

## Thermal properties and tribological characteristics of $\text{CaF}_2$ compact

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### Abstract

By studying the oxidation behavior of  $\text{CaF}_2$  in air, a  $\text{CaF}_2$ -compact was prepared on a substrate and the structure is described in the paper. Effects of temperature, time and humidity on the sliding friction behavior of the compact was studied on a pin-on-disk tribometer. Results indicated that the  $\text{CaF}_2$ -compact prepared for friction in sliding against Steels 100 °C and 700 °C at high velocity and low load. Analytical results suggested two predominant oxidation of places (W/O and the oxidation of  $\text{CaF}_2$  on the two places that affect the lubricating property of  $\text{CaF}_2$ ). Furthermore, the results also showed that  $\text{CaF}_2$ -compact prepared Steels 100 °C with oxidation was able to be applied temperatures up to 700 °C suggested the  $\text{CaF}_2$ -compact in wear at 400 °C in 700 °C. © 1997 Elsevier Science B.V.

**Keywords:**  $\text{CaF}_2$ -compact; tribological characteristics; lubrication conversion

### 1. Introduction

With the increasing operating temperatures of advanced engines and lubricants providing the way to 300 °C and in recent used [1]. The tribological properties of metal oxides, oxides and salts were investigated to identify their abilities on high-temperature solid lubrication in previous works [2-5]. One of the most significant advances made out by Ghazy in Machin was an exploratory study on the tribological properties of van oxide fluorides [4]. Yoda's findings have some characteristics: narrow high melting points, hexagonal crystal structure, WC-coated surfaces may have potential in solid lubricating materials for use in at least 300 °C. Findings revealed that  $\text{CaF}_2$  and  $\text{CaCl}_2$  powder showed good tribological properties above 300 °C above lubricating on Ni-based superalloy couple due to their good film-forming, plastic deformation and transferring abilities [6]. Except all these substances in previous works, very few other solids were studied. One example is that an experimental study about tribological properties of the crystal structure and density of van oxide fluorides in the previous research it was concluded that the crystal structure of  $\text{CaF}_2$  may have some correlation with the friction-reducing property at high temperature above  $\text{CaF}_2$  has a hexagonal crystal structure. Furthermore, it is interesting that  $\text{CaF}_2$  coated film tends to yellow during sliding at high temperature according to our

research [7]. It is well known that  $\text{CaO}$  is yellow. All these imply the potential oxidation and inhibition of  $\text{CaF}_2$  might be involved in the procedure of sliding. To understand the tribological mechanisms of  $\text{CaF}_2$ , therefore, these effects and their influences on tribology of  $\text{CaF}_2$  should be studied in detail.

The authors carried out a series of surveys on the tribology of  $\text{CaF}_2$ . The aim of the research is to understand the lubricating mechanisms of  $\text{CaF}_2$  at high temperature and develop solid lubricant materials containing  $\text{CaF}_2$ . To understand about a  $\text{CaF}_2$ -compact was prepared and the structure is described in this paper. The tribological characteristics of  $\text{CaF}_2$  at temperature in 300 °C were analyzed. Finally, the two main effect the sliding friction behavior of  $\text{CaF}_2$  were studied.

### 2. Experimental details

#### 2.1. Analysis of the oxidation behavior of $\text{CaF}_2$

$\text{CaF}_2$  powder, which was white, was selected from Guangzhou South Grouping China. The purity of the  $\text{CaF}_2$  powder was checked by X-ray diffraction (XRD). The oxidation behavior of the  $\text{CaF}_2$  powder was investigated by using thermogravimetric analysis (TGA), differential thermal analysis (DTA), XRD and X-ray photoelectron spectroscopy (XPS).

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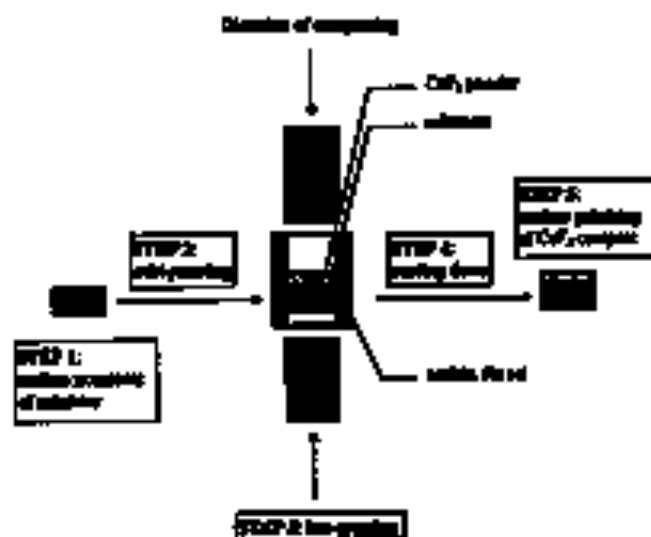


Fig. 1. Manufacturing process for 99.99%  $\text{Cu}_2\text{O}$  compact.

