

Physical and chemical effects of CaF_2 compact in sliding against Hastelloy C in temperatures to 700 °C

Quaji Xian, Jiqun Lu *

Laboratory of Solid Lubrication, Institute of Chemical Physics, Chinese Academy of Sciences, Beijing 100080, China

Received 27 June 1996; accepted 11 March 1997

Abstract

The dependence of friction coefficient vs. temperature of Hastelloy C/ CaF_2 compact was studied in this paper. The wear tracks was studied by using X-ray diffraction (XRD) and scanning electron microscopy (SEM). Frictional coefficient was CaF_2 and played an important role in sliding at different temperatures. The physical effects were known as interstitial intercalation, degree of crystallization and plastic deformation. The preferential intercalation of fluorine (F2) had a positive effect on friction reduction. The friction coefficients were low on the degree of crystallization was high. The chemical effect was known as substrate. The difference between wear and sliding coefficients was not the sliding temperature of the surface was higher than that of the film. The cause was the temperature difference between the sliding surface and intercalation compact by frictional action. The substrate of CaF_2 compact had a negative effect on friction below 300 °C, but CaF_2 exhibited good friction-reducing, strengthening and film-forming properties, which cause the substrate above 300 °C may be a beneficial effect on friction reduction. © 1997 Elsevier Science B.V.

Keywords: Friction; XRD; SEM; Compact; Intercalation; Plastic deformation; Diffusion; CaF_2 compact

1. Introduction

Fluorine, boron and graphite are among typical solid lubricants for wear above 300 °C [1-3]. They were first used to be applied in high temperature solid lubrication up to at least 1800 °C, due to their good film-forming, plastic deformation and transferring properties [3]. Unfortunately however, the degradation involving the crystal substrate and the brittleness of wear tracks have not yet been solved. Furthermore, it is interesting that CaF_2 compact does not slide to yellow during sliding at high temperatures according to literature [4]. It is well known that CaF_2 is yellow, so it may be observed that the addition of CaF_2 might be beneficial to sliding. Apparently, there are effects are very important to help to understand the interesting properties of CaF_2 at high temperatures. The authors' previous survey on the tribological characteristics of CaF_2 compact in nitrogen was to 700 °C showed that the friction coefficient was 0.1 to 0.15 [5]. X-ray diffraction (XRD) results revealed that the crystal phase (JCPD, (113)) of wear tracks showed preferential intercalation and the degree of CaF_2 increased compared to the compact, which suggested that physical and

chemical effects may occur during sliding. As indicated in literature [5], the most interesting parts of the tribological characteristics of CaF_2 are below 300 to 400 °C and 400 to 500 °C. It is likely that there are intercalation on the surface during the sliding of CaF_2 at these temperatures. To have further knowledge on these effects, the dependence of the effects with temperature 300 to 500 °C was studied in this paper. Comparisons on these effects on wear and sliding coefficients were made.

2. Experimental details

2.1. Materials

CaF_2 powder was obtained from China New Salt Co. Ltd. The purity was 99.9%.

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

2.2. Preparation of CaF_2 compact

CaF_2 compact is prepared by using the hot-pressing method in a nitrogen of Hastelloy C. Details on making the CaF_2 compact are given in Ref. [5].

* Corresponding author.

Table 1
The overall compressive and residual strength of Hastelloy C

Composites (wt. %)	Density (g cm^{-3})	Layer thickness (μm)	Compressive strength (MPa)	
			at 25°C	at 300°C
Hastelloy C Cr-Ni-Mo-W-Cu-Co-Nb-Ta 0.58 x 10 ⁶	8.94	1000	1700	870

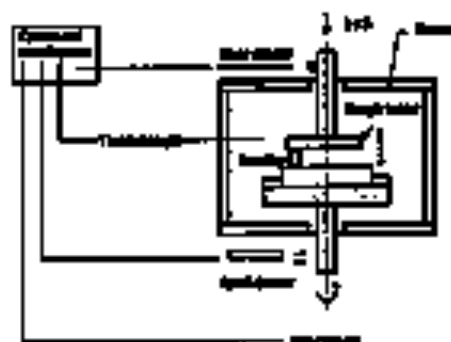


Fig. 1. Schematic of the high temperature apparatus.

2.3. Metallurgical tests

2.3.1. Apparatus and specimen

The cylindrical test were conducted as a pin-on-disk tribometer. The schematic diagram of the tribometer is shown in Fig. 1. The pin is made of Hastelloy C, with a diameter of $253 \pm 15 \mu\text{m}$. The disk is made of CaF_2 compact with a diameter of 4.5 mm.

