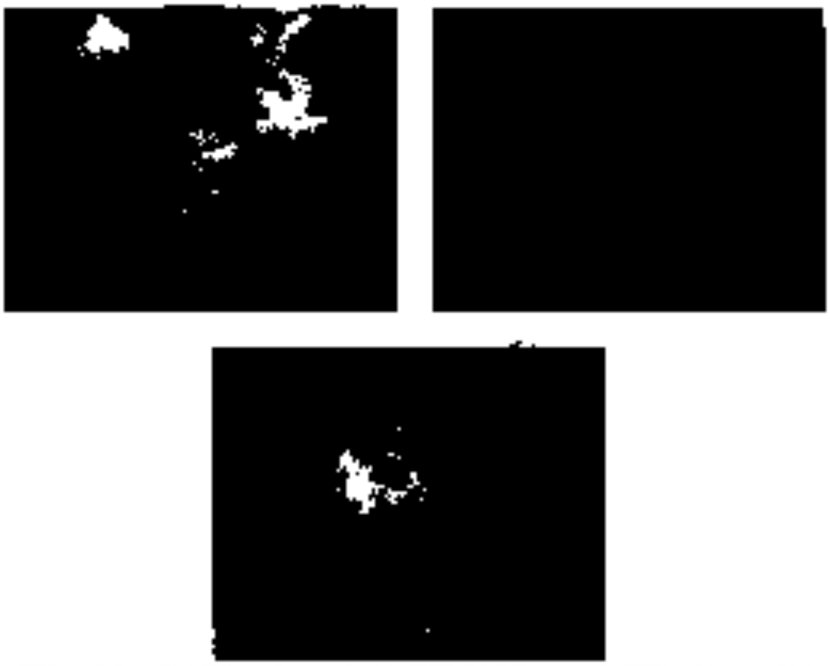

Fig. 5. The SEM morphology of (a) CrF$_3$ powder as received (×[illegible]), (b) CrF$_3$ compact (×[illegible]) and (c) wear debris (×2000).

Table 3
[illegible]

	[illegible]^a			
	Raw material	[illegible] °C	[illegible] °C	700 °C
Static	[illegible]	[illegible]	[illegible]	[illegible]
Sliding	—	[illegible]	[illegible]	[illegible]

^{a}The ratio of the intensity of plane (111) in Cr$_2$O$_3$ and CrF$_3$ respectively.

Table 3). It is suggested that the CrF$_3$ compact was oxidation-resistant up to 600 °C.

3.5.2. The oxidation behavior of CrF$_3$ compact in sliding contact

XRD results show that the oxidation of CrF$_3$ began at 500 °C and the maximum oxidation was observed at 700 °C (see Table 3). The starting oxidation temperature of CrF$_3$ compact in sliding was lower than that under static conditions, which means the oxidation behavior in sliding is different from that of the latter. Due to the frictional action, the temperature of the sliding surface was higher than that of the environment. Hence the oxidation occurred more easily in sliding than static conditions. Wear debris at 700 °C was mainly Cr$_2$O$_3$, which indicated the oxidation of CrF$_3$ was dominant at this temperature.

All this suggests that the tribological behavior of CrF$_3$ was controlled by the formation of [illegible] above 700 °C.

3.5.3. The tribological characteristics of Cr$_2$O$_3$ compact at 700 °C

Fig. 8 shows the tribological characteristics of Cr$_2$O$_3$ compact from room temperature to 700 °C. It is clear that Cr$_2$O$_3$ showed lubricity only at 700 °C. As seen in Fig. 7, Cr$_2$O$_3$ was a good lubricant at 700 °C. At this temperature, transferred film was formed on the counterpart surface (see Fig. 9) and the

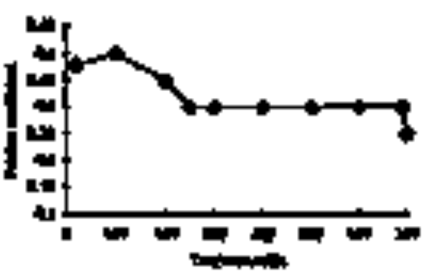

Fig. 8. Friction coefficient of [illegible] Cr$_2$O$_3$ compact sample at elevated temperatures.

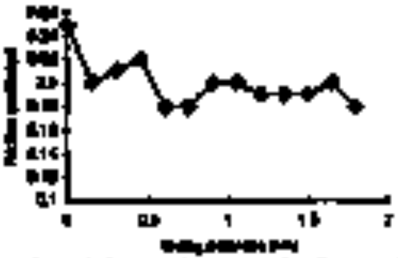

Fig. 2. Dependence of friction coefficient vs. sliding distance of [illegible] CeO$_2$ [illegible] at 700°C.

friction coefficient remained at 0.18 ~ 0.20 after sliding a distance of 0.25 km. The [illegible] existence of CeO$_2$ at [illegible] so the friction-reducing property is probably due to the [illegible] of CeO$_2$. Observation on the worn surface of CeO$_2$ specimen at 700 °C indicated that the worn surface was smooth and glass-like. The [illegible] that can reduce the wear of the alloy C since [4] wear rate is very low (3.7[illegible] × 10$^{-[illegible]}$ m^3 N^{-1} m^{-1}). Unlike MoO$_3$ which sublimates at 800 °C, CeO$_2$ is more stable [4] and can be used to a temperature of 1000 °C or even higher.