## 2.2. Preparation and characterization of $\text{Cu}_2\text{O}$ compact

A  $\text{Cu}_2\text{O}$  compact (3 mm in thickness) on the substrate of Hensley C was prepared by using the hot-pressing method in a silicon die. The pressing was done under the  $\text{Cu}_2\text{O}$  compact is shown in Fig. 1. Five steps are included in the pressing process. The first step is the silicon crushing of the substrate. The substrate is mechanically polished to get a surface roughness of 0.05  $\mu\text{m}$ . This step is used to get a good adhesion between the compact and the substrate. Step 2 is the sub-pressing of  $\text{Cu}_2\text{O}$  powder in the silicon die in an oxygen-free air in the pressure. The pressing pressure is 40 MPa. The third step is the hot-pressing of  $\text{Cu}_2\text{O}$  compact. The pressure is 12 MPa and changing temperatures are 400  $^\circ\text{C}$  and 700  $^\circ\text{C}$  respectively. The changing from 75 MPa to 12 MPa is to prevent some damage to the  $\text{Cu}_2\text{O}$  compact and the silicon die in doing the pressing. A thin film film was prepared on the surface of the silicon die. As a result, the  $\text{Cu}_2\text{O}$  compact was finished with a clean and unpolished surface. Step 4 is the cooling down of the compact. The finishing step is the surface polishing of the compact by diamond paper.

The composition of the compact was analyzed by XED and ICP. The diameter of the  $\text{Cu}_2\text{O}$  compact was characterized by scanning electron microscopy (SEM). The diameter of the compact was measured on a fracture face by using a JLSJ by Hitachi.

## 2.3. Frictional test

### 2.3.1. Apparatus and specimen

The frictional test was conducted on a pin-on-disk tribometer. The schematic diagram of the tribometer is shown in Fig. 2.

The pin was made of Hensley C, with heat of 855 H (13 mm). Hensley C is an Fe-based alloy prepared by the powder

metallurgy method in the authors' laboratory. The overall composition and some mechanical properties of Hensley C are shown in Table I. Hensley C was chosen as pin of the sliding tribometer because it is used as a commercial material in some engines that perform at very high temperatures. The disk was made of the  $\text{Cu}_2\text{O}$  compact and was 40 mm in diameter. The pin was attached perpendicular to the surface with a nut on the surface before the friction.

### 2.3.2. Procedure

The tests were conducted by sliding Hensley C against the  $\text{Cu}_2\text{O}$  compact. The wear rates of the pin are calculated by using the formula as follows:

$$W_p = \Delta V / (L \cdot \pi r)$$

where  $W_p$  represents the wear rate,  $\Delta V$  represents the volume loss of the pin before and after the test,  $L$  represents the load,  $r$  represents the radius, and  $\pi$  represents the diameter. In this paper, the wear rate of the Hensley C pin is expressed over the entire temperature range.

## 3. Results and discussion

### 3.1. The maximum diameter of $\text{Cu}_2\text{O}$ powder up to 1200 $^\circ\text{C}$ in air

The XED results show that there was a very small amount of  $\text{Cu}_2\text{O}$  existing in the pore space of the  $\text{Cu}_2\text{O}$  powder. The presence of the crystalline phase  $\text{Cu}_2\text{O}$  in the powder is due to the preparation of the compact.