2.3.2. Procedure

The test were conducted by sliding Hastelloy C against CaF_2 compact to study its tribological behaviour. Friction coefficient was studied at 500, 600, 700, 800, and 900 $^\circ\text{C}$. Test conditions were load 20.1 N , velocity 0.5 m s^{-1} , the diameter of the pin with width area, which is 1.8 cm^2 in diameter. The friction coefficient was measured at 5 points around (0.25 cm in diameter).

2.4. Results

The physical and chemical effects were studied by using XRD (Hilitec-D8) to detect the composition and structure of the test discs after the tribological test at various temperatures. The phase distribution of the test discs and the morphology of the CaF_2 compact were studied by using scanning electron microscopy (SEM) (JEOL-10000/S). The morphology also was studied by using Auger electron spectroscopy (AES) (P.E. P86-600).

2. Results and discussion

2.1. The dependence of friction coefficient on sliding distance at ambient temperature

Fig. 1 shows friction coefficient as a function of sliding distance of Hastelloy C/ CaF_2 couple at ambient temper-



Fig. 2. Dependence of friction coefficient on sliding distance at various temperatures (load 20.1 N , velocity 0.5 m s^{-1}).

ture. At 200°C , the starting friction coefficient was 0.23, and increased to $0.28 \sim 0.29$ after sliding 0.25 cm . Then the friction coefficient stayed at 0.26 to the distance of 1.5 cm . Finally, the friction coefficient dropped to the value of 0.24. The friction coefficient at 200°C was not too sensitive to tribolite Hastelloy C. At 300°C , the friction coefficient was relatively constant as a function of sliding distance. Only within the distance of $0 \sim 0.5 \text{ cm}$ did the friction coefficient increase from 0.15 to 0.18 and then remained at 0.17 for the rest of the distance. At 400°C , the starting friction coefficient was $0.16 \sim 0.14$, then increased to 0.20 after sliding 0.25 cm . Finally it reached 0.26 after sliding a distance of 0.50 cm . At 500 and 700°C , the friction coefficient vs. sliding distance was stable. The friction coefficient was stable for a range of $0.15 \sim 0.26$.

At 700°C , the test discs of Hastelloy C were flat and the results were unchanged. At 600 , 600 , 800 , and 700°C , Hastelloy C and negative wear locus ($0.7 \sim 1 \mu\text{m}$ thickness) were the formation of residual film on its wear surface. Although the wear rate of the compact was high ($24.7 \sim 33.0 \mu\text{g}$), it can be concluded that CaF_2 compact (provided laminae were thinner as to completely lubricate C by forming residual film on the wear surface of Hastelloy C at various temperatures).

2.2. Physical effect

2.2.1. Preferential orientation and degree of crystallization

XRD results reveal that no preferential orientation resulted by simply heating CaF_2 compact except at 700°C , where the crystal planes (200), (111), and (100) of CaF_2 had preferential orientations (see Fig. 3).

Table 2 lists the crystal planes of CaF_2 test discs that had preferential orientations after friction tests at 600 , 600 , 600 ,

400, and 700 °C. Crystal phase (CP) and preferential orientation except at 700 °C. The original structure of CaF_2 is destroyed and along the so-called spinning sequence which appears as a layer-like. The layers are held together only by weak van der Waals' forces. This type of structure is rarely observed in the direction parallel to layer orientation [3]. In the preferential orientation of original phase (OP) is brought to friction reduction of CaF_2 . As seen in Fig. 4(a,b), the intensity of phase (OP) exceeded that of phase (111). Combined with the effect of friction coefficient-reducing effect at 400 °C. It can be concluded that the preferential orientation of phase (OP) was the dominant factor in friction reduction. Phase (111), (100) and preferential orientation peak preferred appearance. This may be due to the intermolecular forces.

As seen in Fig. 4, the degree of crystallization of the wear debris at various temperatures was influenced by sliding. At 300 °C, the degree of crystallization was low (see Fig. 2(a)), and as a result the friction coefficient was higher despite the preferential orientation of phase (OP). At other temperatures, the degree of crystallization of wear debris was higher than that at 300 °C in about lower sliding.

