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Tribological Properties of Self-lubricating Laminated Ceramic Materials

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Abstract: In order to improve the tribological properties of ceramic composites, Al_2O_3/TiC-Al_2O_3/TiC/CaF_2 self-lubricating laminated ceramic composites were prepared by vacuum hot pressing sintering. Experiments were conducted to get mechanical properties and the friction and wear properties were also measured with friction and wear tester. The worn surfaces were observed by scanning electron microscope (SEM) and energy dispersion spectrum (EDS). The wear resistance properties and the self-lubricating effect of ceramic composites were analyzed. Results show that the Al_2O_3/TiC-Al_2O_3/TiC/CaF_2 self-lubricating laminated ceramic composites layers are well-defined with a higher bonding strength and the mechanical performances are uniform enough to overcome the anisotropy of weak laminated ceramic composites. In addition, the fracture toughness of Al_2O_3/TiC layers is also improved. Its friction coefficient and wear rates decrease with the increase of rotation speed and load. Al_2O_3/TiC-Al_2O_3/TiC/CaF_2 self-lubricating laminated ceramic composites have good wear resistance because of the tribofilm formed by the CaF_2 solid lubricants. The wear mechanisms of Al_2O_3/TiC/CaF_2 layers are abrasive wear and Al_2O_3/TiC layers are adhesive wear.

Key words: composites; laminated ceramic materials; self-lubricating; wear and friction

1 Introduction

In the modern industry, ceramic composites have great application potentials because of excellent general mechanical properties in terms of wear resistance, oxidation resistance and corrosion resistance[1-4]. Nowadays, the advanced ceramics are widely used in wire drawing dies, cutting tools, bearing parts and varieties of high temperature engine parts[5]. However, many ceramic composites have weakness, such as sensitive to defects, bigger friction coefficient and wear rates under dry sliding conditions[6-8], which impact the wear performance.

To improve the mechanical properties and realize self-lubrication performance of the ceramic composites, several actions have been made recently. The main methods are shown as follows: adding solid-lubricants into the ceramic matrix to develop the self-lubricating ceramic composites[9-11], by *in situ* reaction method to fulfill ceramic composites self-lubricating properties[12-14], impregnating solid-lubricants[15,16], coating lubricating films[17,18], laminating different composites to realize self-lubricating performance[19], and so on.

For laminated ceramic composites, focusing on its toughening effect is significant. Combining laminated structure of shells and tribology design methods, Clegg[20] fabricated SiC-C laminated ceramic composites which possess higher toughness values than SiC ceramic materials in 1990.

Since Al_2O_3/TiC composites[21-22] have high hardness and intensity values and Al_2O_3/TiC/CaF_2 composites[23] possess better tribological properties, Al_2O_3/TiC- Al_2O_3/TiC/CaF_2 self-lubricating laminated ceramic materials were proposed and the mechanical properties, friction and wear performance under dry friction conditions were investigated.

2 Experimental

2.1 Preparation of materials

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Table 1 The mechanical properties of $Al_2O_3/TiC/CaF_2$ ceramic composites with different CaF_2 contents

	Composition/wt%			Hardness/GPa	Mechanical properties	
	Al_2O_3	TiC	CaF_2		Fracture toughtness/MPa • $m^{1/2}$	Fleurxal strength/MPa
1	32.5	62.5	5	14.6 ± 0.7	2.8 ± 0.5	335 ± 1
2	30	60	10	18.2 ± 0.8	3.5 ± 0.4	348 ± 2
3	27.5	57.5	15	13.2 ± 0.5	2.5 ± 0.5	330 ± 1