Fig. 3 shows the DTA and TGA spectra of  $\text{Cu}_2\text{O}$  powder at temperatures up to 1200  $^\circ\text{C}$  in air. Compared with the results of DTA and TGA spectra, according to 800  $^\circ\text{C}$ , the material

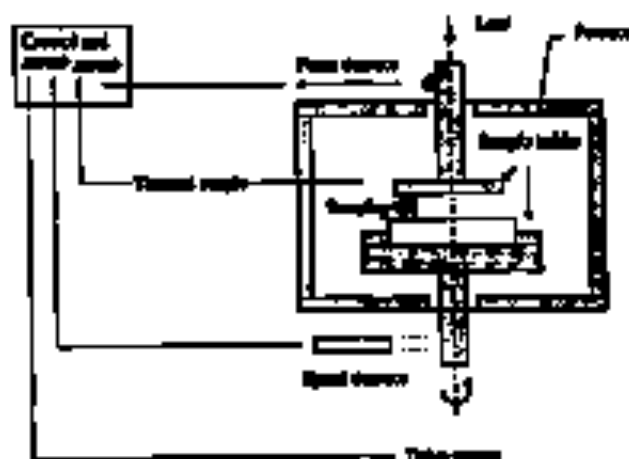


Fig. 3. Schematic of the high temperature furnace.

Table 1

The furnace composition and main mechanical property of Fe–Al–C.

Material	Composition (wt %)	Density ( $\text{g cm}^{-3}$ )	Impact toughness ( $\text{kJ m}^{-2}$ )	Compressive strength (MPa)	
				20°C	300°C
Fe–Al–C	Co 56, Ni 16, W 3, Mo 4, Fe 24, Nb 24	8.0	100	1700	1600

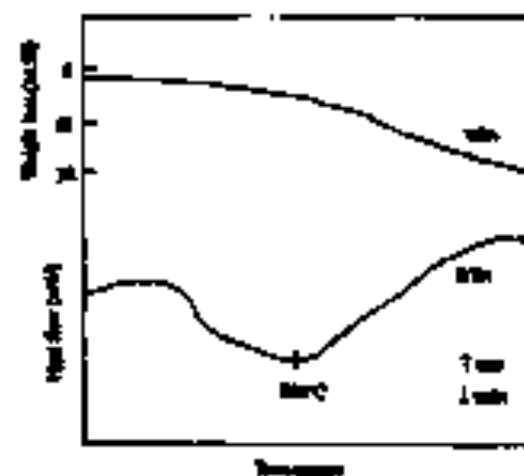
Fig. 4. TGA and DTA graphs of  $\text{CaF}_2$  powder from temperature to 1200 °C in air.

Table 2

Phase content of  $\text{CaF}_2$  powder after heating at 200 °C, 700 °C, and 900 °C for an hour in air.

Oxide phase	Control		
	200 °C	700 °C	900 °C
$\text{CaF}_2$	High	High	Low
$\text{CaO}$	None	None	High

Table 2 shows the phase content of  $\text{CaF}_2$  powder obtained by XRD after heating in a furnace at 200 °C, 700 °C, and 900 °C respectively for an hour at 200 °C, 700 °C, and 900 °C respectively because no significant  $\text{CaO}$  was detected. At 200 °C, the oxidation of  $\text{CaF}_2$  was slight. At 700 °C, the oxidation of  $\text{CaF}_2$  was completed. Table 3 shows the binding energy of Ca, F and O of  $\text{CaF}_2$  powder obtained by XPS. These data proved that  $\text{CaF}_2$  had no oxidation at 900 °C because the binding energy of O<sub>1s</sub> in the range of 510–530 eV can be concluded that  $\text{CaF}_2$  is oxidation-resistant at 900 °C in air.

As a result, the appropriate temperature for processing  $\text{CaF}_2$  composite should be below 600 °C. As seen in Table 3, the  $\text{CaF}_2$  did not oxidize by processing the  $\text{CaF}_2$  remains at 600 °C. While compressing at 700 °C, slight oxidation of  $\text{CaF}_2$  occurred. In the  $\text{CaF}_2$  composite prepared at 900 °C this trend in the experimental specimen.

Table 3

Binding energy of Ca, F, O.

Sample	Binding energy (eV)		
	Ca <sub>2p</sub>	F <sub>1s</sub>	O <sub>1s</sub>
$\text{CaF}_2$ powder before control	284.2	688.2	532.2
Control sample $\text{CaF}_2$	284.2	—	532.2
Sample after heating at 200 °C	284.2	688.2	532.2
Sample after heating at 700 °C	284	—	532
Control prepared at 200 °C	284.2	688.2	532.2
Control prepared at 700 °C	284.2	688.2	532.2



Fig. 4. Micrographs (SEM) of (a)  $\text{CaF}_2$  particles (b)  $\text{CaF}_2$  compact.