Considering these discussions, it can be concluded that the oxidation of CeF$_3$ in sliding below 700 °C and a negative

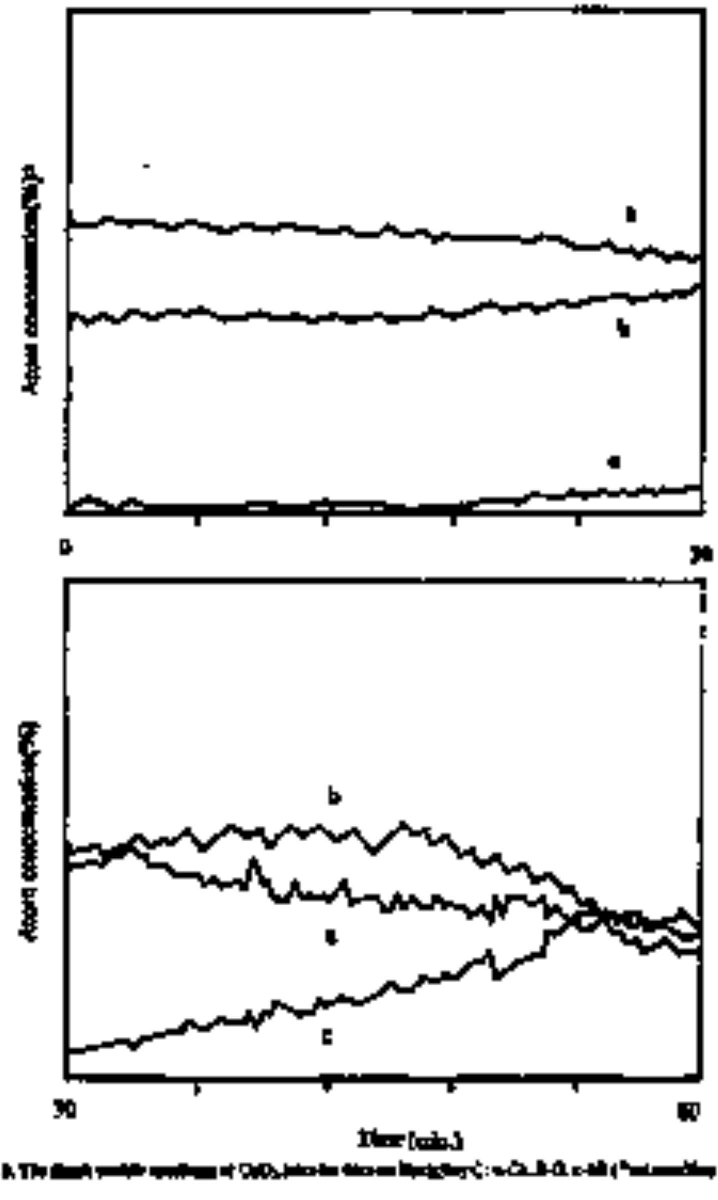

Fig. 3. The depth profile spectrum of CeO$_2$ [illegible] (: a-Ce, b-O, c-Al ([illegible]

effect on the lubricity since CrO$_3$ showed good lubricity by providing low friction and low wear rate. All this implies that when using CaF$_2$ containing compact for lubrication below 700 °C, the formation of CrO$_3$ film on the surface of mating counterpart should be avoided.

4. Conclusions

1. The physical effects of CaF$_2$ compact including were preferential orientation, plastic deformation, and degree of crystallization. The preferential orientation of plane (100) had a positive effect on reducing friction. The degree of crystallization of wear debris showed a positive effect when the wear rate was high.
2. The chemical effect of CaF$_2$ compact in sliding was oxidation. It had a negative effect on reducing friction between 300 °C and 700 °C since the tribological properties of CrO$_3$ at these temperatures were poor.
3. CrO$_3$ had good friction-reducing properties at 700 °C in which the softening and film-forming properties of CrO$_3$ were perfectly performed.

Acknowledgements

Professor Q.Z. Cheng is thanked for valuable help.

References

[1] [illegible] ASLE Transactions 3 (1) (19[illegible]) [illegible].

[2] H.E. [illegible], ASLE Transactions [illegible] (19[illegible]) [illegible].

[3] [illegible] NASA [illegible] (19[illegible]).

[4] [illegible] [illegible] Engineering [illegible] (19[illegible]) [illegible].

[5] [illegible], Wear, in press.