The main powders used to fabricate the laminated ceramic composites were Al_2O_3 powder, TiC powder, CaF_2 powder, Mo powder, and Ni powder. The density of high-purity α-Al_2O_3 powder with an average particle size of 0.5 μm was 3.99 g/cm^3 and the density of high-purity TiC powder with an average particle size of 0.5 μm was 4.25 g/cm^3.The purity of CaF_2 powder was more than 98.5% and its density was 3.18 g/cm^3. The purity of Mo powder and Ni powder was more than 99%. Table 1 shows the mechanical properties of $Al_2O_3/TiC/CaF_2$ ceramic composites with different CaF_2 contents. Table 2 shows the matching principle of the Al_2O_3/TiC- $Al_2O_3/TiC/CaF_2$ self- lubricating laminated ceramic composites. The combined powers were prepared by planetary ball milling in pure water for 120 h with ceramic balls. After being roasted in vacuum oven, the mixed powers were sifted in screen.

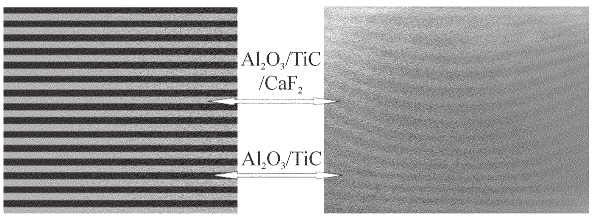

Fig.1 The schematic of laminated structure and laminated experimental sample

Table 2 Chemical contents of Al_2O_3/TiC–$Al_2O_3/TiC/CaF_2$ self-lubricating laminated ceramic composites

Sample	Composition/wt%				
	Al_2O_3	TiC	CaF_2	Mo	Ni
$Al_2O_3/TiC/CaF_2$ composites	30	60	10	0	0
Al_2O_3/TiC composites	38	52	0	1	9

Table 3 Sintering parameters of Al_2O_3/TiC–Al_2O_3/TiC/ CaF_2 self-lubricating laminated ceramic composites

Temperature/℃	Time/min	Pressure/MPa	Vacuum/Pa
1 750 ± 5	30	30 ± 0.1	10^{-3}

After mixing, Al_2O_3/TiC ceramic composites and $Al_2O_3/TiC/CaF_2$ ceramic composites were put into graphite mould (volume ratio 1:1), making sure that each layer was 1 mm thick. Table 3 describes sintering parameters of Al_2O_3/TiC-$Al_2O_3/TiC/CaF_2$ self-lubricating laminated ceramic composites. The schematic of laminated structure and laminated experimental sample are shown in Fig.1.

2.2 Mechanical properties

Bars of 3 mm×4 mm×30 mm were cut from the sintered laminated self-lubricating ceramic composites to measure the flexural strength, Vickers hardness and fracture toughness. Their surfaces were ground and polished. The Vickers hardness was measured with a load of 196 N. Three-point-bending mode was used to measure the flexural strength with a crosshead speed of 0.5 mm/min and a span of 20 mm. Considering the laminated structure, flexural strength in two different directions on the specimen was measured and the specific process is shown in Fig.2. Fracture toughness measurement was applied with an indentation method in a hardness tester using the formula proposed by Cook[24]. The values of hardness, strength and toughness were gathered from five tests and averaged.

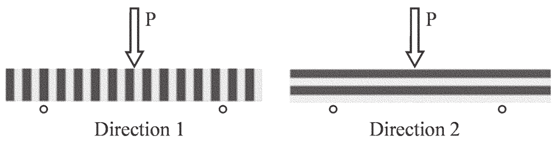

Fig.2 Two different directions about the force

2.3 Friction and wear tests

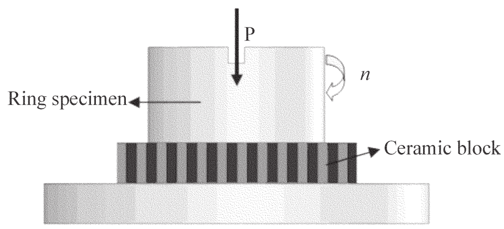

Fig.3 Schematic diagram of friction and wear test apparatus (dimension: ceramic block 24 mm × 34 mm × 5 mm, ring specimen 22 mm × 18 mm × 12 mm)