Fig. 5. Micrograph of PVDF layer (thickness  $\times 2000$ ).

Table 4  
Depth distribution of PV in  $\text{CaF}_2$  compact by SEM on SEM

Position (mm)	Thickness (mm)				
	0	0.5	20	30	70
Thickness (mm)	27.2	22.8	20.6	22.8	0

### 3.2. Microstructure of $\text{CaF}_2$ compact

Figs. 4(a) and 4(b) show the morphology of  $\text{CaF}_2$  particles in compact and cross-section morphology of the  $\text{CaF}_2$  compact respectively. Particles in the  $\text{CaF}_2$  compact grew after sintering at 280 °C. The particles were held together by the interfacial energy of particles. The compact had a thickness of 21 mm, which suggested that the sintering strengthening

of the particles was high. The thickness was equal to the width thickness of  $\text{CaF}_2$ , according to Ref. [14]. As such, the particles were held in the same size as the same surface as powder form. A thin layer of Ni, Cu, W, etc. (shown the substrate) and  $\text{CaF}_2$  between the  $\text{CaF}_2$  compact and the substrate formed by mutual diffusion was observed (see Fig. 3). This layer was about 50 to 75  $\mu\text{m}$  in thickness according to the data listed in Table 4 obtained by energy dispersive spectroscopy (EDS) on SEM. The average thickness of the layer was calculated by assuming the concentration distribution of Ni as a function of the depth. The existence of this layer may prevent the diffusion enough between the substrate and  $\text{CaF}_2$  compact. The substrate had a thickness of 280 mm and was heated evenly and applied on the compact. Presumably, the compact was not in a solid condition acting as a total substrate. However, the layer was so thin and fine that the bonding enough between compact and substrate was weak. So casting and the techniques, such as PVD or plating, are more appropriate than using  $\text{CaF}_2$  as a compact when applied  $\text{CaF}_2$  in a micro-system.

### 3.3. The tribological characteristics of $\text{CaF}_2$ compact

#### 3.3.1. Effect of temperature on the tribology behavior of Hertzian $\text{CaF}_2$ compact sample

Fig. 6 shows the tribological characteristics of the  $\text{CaF}_2$  compact from room temperature to 200 °C. Unlike the low velocity C and steel sample, which provided high and unstable friction coefficient at ambient temperature, the  $\text{CaF}_2$  compact provided low friction in sliding against Hertzian C

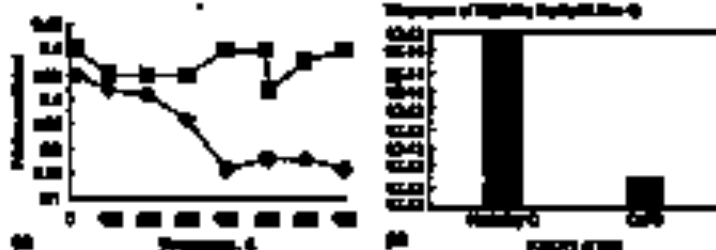


Fig. 6. Tribological characteristics of  $\text{CaF}_2$  compact from room temperature to 200 °C in the: (a) Hertzian temperature over; (b) average value of friction coefficient. Test conditions: 200 MPa, velocity 0.1 m s<sup>-1</sup>, loading rate 10–20 °C per min.

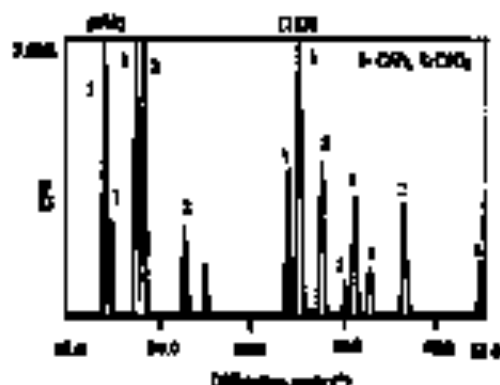


Fig. 7. XRD spectra of wear debris of  $\text{CaF}_2$  measured after sliding against Haeffley C from room temperature to 700 °C. Load 20.0 N, velocity 0.1 m s<sup>-1</sup>, time 60 and 10–20 °C per min.