Combining these observations, PANG concluded that the preferential orientation of phase (OP) and the degree of crystallization of wear debris were the two underlying physical factors. One effect of friction-reducing property of CaF_2 was that. The preferential orientation of phase (OP) and a positive effect on the friction-reducing property of CaF_2 and

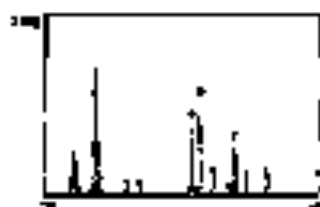


Fig. 2. XRD pattern of CaF_2 versus time heating at 300 °C in air at 1000, 2000, 4000, 6000, 8000, 10000, 12000, 14000, 16000, 18000, 20000, 22000, 24000, 26000, 28000, 30000, 32000, 34000, 36000, 38000, 40000, 42000, 44000, 46000, 48000, 50000, 52000, 54000, 56000, 58000, 60000, 62000, 64000, 66000, 68000, 70000, 72000, 74000, 76000, 78000, 80000, 82000, 84000, 86000, 88000, 90000, 92000, 94000, 96000, 98000, 100000, 102000, 104000, 106000, 108000, 110000, 112000, 114000, 116000, 118000, 120000, 122000, 124000, 126000, 128000, 130000, 132000, 134000, 136000, 138000, 140000, 142000, 144000, 146000, 148000, 150000, 152000, 154000, 156000, 158000, 160000, 162000, 164000, 166000, 168000, 170000, 172000, 174000, 176000, 178000, 180000, 182000, 184000, 186000, 188000, 190000, 192000, 194000, 196000, 198000, 200000, 202000, 204000, 206000, 208000, 210000, 212000, 214000, 216000, 218000, 220000, 222000, 224000, 226000, 228000, 230000, 232000, 234000, 236000, 238000, 240000, 242000, 244000, 246000, 248000, 250000, 252000, 254000, 256000, 258000, 260000, 262000, 264000, 266000, 268000, 270000, 272000, 274000, 276000, 278000, 280000, 282000, 284000, 286000, 288000, 290000, 292000, 294000, 296000, 298000, 300000, 302000, 304000, 306000, 308000, 310000, 312000, 314000, 316000, 318000, 320000, 322000, 324000, 326000, 328000, 330000, 332000, 334000, 336000, 338000, 340000, 342000, 344000, 346000, 348000, 350000, 352000, 354000, 356000, 358000, 360000, 362000, 364000, 366000, 368000, 370000, 372000, 374000, 376000, 378000, 380000, 382000, 384000, 386000, 388000, 390000, 392000, 394000, 396000, 398000, 400000, 402000, 404000, 406000, 408000, 410000, 412000, 414000, 416000, 418000, 420000, 422000, 424000, 426000, 428000, 430000, 432000, 434000, 436000, 438000, 440000, 442000, 444000, 446000, 448000, 450000, 452000, 454000, 456000, 458000, 460000, 462000, 464000, 466000, 468000, 470000, 472000, 474000, 476000, 478000, 480000, 482000, 484000, 486000, 488000, 490000, 492000, 494000, 496000, 498000, 500000, 502000, 504000, 506000, 508000, 510000, 512000, 514000, 516000, 518000, 520000, 522000, 524000, 526000, 528000, 530000, 532000, 534000, 536000, 538000, 540000, 542000, 544000, 546000, 548000, 550000, 552000, 554000, 556000, 558000, 560000, 562000, 564000, 566000, 568000, 570000, 572000, 574000, 576000, 578000, 580000, 582000, 584000, 586000, 588000, 590000, 592000, 594000, 596000, 598000, 600000, 602000, 604000, 606000, 608000, 610000, 612000, 614000, 616000, 618000, 620000, 622000, 624000, 626000, 628000, 630000, 632000, 634000, 636000, 638000, 640000, 642000, 644000, 646000, 648000, 650000, 652000, 654000, 656000, 658000, 660000, 662000, 664000, 666000, 668000, 670000, 672000, 674000, 676000, 678000, 680000, 682000, 684000, 686000, 688000, 690000, 692000, 694000, 696000, 698000, 700000, 702000, 704000, 706000, 708000, 710000, 712000, 714000, 716000, 718000, 720000, 722000, 724000, 726000, 728000, 730000, 732000, 734000, 736000, 738000, 740000, 742000, 744000, 746000, 748000, 750000, 752000, 754000, 756000, 758000, 760000, 762000, 764000, 766000, 768000, 770000, 772000, 774000, 776000, 778000, 780000, 782000, 784000, 786000, 788000, 790000, 792000, 794000, 796000, 798000, 800000, 802000, 804000, 806000, 808000, 810000, 812000, 814000, 816000, 818000, 820000, 822000, 824000, 826000, 828000, 830000, 832000, 834000, 836000, 838000, 840000, 842000, 844000, 846000, 848000, 850000, 852000, 854000, 856000, 858000, 860000, 862000, 864000, 866000, 868000, 870000, 872000, 874000, 876000, 878000, 880000, 882000, 884000, 886000, 888000, 890000, 892000, 894000, 896000, 898000, 900000, 902000, 904000, 906000, 908000, 910000, 912000, 914000, 916000, 918000, 920000, 922000, 924000, 926000, 928000, 930000, 932000, 934000, 936000, 938000, 940000, 942000, 944000, 946000, 948000, 950000, 952000, 954000, 956000, 958000, 960000, 962000, 964000, 966000, 968000, 970000, 972000, 974000, 976000, 978000, 980000, 982000, 984000, 986000, 988000, 990000, 992000, 994000, 996000, 998000, 1000000.