Friction and wear tests under dry sliding conditions were conducted with MMG-10 high speed and temperature friction and wear machine. The friction pair was Ring-on-Disc. Fig.3 indicates the schematic diagram of this equipment. In the tests, the ring specimen rotated at the speed of 50-200 r/min and the load changed in the range of 50-250 N. The block specimen (24 mm×34 mm×5 mm) was made of Al_2O_3/TiC-Al_2O_3/TiC/CaF_2 self-lubricating laminated ceramics composites with a polished surface. The ring specimen (Φ22 mm×Φ18 mm×12 mm) was made of chilled 45# steel with a hardness of HRC42 and it was also polished. Before tests, both of the block and the ring were cleaned in an ultrasonic alcohol bath for 30 min. The loss of the mass of worn ceramic block was measured by the high precision electronic scale and the precision of the electronic scale was 0.000 1 g. The wear rates were calculated by Formula 1 as follows:

$$W = \frac{\Delta w}{2\pi Rtn\rho\mu P} \quad (1)$$

where Δw— wear volume (g); ρ—the density of the ceramic blocks (g/cm^3); R—average friction radius, that is the distance between the middle diameter and the rotating axle of the ring (m); t—the working time (min); n—the rotation speed of the ring (r/min); μ—average friction coefficient; P—the force on the disc (N).

After tests, due to the requirement of the subsequent experiment, the ceramic composites were cleaned in an ultrasonic alcohol bath again. The microstructures and energy dispersive spectrum (EDS) analysis of worn surfaces were observed via FEI QUANTA FEG 250 scanning electron microscope.

3 Results and discussion

3.1 Microstructure and mechanical properties

The mechanical properties of Al_2O_3/TiC/CaF_2 ceramic composites with different CaF_2 contents are listed in Table 1. It shows that the hardness values, fracture toughness and flexural strength varied with the content of CaF_2. With 10 wt% CaF_2, the Al_2O_3/TiC/CaF_2 ceramic composites exhibited a better mechanical properties and the hardness values, fracture toughness and flexural strength were separately 18.2±0.8 GPa, 3.5±0.4 MPa•m$^{1/2}$, and 348±2 MPa. The mechanical properties of Al_2O_3/TiC- Al_2O_3/TiC/CaF_2 self-lubricating laminated ceramic composites are listed in Table 4. Fig.4 shows the microstructure of the interface between two layers. Obvious residual porosity, cracking and delaminating are not detected from SEM observations of the interfaces. Combining with Fig.4 and hardness values of the interface (18.0±2 GPa), it can be seen that the two types of ceramic composites layers are well-defined with a higher bonding strength.

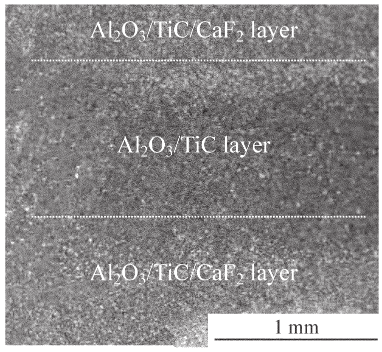

Fig.4 The microstructure of the interface between two layers

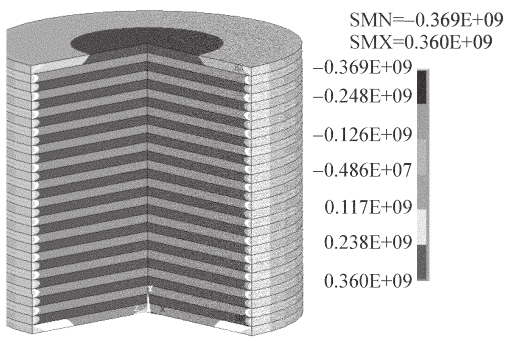

Fig.5 The residual stress of the laminated ceramic composites

Flexural strength values in direction 1 and direction 2 are 320±3 MPa and 350±3 MPa, respectively. It is indicated that the strong-binding interface laminated mode overcomes the anisotropy and the laminated ceramic composites possessed a balanced flexural strength.