between 400 °C and 700 °C. Meanwhile, compared with the Haeffley C self-wear sample, the wear rate of the Haeffley C pin was significantly reduced due to the lubrication of the  $\text{CaF}_2$  asperity. This causes the  $\text{CaF}_2$  asperity to be a good lubricant for the range of 400 °C to 700 °C. It is interesting that the friction-coefficient curve of the Haeffley C/ $\text{CaF}_2$  contact couple can be divided into three sections. Section 1 is low wear, corresponding to 100 °C, in which the friction coefficient gradually decreased with temperature. Section 2 is from 200 °C to 400 °C, when the friction coefficient decreased rapidly with temperature. Section 3 is from 400 °C to 700 °C, with the friction coefficient stabilised at a level of 0.16–0.18. In sections 1 and 2, the wear debris had an apparent order change while in section 3 the wear debris was stable. These places believed that the oxidation of  $\text{CaF}_2$  was more in sliding in section 2. As seen in Fig. 7, the intensity of  $\text{CaF}_2$  peaks of wear debris increased compared to powder or self-wear, which suggested that the amount of  $\text{CaF}_2$  in wear debris increased. It can be believed that the lubrication of  $\text{CaF}_2$  in wear debris is due to the oxidation of  $\text{CaF}_2$  in sliding. According to Ref. [3],  $\text{CaF}_2$  showed poor friction reducing ability. For the oxidation of  $\text{CaF}_2$  in sliding may have a negative effect on its lubricity. Furthermore,

plates (100) and (111) of  $\text{CaF}_2$  wear debris had preferential orientation, which suggested that the lubricity of  $\text{CaF}_2$  was more associated with the crystal structure.  $\text{CaF}_2$  has a hexagonal crystal structure and can be named as a layer structure. The layers are held together by weak van der Waals' force. So it is easy to shear in the direction parallel to the layer. Once the layer separates plates (100) is weak, it can be believed that rubbing easily shear plates between the layer of plates (111). By slipping between plates (100), the fractured layer is low, which has to rely the friction coefficient to low to section 2. All these allow one to be studied in detail in another paper [8].

Fig. 8(a) and 8(b) show the morphology and cross-sectional morphology of the wear surface of the asperity. It is suggested that the friction took place at the surface of the asperity. The wear debris was also shaped and over-curved on the surface. The above-shaped wear debris suggested that the  $\text{CaF}_2$  powder had plastic deformation in sliding.

### 3.3.2. Effect of load and velocity on friction coefficient of Haeffley C/ $\text{CaF}_2$ contact couple at elevated temperatures

As seen in Fig. 5, the friction coefficient increased with the increasing load, while in case of increasing velocity, the friction coefficient tended to decrease. XRD showed that the wear debris at 700 °C was mainly composed of  $\text{CaF}_2$ . So it is believed that the increasing friction coefficient with the increasing load is due to the oxidation of  $\text{CaF}_2$  in sliding. In the case of increasing velocity, the composition of wear debris was not affected by the oxidation. Furthermore, the wear debris was more easily wear away from the wear surface in high velocity. For the over-curved of the asperity is replaced by fresh asperity. This is why the friction coefficient tended to decrease with increasing velocity. It can be concluded that  $\text{CaF}_2$  has high velocity and low load.

### 3.3.3. Temperature of $\text{CaF}_2$ asperity on Haeffley C

By using  $\text{CaF}_2$  powder on the surface of Haeffley C and heating at 400 °C, amorphous  $\text{CaF}_2$  was formed by physical absorption can be observed (see Fig. 10). So it can be believed that transfer film of  $\text{CaF}_2$  is mainly formed on the wear surface. In that transfer film of  $\text{CaF}_2$  can be formed on



Fig. 8. Micrographs of the wear surface of Haeffley C (a) and CaF<sub>2</sub>-impregnated Haeffley C (b).

