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Effect of Mo and Ag on the friction and wear behavior of $ZrO_2(Y_2O_3)$–Ag–CaF_2–Mo composites from 20 °C to 1000 °C

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ABSTRACT

In this paper, a series of ZrO_2 matrix high-temperature self-lubricating composites were prepared by hot-press technique. The effect of Mo and Ag on the friction and wear behavior of the $ZrO_2(Y_2O_3)$–Ag–CaF_2–Mo composites in a wide temperature range was investigated. The XRD results showed that $CaMoO_4$ formed on the worn surface above 400 °C. The excellent lubrication performance of $CaMoO_4$ endowed the low coefficient of friction of the $ZrO_2(Y_2O_3)$–Ag–CaF_2–Mo composites at high temperatures. The $ZrO_2(Y_2O_3)$–10Ag–10CaF_2–10Mo composites showed favorable wear resistance at all the tested temperatures which was attributed to the combined action of hardness and phase transformation.

1. Introduction

Zirconia is preferred as mechanical seals, engine components, cutting tools, sensors and thermal barrier coatings because of its excellent wear resistance and fracture toughness [1,2]. Especially, partially stabilized zirconia (PSZ) which possesses stress-induced phase transformation presents a good combination of toughness and strength [2–4]. Although the zirconia ceramic shows a good wear resistance at room temperature (RT), it has high wear rates and coefficients of friction (CoF) at high temperatures (above 100 °C) [5–7]. It is of great significance to find ways to lubricate the ZrO_2 ceramic in a wide temperature range (from 20 °C to 1000 °C) and develop $ZrO_2(Y_2O_3)$ matrix self-lubricating composites.

In recent years, many efforts have been done in order to reduce the friction and wear of $ZrO_2(Y_2O_3)$ composites [8–11]. But up to now, the high friction and wear still restrict the application of $ZrO_2(Y_2O_3)$ ceramic. As is known, CaF_2 is a good high-temperature solid lubricant and has been widely reported [12–16]. PM304 composite and PS304 coating are the most famous examples which take advantage of CaF_2 as a high-temperature solid lubricant. The composites which were first reported by NASA are widely investigated in recent decades [12,17,18]. In these composites, CaF_2 provides good lubrication at high temperatures from 500 °C to 1000 °C. While, in the authors' previous work, Mo together with fluoride provide a better lubrication at high temperatures compared with sole fluoride [14].

It is obvious that the tribological behavior of $ZrO_2(Y_2O_3)$–10 wt% BaF_2/CaF_2–10 wt% Mo composite is rather better than that of $ZrO_2(Y_2O_3)$–10 wt% BaF_2/CaF_2 composite [14]. For example, the CoF at 1000 °C is 0.28 of $ZrO_2(Y_2O_3)$–10 wt% BaF_2/CaF_2–10 wt% Mo composite and 0.48 of $ZrO_2(Y_2O_3)$–10 wt% BaF_2/CaF_2 composite. The reason was that BaF_2 and CaF_2 will react with Mo at high temperatures to form $BaMoO_4$ and $CaMoO_4$ on the worn surface. $BaMoO_4$ and $CaMoO_4$ are good high-temperature solid lubricants [19–22], and play an important role in reducing the friction and wear of the $ZrO_2(Y_2O_3)$–10 wt% BaF_2/CaF_2–10 wt% Mo composite [14].

In this work, $ZrO_2(Y_2O_3)$–Ag–CaF_2–Mo composites were prepared using hot pressed technique by tailoring the content of Mo to obtain favorable tribological properties in a wide range of temperatures. Mo reacted with CaF_2 at high temperatures to form $CaMoO_4$ on the worn surface to provide lubrication. Ag in the composite was used to provide lubrication at low temperatures. The tribological behavior of the $ZrO_2(Y_2O_3)$–Ag–CaF_2–Mo (AFM) composites from RT to 1000 °C was investigated, and the wear and lubricating mechanisms were also explored.

2. Experimental procedures

2.1. Material preparations

$ZrO_2(Y_2O_3)$ matrix composites with 10 wt% CaF_2, 10 wt% Ag and different contents (0, 10 wt%, 20 wt% and 30 wt%) of Mo (denoted as AF, AFM10, AFM20, AFM30) were fabricated by hot pressed

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sintering. The content of Y_2O_3 in the $ZrO_2(Y_2O_3)$ powder is 5.2 wt%, and the size of $ZrO_2(Y_2O_3)$ powder is 0.2–1.0 μm. The grain sizes of Ag, CaF_2 and Mo powders are about 10–30 μm (Analytically pure, Sinopharm Chemical Reagent Co., Ltd).

The prepared process of the $ZrO_2(Y_2O_3)$ matrix composites can be briefly described as follows: First, the raw powders were ball milled for 8 h with a rotational speed of 300 rpm, and then, they were put into a hot press furnace using a graphite mold; when the furnace was evacuated to a dynamic vacuum about 10^{-2} Pa, the furnace was heated to 1200 °C at a rate of 10 °C/min. The powders were consolidated at 1200 °C under 35 MPa, holding 30 min.

2.2. Mechanical and tribological tests

The hardness of the $ZrO_2(Y_2O_3)$ composites was evaluated by using a conventional Vicker's indentation tester (MH-5-VM microhardness tester, Shang Hai Heng Yi Technology Company, China). The test load is 9.8 N and the dwell time is 10 s. The actual density was tested using Archimedes' principle, and the relative density was obtained when the actual density was divided by the theory density. The measurements for each sample were carried out at least ten times, and the data of each sample in the table were average values.