Fracture toughness value of Al_2O_3/TiC layers was 6.0±0.3 MPa which was larger than monolithic Al_2O_3/TiC ceramic composites (4.9 MPa)[22], and Al_2O_3/TiC/CaF_2 layers was 3.5±0.4 MPa which was similar to monolithic Al_2O_3/TiC/CaF_2 ceramic composites (3.6±0.3 MPa)[23]. The average fracture toughness value was 4.2±0.3 MPa. Due to the different thermal expansion coefficients of the layers, the laminated ceramic composites were constrained to be flat,

Table 4 Mechanical properties of the laminated ceramic composites

Specimen	Hardness/GPa	Flexural strength/MPa		Fracture toughness/(MPa・m$^{1/2}$)
		Direction 1	Direction 2	
Al_2O_3/TiC layers	20.0 ± 3	–	–	6.0 ± 0.3
Al_2O_3/TiC/CaF_2 layers	18.0 ± 1	–	–	3.5 ± 0.4
Interface	18.0 ± 2	–	–	3.0 ± 0.2
Average values	18.6 ± 2	320 ± 3	350 ± 3	4.1 ± 0.3

contributing to the residual stress during cooling. Fig.5 shows the residual stress of the laminated ceramic composites by FEM. It indicates that Al_2O_3/TiC layers were under compressive stress which can enhance the fracture toughness. Besides, the values of surface residual stress were not constant, which depended on the location.

3.2 Friction coefficient and wear rates

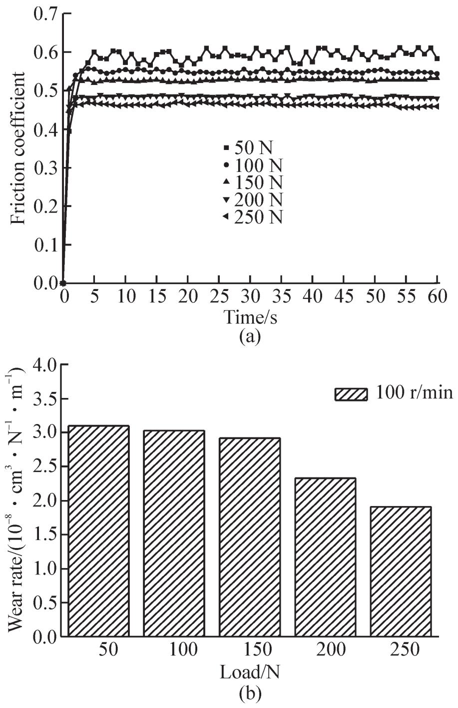

Fig.6 The effect of loads on friction coefficient (a) and wear rates (b) of Al_2O_3/TiC-Al_2O_3/TiC/CaF_2 self-lubricating laminated ceramic composites

Figs.6 (a) and (b) illustrate the effect of loads on friction coefficient and wear rates of Al_2O_3/TiC-Al_2O_3/TiC/CaF_2 self-lubricating laminated ceramic composites, respectively. Obviously, the friction coefficient and wear rates show downward trend with an increase in the load under certain rotation speed. When the rotation speed was 100 r/min and the load was in a lower scales (50-150 N), both of the values of friction coefficient and wear rates were in a smaller location. When the load was 250 N, friction coefficient decreased to 0.46 and the corresponding wear rate was 1.03×10^{-8}•cm^3•n^{-1}•m^{-1}.

Under the same speed conditions with a smaller load, the contact surfaces with tiny and hard particles or micro convex peaks had an adverse effect to friction process. These tiny particles acted as cutting tools for quenching 45 # steel materials, resulting in mass loss of friction pairs. The mechanism shows the reason why the friction pair exerts high friction coefficient and wear rates in a smaller load. With the increase of loads, temperature of friction surface increases and plastic deformation is generated at the contact areas on friction surface, which improve friction conditions contributing to the decrease of friction coefficient and wear rates. Furthermore, improvement of lubrication effect of Al_2O_3/TiC/CaF_2 layers caused by the rising temperature also has a positive function.