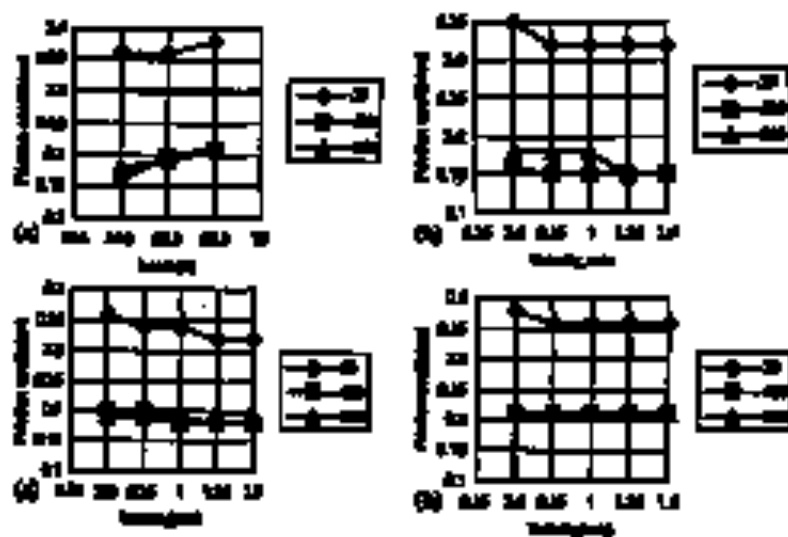


Fig. 5. Effect of (a) low-level (20–40) mg/L, (b) medium-level (100–200) mg/L, (c) high-level (200–400) mg/L, and (d) very high-level (400–600) mg/L of initial concentration on the adsorption capacity of P(Ch) for Pb(II) at 20 °C, 30 °C, and 40 °C. The conditions are: initial pH = 6.0, initial ionic strength = 0.1 M, and initial P(Ch) = 0.1 g.



Fig. 6. Micrographs (a) before, (b) after, and (c) after adsorption of Pb(II) on P(Ch) at 20 °C and 40 °C.

the surface of Hastelloy C by sliding  $\text{CoF}_2$  against Hastelloy C in different temperatures. At 400 °C, the transfer film was mainly composed of  $\text{Co}_2\text{O}_3$ . While at 700 °C, the transfer film was  $\text{CoF}_2$ . Obviously, the composition of the transfer film was influenced by the oxidation of  $\text{CoF}_2$ . According to Ref. [4],  $\text{CoF}_2$  can protect the Ni-based alloy from suffering severe wear. So the transfer film on the wear surface had the beneficial effect of reducing wear of the counterpart.

#### 4. Conclusions

Based on the discussion above, the following conclusions can be made:

- The maximum oxidation-reduction temperature of  $\text{CoF}_2$  powder in air was 600 °C. At 600 °C, the oxidation of  $\text{CoF}_2$  was complete. By compressing  $\text{CoF}_2$  at 600 °C, a  $\text{CoF}_2$  compact was of excellent with a good microstructure to be applied.
- The  $\text{CoF}_2$  compact provided low friction in sliding against Hastelloy C between 400 °C and 700 °C in high velocity and low load. The preferential orientation of plate (001) and oxidation of  $\text{CoF}_2$  was the main reason that affect the friction-reducing property of  $\text{CoF}_2$ . The latter factor had a beneficial effect on reducing friction while the former had a negative effect on reducing friction.
- The wear rate of Hastelloy C was very low due to the transfer film provided by the  $\text{CoF}_2$  compact. At 400 °C, the film was composed of  $\text{CoF}_2$ , while the transfer film of  $\text{Co}_2\text{O}_3$  was formed at 700 °C.
- $\text{CoF}_2$  can be used as solid lubricant film from 400 °C to 700 °C.

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#### Bioographies

Jun Li received his M.S. in Applied Chemical Engineering from the Department of Chemical Engineering, Tsinghua University, in 1998. He has been engaged in the study of tribology theory since. His scientific interests are high-temperature solid lubricant, solid matrix self-lubricating composite and self-lubricating metal-ceramic. Besides these, he has a wide range of interests in the use of solid lubricants. Now he is pursuing a doctoral degree in Lubrication Institute of Chemical Physics, Chinese Academy of Sciences.

Qunji Liu graduated from the Department of Chemistry, Beijing University of China, and received his M.S. degree at Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, in 1967. From 1969 to 1980, he worked at the University of Michigan. Since 1981, he has worked in the field of tribology with special emphasis on lubricating materials and  $\gamma$ -irradiated wear-free film materials papers in national and international journals. Currently, he is a professor and head of the Laboratory of Solid Lubrication and deputy director of Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences.

Shilin Cao graduated from the Department of Chemical Engineering, Tianjin University of China, in 1988. Since then, he has been working in the field of tribology with special emphasis on solid and liquid self-lubricating materials. He is the author of 20 scientific papers in national and international journals and two patents in China. He is published a book on the theory and practice of tribology.