Table 2
Crystal phase of wear debris that had preferential orientation (+) obtained at ambient temperatures.

Crystal phase	Temperature				
	300 °C	400 °C	500 °C	600 °C	700 °C
(100)	+	+	+	+	
(110)					
(111)					
(112)					
(101)					
(102)	+				+
(113)	+	+		+	+
(114)	+	+	+	+	+
(115)	+				+
(116)	+				
(117)	+				
(118)	+				
(119)	+				
(120)	+				

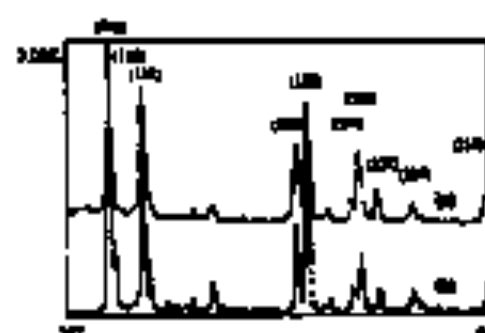


Fig. 4. XRD spectra of CaF_2 over which a ambient temperature (a) 300 °C, (b) 400 °C.

the degree of crystallization had a positive effect on tribological behavior when it was large.

1.2.2. Phase deformation.

Fig. 5 shows the morphology of CaF_2 powder as received, CaF_2 compact and water debris. CaF_2 powder as received was spherical-like, about 1 μm in size. After sliding, the morphology of CaF_2 phase. The wear debris was also spherical, which were phase deformation resulted in sliding. Plastic deformation occurred in many places and the forming on the wear surface. Because CaF_2 has low modulus [3], the deformation can easily occur. However, the compressive strength in the direction of c_2 (direction vertical to phase (OP)) is higher than that was in the direction of a_2 (direction parallel to phase (OP)) while the shear strength is just the opposite. In the plastic deformation occurred in the direction parallel to a_2 and slip followed the direction. This explains the shape of the wear debris.

1.3. Chemical effect

1.3.1. The early oxidation behavior of CaF_2 samples

XRD results show that the CaF_2 compact begins to oxidize between 300 and 350 °C, and mainly converted to CaO at 300 °C after being heated in a stream for an hour (see