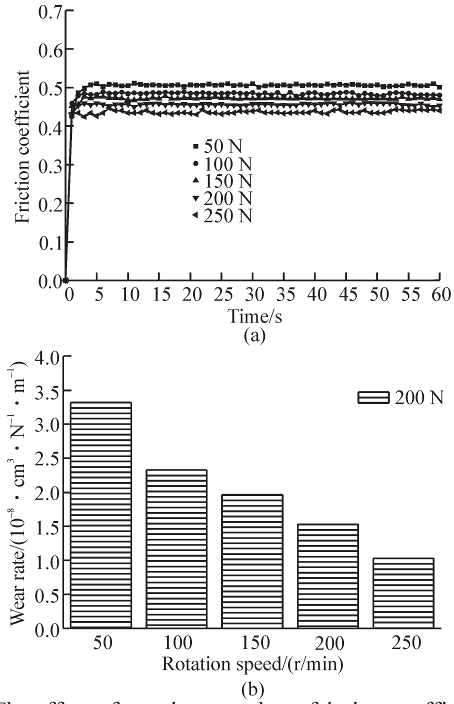

Fig.7 The effect of rotation speeds on friction coefficient (a) and wear rates (b) of Al_2O_3/TiC-Al_2O_3/TiC/CaF_2 self-lubricating laminated ceramic composites

Figs.7 (a) and (b) illustrate the effect of the rotation speeds on friction coefficient and wear rates of Al_2O_3/TiC-Al_2O_3/TiC/CaF_2 self-lubricating laminated ceramic composites when the load was 200 N, respectively. Obviously, the two figures show that the friction coefficient and wear rates decrease with the rise of rotation speeds. When the rotation speed is 50 r/min, the friction coefficient and wear rates are 0.51 and 3.78×10^{-8}•cm^3•N^{-1}•m^{-1}. Besides, when the rotation speed was 50 r/min, the corresponding values reduced to 0.44 and 1.91×10^{-8}•cm^3•N^{-1}•m^{-1}.

Under the same load condition with a lower speed, the temperature of friction surface was not high enough to make CaF_2 particles change from brittle state to the plastic state. CaF_2 particles are difficult to separate out from matrix and adhere to the friction surface, so the complete lubrication films could not form. When speed increases, the contact areas are under high temperature and pressure conditions which are necessary for CaF_2 particles to transform into plastic state. Meantime, CaF_2 particles are squeezed out from matrix materials because of high coefficient of thermal expansion. Due to dragging effect in the process of friction, solid lubricant-CaF_2 particles are towed and covered on the friction surface, improving the friction and wear conditions. Because of the tribofilms formed by CaF_2 particles, the friction coefficient and wear rates at high rotation speed are smaller than those at low rotation speed.

3.3 Wear surface studies

Typical SEM micrographs and EDS patterns of the worn surface of Al_2O_3/TiC/CaF_2 layer are shown in Figs.8 (a), (b), (c) and (d), respectively. Through these SEM micrographs and EDS patterns, the morphology of the composites can be seen clearly. Fig.8 (a) shows that there are numerous small pits on the worn