The tribological tests were conducted on a HT-1000 ball-on-disk high-temperature tribometer (Zhong Ke Kai Hua Corporation, China). The size of the specimen disc is ø 30×2 mm. All the specimens were polished by emery paper to a roughness (Ra) of about 0.3 μm. Commercial Al_2O_3 ceramic ball with a hardness of 1650 HV was used as the counter face ball. The selected tested temperatures were 20 °C, 200 °C, 400 °C, 600 °C, 800 °C and 1000 °C. All the tests were carried out at an applied load of 10 N and a sliding speed of 0.20 m/s with a testing time of 30 min. The radius of the wear track is 5 mm.

The wear volume was determined as $V=AL$, in which A was the cross-section area of wear track, and L was the circumference of the wear track. For each wear track four locations were measured to determine the value of A by a surface profilometer. The wear rate W is defined as the wear volume V divided by the total sliding distance S and the applied load P, written as $W=V/SP$. All the tribological tests were carried out at least three times under the same conditions.

The microstructures, morphologies of the worn surfaces and phase structures were examined by JSM-5600LV scanning electron microscope (SEM) and X-ray diffractometer (XRD, Rigaku D/Max-2400). A PHI-5702 multifunctional X-ray photoelectron spectroscope (XPS) was employed to examine the chemical states of elements on the worn surface. The XPS analysis used Al Ka radiation as the exciting source and the binding energy of carbon contaminant (C1s-284.8 eV) as the reference. Before observations, samples were cleaned with acetone and then dried in hot air.

3. Results

Characteristics of the ZrO_2 (Y_2O_3) composites are listed in Table 1. It can be found that AF has the highest average hardness of 767 HV and the lowest relative density of 94.8%. The hardness of the $ZrO_2(Y_2O_3)$ matrix composites decreases as the content of Mo increases, but in the meanwhile, the relative density increases along with the increase of the Mo content.

The SEM backscattered electron image (BEI) in Fig. 1 shows the typical morphology and distribution of different constituents of AFM10. Through energy dispersive spectroscopy (EDS) analysis which is not shown here, almost all the black area is CaF_2; the rest gray area is ZrO_2 (Y_2O_3) matrix; meanwhile the bright area is the Ag and Mo rich phase. It can also be found that the grain size of the composite is 5–30 μm.

Fig. 2 shows the XRD pattern of AFM10 sintered sample. It can be found that the composite consists of ZrO_2, CaF_2, Ag and Mo. This indicates that there is no reaction between them and no oxidation during the sintered process.

The wear and friction behavior of the composites was investigated from RT to 1000 °C. The CoFs as a function of test temperature were plotted in Fig. 3. It presents that when the temperature was below 600 °C, the CoFs of AFM were a little higher than those of AF. While above 600 °C, the CoFs of AFM were much lower than those of AF. In general, AFM10 has the optimal CoF over the tested temperature range. The CoF is 0.28 at 800 °C and rises to 0.32 at 1000 °C.

Fig. 4 presents the wear rates of the ZrO_2 (Y_2O_3) matrix composites at different tested temperatures. It can be found that when Mo was doped into the AFM composites, their wear rates were greatly improved from RT to 1000 °C. In all three AFM composites, AFM10 has the lowest wear rate at almost all the tested temperatures (only at 600 °C and 800 °C, its wear rates were similar to those of AFM20). Take AFM10 as an example, the wear rate is 1.70×10^{-5} mm^3/Nm at RT and 1.82×10^{-5} mm^3/Nm at 800 °C. At the same time, we can find that the wear rate of AFM10 is eighteen times lower than that of AF at 800 °C. This clearly suggests that Mo plays a crucial role in improving the wear behavior of the composites.

In order to analyze the wear mechanism of three AFM at different temperatures, the microstructures and morphologies of the worn surfaces of AFM10 were examined by SEM. Fig. 5 depicts the worn surfaces of AFM10 at different tested temperatures. As can be seen in Fig. 5, from RT to 400 °C there are many delamination pits and brittle fracture trace, suggesting that the wear mechanism is fatigue wear. As the temperature increases to 600 °C, in spite of the severe wear, much debris begins to form glaze film on the worn surface. The glaze layer can improve the friction behavior of AFM which can be proved in Fig. 3, and the lubricating mechanism will be discussed in detail later. At 800 °C and 1000 °C, the lubricious glaze layers were more complete and even covered the entire worn surface. We can also find that at 1000 °C, there was slight plastic deformation on the glaze layers. The plastic deformation can lead to the great increase in wear rate.

The worn surfaces of the Al_2O_3 ceramic balls sliding against AFM10 were given in Fig. 6. As we know, the wear rate of the counterpart ball is proportional to the size of the wear scar. In Fig. 6, we can find that the size of wear scar decreases as the temperature increases from RT to 1000 °C. That is to say, the wear

Table 1
Characteristics of the $ZrO_2(Y_2O_3)$ matrix composites.

Specimen	Compositions	Hardness (HV)	Density (g/cm^3)	Relative density (%)
AF	$80ZrO_2(Y_2O_3)$–10Ag–$10CaF_2$	767 ± 100	5.45 ± 0.13	94.8 ± 2.3
AFM10	$70ZrO_2(Y_2O_3)$–10Ag–$10CaF_2$–10Mo	615 ± 70	5.70 ± 0.08	95.2 ± 1.3
AFM20	$60ZrO_2(Y_2O_3)$–10Ag–$10CaF_2$–20Mo	531 ± 70	6.08 ± 0.08	97.4 ± 1.3
AFM30	$50ZrO_2(Y_2O_3)$–10Ag–$10CaF_2$–30Mo	461 ± 40	6.39 ± 0.06	98.2 ± 0.9