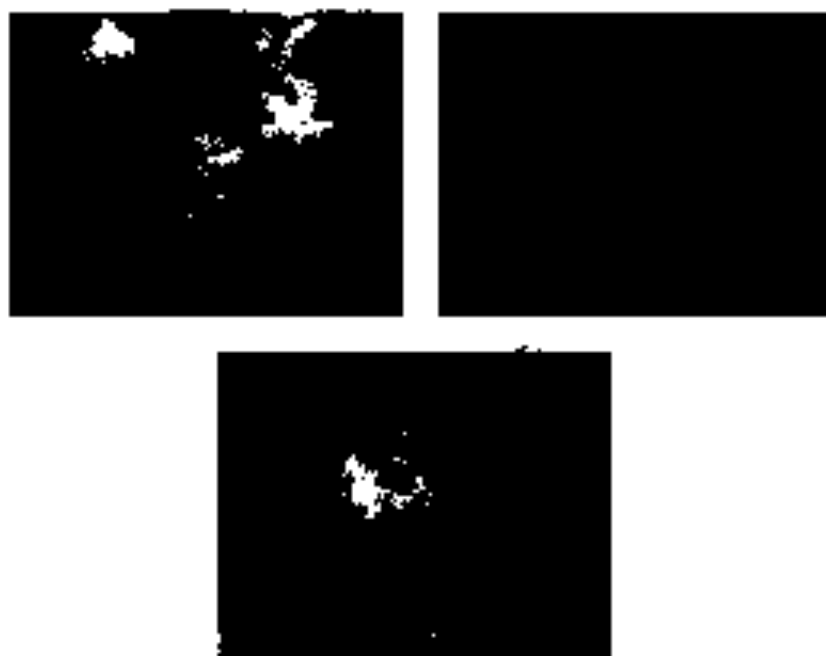


Fig. 5. The SEM morphology of (a) CaO particles on sapphire ($\times 3000$), (b) CaO on sapphire ($\times 3000$) and (c) wear track ($\times 10000$).

Table 3

Relative degree of CaO on sapphire in each condition for the sliding system. Sliding C is 200, distance 1000 μm

	$\mu\text{m}^2/\text{rev}^*$			
	Raw sapphire	700 $^\circ\text{C}$	800 $^\circ\text{C}$	1000 $^\circ\text{C}$
State	10 SEM	10 SEM	60 SEM	40 SEM
Wear	—	21 SEM	60 SEM	100 SEM

*The size of the scratch of glass (11) is CaO, and CaO, respectively.

Table 3). It is suggested that the CaO on sapphire was oxidized up to 1000 $^\circ\text{C}$.

3.3.2. The oxidation behavior of CaO on sapphire in sliding contact

XRD would show that the oxidation of CaO begins at 200 $^\circ\text{C}$ and the maximum oxidation was observed at 700 $^\circ\text{C}$ (see Table 3). The specific oxidation temperature of CaO on sapphire 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 continuous nature, the temperature of the sliding surface was higher than that of the latter. Hence the oxidation occurred more easily in sliding than static conditions. Wear starts at 700 $^\circ\text{C}$ and mainly CaO, which indicated the oxidation of CaO was finished at that temperature.

All the samples that the oxidized behavior of CaO was removed by the chemical effect above 700 $^\circ\text{C}$.

3.3.3. The tribological characteristics of CaO on sapphire at 700 $^\circ\text{C}$

Fig. 6 shows the tribological characteristics of CaO on sapphire under various temperatures at 700 $^\circ\text{C}$. It is clear that CaO on sapphire showed tribology only at 700 $^\circ\text{C}$. As seen in Fig. 7, CaO on sapphire acted as a good lubricant at 700 $^\circ\text{C}$. At this temperature, transformed the wear form on the counterpart surface (see Fig. 8) and the

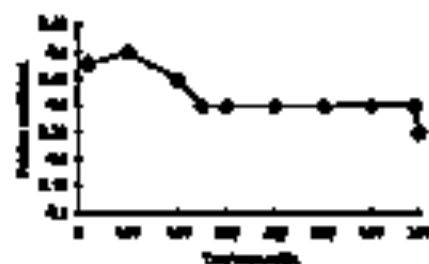


Fig. 6. Tribological characteristics of CaO on sapphire at various temperatures.

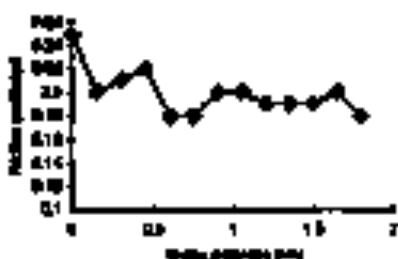


Fig. 2. Dependence of friction coefficient on sliding distance of flowing CaCO_3 suspension at 100°C .

friction coefficient remained at $0.15 \sim 0.20$ after sliding a distance of 0.25 cm. The typical structure of CaF_2 at *fcc* as the friction-reducing property is probably due to the evolution of CaO . Observation on the cross-section of CaO crystals at 700°C indicated that the cross-section was smooth and glass-like. The calculated flux rate under the case of the sliding Γ after the water was in very low ($3.76 \times 10^{-10} \text{ mol m}^{-2} \text{ s}^{-1}$). Unlike SiO_2 , which sublimes at 800°C , CaO is more stable and can be used in a spectrum of 1800°C or even higher.