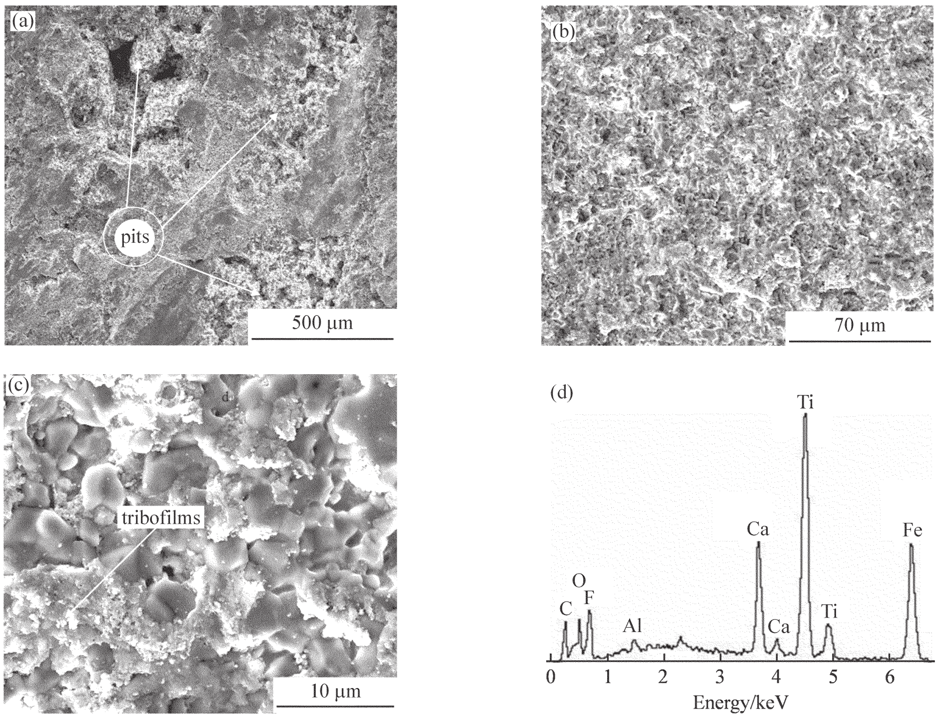

Fig.8 Typical SEM images (a),(b),(c) and EDS patterns (d) of the worn surface of Al_2O_3/TiC/CaF_2 layer