Considering these observations, it can be concluded that the reduction of CaF_2 is sliding below 700°C and a negative

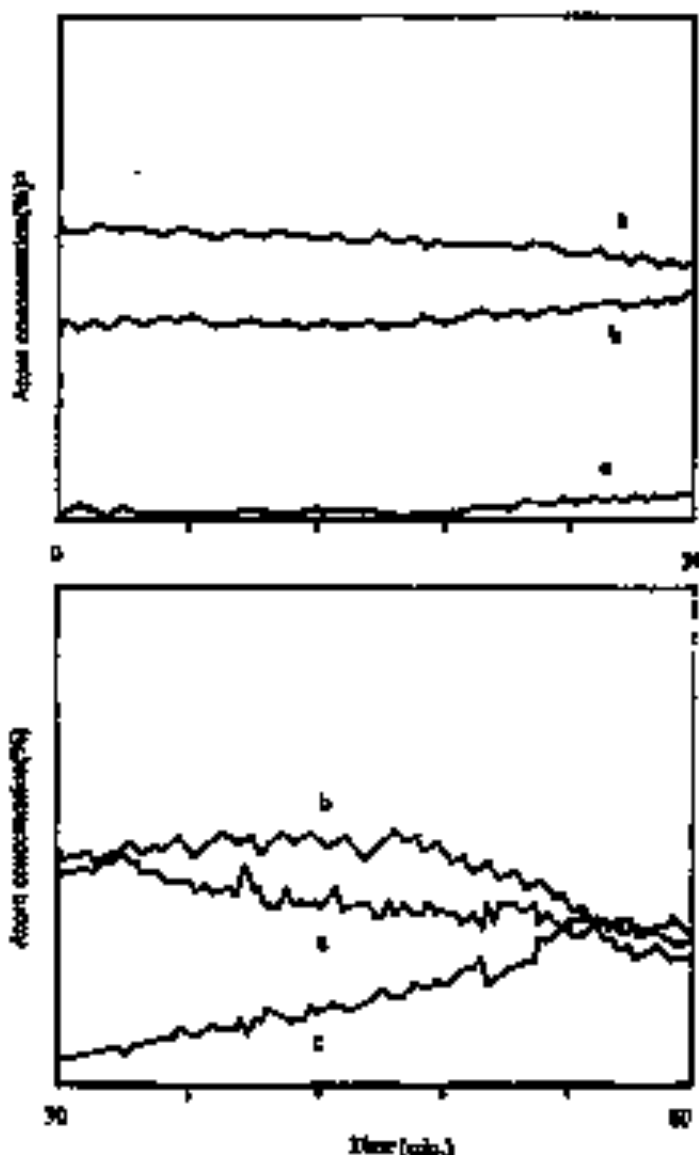


Fig. 3. The mass yield spectrum of CaCO_3 into the three on 1000°C : a-Ca, b-O, c-H₂O (Post-sliding state).

effect on the tribology of CaO_2 showed good tribology by providing low friction and low wear rate. All this implies that when using CaO_2 as a coating material for lubrication at 700 °C, the formation of CaO film on the surface of mating components should be avoided.

4. Conclusions

1. The physical effects of CaO_2 on metal bonding, wear, post-wear oxidation, plastic deformation, and degree of crystallization. The post-wear crystallization of glass (80%) had a positive effect on reducing friction. The degree of crystallization of wear debris showed a positive effect after the wear test, high.
2. The chemical effect of CaO_2 compared to sliding was not obvious. It had a negative effect on reducing friction between 500 °C and 700 °C after the tribological preparation of CaO_2 at these temperatures was poor.

3. CaO_2 had good friction-reducing properties at 700 °C in addition to reducing the film-forming properties of CaO , wear particles produced.

Acknowledgements

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

References

- [1] H.H. Poon, S.F. Wang, J.J. Peng, Characterization of tribochemical byproducts from $\text{SiO}_2/\text{Al}_2\text{O}_3$ tribosystem, *J. Tribol.* 22 (2000) 20–26.
- [2] H.H. Poon, Kinetics of tribochemical reactions on alumina and amorphous silica, *ASLE Transactions* 8 (1991) 207–208.
- [3] H.H. Poon, *Surface and Interface* and *Tribol.* as tribology units of tribology world tribology conference in HONG KONG, CHINA, 10–14 SEPTEMBER 1994.
- [4] H.H. Poon, S.F. Wang, Effect of water film on low speed tribology of $\text{SiO}_2/\text{Al}_2\text{O}_3$ tribosystem at temperature below 100 °C, *Lubrication Engineering* 49 (2003) 207–208.
- [5] H. Li, Q.Z. Cheng, J.L. Cheng, Thermal property and tribological characteristics of CaO_2 prepared from CaCO_3 .