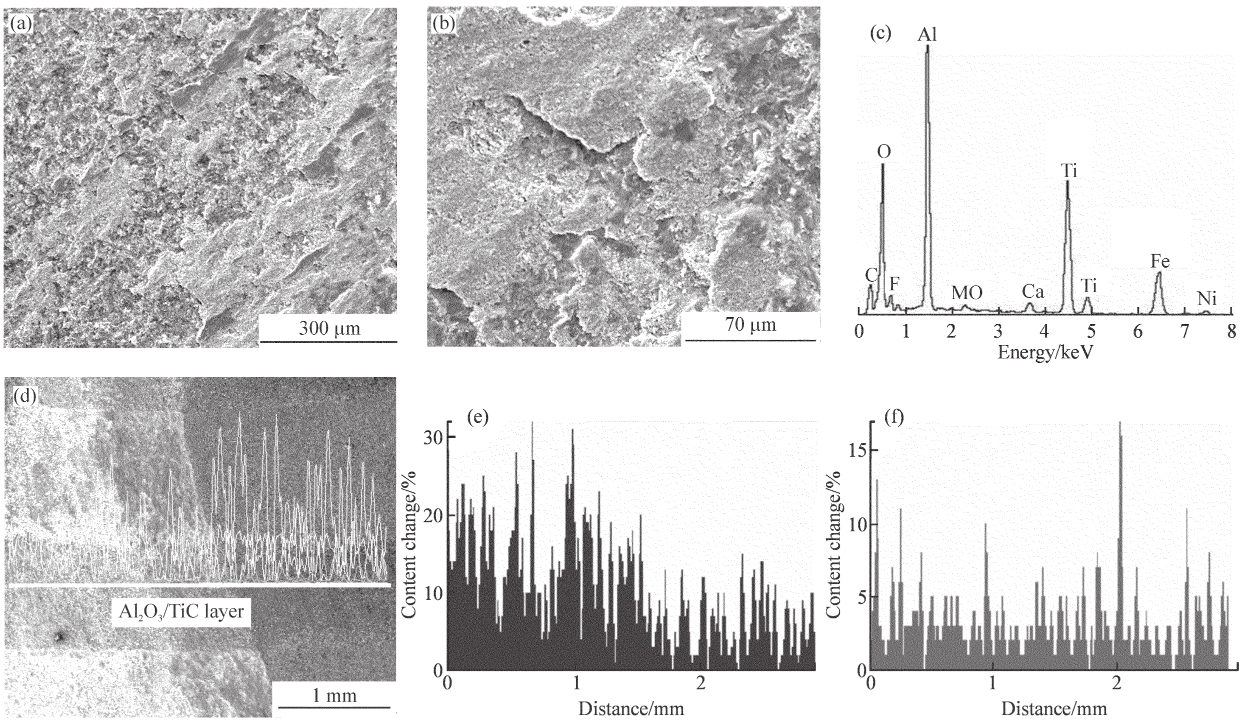

Fig.9 (a) and (b) are typical SEM images of Al_2O_3/TiC layer; (c) is EDS patterns of the worn surface; (d) is line-scanning component analysis diagram; (e) and (f) respectively show F and Ca relative contents changing with the given distance surface and the results observed under the higher magnification factor conditions are shown in Figs.8 (b), (c), indicating particles around pits present obviously cracked traces. Because of high hardness of ceramic composites compared with chilled 45# steel (HRC42), during the friction process, some ceramic particles are squeezed into chilled 45# steel. The effect of cyclic stress and collision between particles makes more and more ceramic particles peeling off. These particles act as abrasive and cause further wear. Therefore the wear mechanism of Al_2O_3/TiC/CaF_2 material layers is mainly abrasive wear. What's more, partial tribofilms could also be seen in Fig.8 (c) and the corresponding EDS patterns shown in Fig.8 (d).

Fig.9 show the SEM images and EDS patterns of the worn surface of Al_2O_3/TiC layer. From Figs.9 (a) and (b), there are many flake grindings covered on the ceramic matrix. The contents of these flake grindings are CaF_2 and iron that can be demonstrated in Fig.9 (c). Under the dry friction conditions, the tribofilms formed by the releasing and smearing of solid lubricants CaF_2 on the Al_2O_3/TiC/CaF_2 layers are transferred to Al_2O_3/TiC layers because of the "dragging effective". The transferred-tribofilms cover on the Al_2O_3/TiC layers, enhancing the wear resistance. The results of Figs.9 (d), (e) and (f) also prove the statement. Figs.9 (d), (e) and (f) are the line scanning analysis patterns and Fluorine element and Calcium element apparently exist in Al_2O_3/TiC layers. Compared with Al_2O_3/TiC/CaF_2 layers, Al_2O_3/TiC layers possess higher hardness and have no matrix materials loss, the particles are difficult pulled out. On the contrary, the iron is ripped and migrated on the ceramic surface. Al_2O_3/TiC layers wear mechanism is mainly adhesive wear.

4 Conclusions

a) Al_2O_3/TiC-Al_2O_3/TiC/CaF_2 self-lubricating laminated ceramic materials were prepared by vacuum hot pressing sintering. The two types of ceramic composites are well-defined with a higher bonding strength and the strong-binding interface laminated mode overcomes the anisotropy; the laminated ceramic composites possess a balanced flexural strength. Due to the different thermal expansion coefficients of the two composites, Al_2O_3/TiC composites are under compressive stress and its fracture toughness is improved;

b) Friction and wear tests against chilled 45# steel were carried out with wear and tear machine. Its friction coefficients and wear rates decrease with the increase of rotation speeds and loads. Detailed observations and analyses of worn surface reveal that the wear mechanism of Al_2O_3/TiC/CaF_2 composites is abrasive wear and the wear mechanism of Al_2O_3/TiC composites is adhesive wear. Because of the "dragging effective", the tribofilms formed by solid lubricants CaF_2 cover on the worn surface and ensure the laminated ceramic materials self-lubrication properties.

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