Available online at www.sciencedirect.com
ScienceDirect
Trans. Nonferrous Met. Soc. China 22(2012) 585−589
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Dry sliding tribological behavior of Zr-based bulk metallic glass

WU Hong[1, 2], Ian BAKER[2], LIU Yong[1], WU Xiao-lan[2]

1. State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, China;
2. Thayer School of Engineering, Dartmouth College, Hanover, NH 03755-8000, U.S.A.

Received 9 September 2011; accepted 16 January 2012

Abstract: The tribological behavior of a Zr-based bulk metallic glass (BMG) was investigated using pin-on-disk sliding measurements in two different environments, i.e., air and argon, against an yttria-stabilized zirconia counterface. It was found that the wear of the Zr-based BMG was reduced by more than 45% due to the removal of oxygen from the test environment at two different loads, i.e., 16 N and 23 N. The wear pins were examined using X-ray diffractometry, differential scanning calorimetry, scanning electron microscopy and optical surface profilometry. A number of abrasive particles and grooves presented on the worn surface of the pin tested in air, while a relatively smooth worn surface was observed in the specimens tested in argon. The wear mechanism of the pin worn in air was dominated by abrasive wear compared with an adhesive wear controlled process in the tests performed in argon.

Key words: bulk metallic glasses; tribological behavior; oxidation; wear mechanism

1 Introduction

Over the past two decades the tribological properties of bulk metallic glasses (BMGs) have been of great attraction as promising candidates for high wear applications because of their comparatively high hardness and strength [1−3]. For instance, MA et al [4] used a Zr-based BMG as bearing rollers, which showed a better wear resistance than the commercial GCr15 steel. ISHIDA et al [5] reported a new type of Ni-based BMG microgear, which had a much longer lifetime of 2500 h compared with 8 h for SK-steel.

Nonetheless, recent studies on the friction and wear behaviors of BMGs indicated contradictory performance [6,7]. Since BMGs are in a non-equilibrium state, their tribological behaviors are strongly dependent on the test conditions and local chemical compositions, such as applied load, sliding distance, sliding speed, friction mode [5], lubrication condition [7] as well as annealed state [6,8]. In addition, it is well-known that oxygen not only has adverse effects on the glass-forming ability and thermal stability [9], but also affects the deformability of BMGs [10]. Even though some studies reported that the friction and wear of metallic glasses have shown sensitivity to oxygen in test environment, the underlying mechanism is not completely understood [11−14]. For example, some BMGs show a negative effect of oxidation on wear resistance [11,12], while others show a positive effect [13]. In the view of fundamental research and industrial application, therefore, it is of great importance to systematically characterize the tribological behavior of metallic glass and to reveal the related mechanism for sliding in different environments.

This paper outlines our preliminary investigation on the friction and wear behavior of a Zr-based BMG during dry sliding in two different environments, air and argon.

2 Experimental

A master alloy with a nominal composition of $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ (mole fraction, %) was prepared by arc melting a mixture of pure Zr (99.8%, mass fraction), Cu (99.9%), Ni (99.9%), Al (99.99%), and Ti (99.9%) in a Ti-gettered high-purity argon atmosphere. The ingot was remelted four times to ensure a homogeneous composition, and then suction cast into 3 mm in diameter and 70 mm in length, in a water-cooled

Foundation item: Project (DE-FG02-07ER46392) supported by U.S. Department of Energy, Office of Basic Energy Science; Project (2011JQ002) supported by the Fundamental Research Funds for the Central Universities, China; Project supported by the Open-End Fund for the Valuable and Precision Instruments of Central South University, China
Corresponding author: LIU Yong; Tel: +86-731-88830406; E-mail: yonliu11@yahoo.com.cn
DOI: 10.1016/S1003-6326(11)61217-X

copper mold. Wear pins of 6 mm in length were cut from the suction-cast rods using a high speed abrasive saw, cooled with water to avoid possible crystallization. The two ends were polished with 600 grit silicon carbide papers and finished with 0.3 μm-alumina powders.

Pin-on-disk tribotests were performed against an yttria-stabilized zirconia counterface material polished to a surface roughness of 0.01−0.05 μm. The test system was described in detail in Ref. [15]. Cylindrical pin specimens were fixed on a holder and loaded against the rotating disk. The tests were conducted under constant applied normal loads of 16 N and 23 N, at a sliding speed 1 m/s and for a sliding distance of 1 km, in air and argon. Three tests were performed in each environment.

The phases of the specimens both before and after wear testing were analyzed on a Rigaku D/Max 2000 X-ray diffractometer (XRD) with Cu K_α radiation operated at 40 kV and 300 mA. Measurements were performed by step scanning 2θ from 10° to 120° with 0.02(°)/step. A count time of 1 s/step was used, giving a total scan time of ~1.5 h. The thermodynamic behavior of the wear pins was investigated on a Perkin Elmer DSC 7 differential scanning calorimeter (DSC), from room temperature to 600 °C at a heating rate of 20 °C/min under flowing argon. The worn surfaces were examined with an FEI XL−30 scanning electron microscope operating at 15 kV, equipped with an EDAX Li-drifted energy dispersive X-ray spectrometer. Worn surface topographies of the pins were determined using a Zygo 7300 profilometer. The mass loss of the specimens was measured in an electronic balance of ±0.1 mg precision before and after the wear test. The density of the metallic glass was determined according to Archimedes' method and the mass loss was then converted to a volume loss value.

3 Results and discussion

The mass loss results for the sliding tests run in both air and argon at two different loads are shown in Fig. 1. For a given load, it can be clearly seen that the wear loss of the pins is dramatically reduced by the removal of oxygen in the test environment. Wear rate in both environments increased with increasing normal load. As listed in Table 1, the wear loss of the pins after 1 km of sliding decreased by more than 45% when varying the environment from air to argon under both loads. This indicates the adverse effect of oxygen in the test environment on the wear resistance of BMG during sliding. A similar study conducted by FU et al [11], reported that less wear was obtained in a Zr-based BMG by changing the test environment from air to vacuum.

The measured friction force was somewhat variable during the tests, and decreased from a higher initial value to a lower steady state value under all test conditions, as shown in Fig. 2. The steady state friction coefficient ranged from 0.15 to 0.28 depending on the normal load and the test environment. For a given load, the measured friction coefficient (steady state) was somewhat higher for tests conducted in air than that for tests performed in argon. These are considerably lower than the result of BLAU [7], and comparatively close to the values reported by LIU et al [16], in dry sliding tests of the same composition of BMG. Since the friction coefficient decreases with increasing load [11], the low friction coefficient obtained from the sliding tests may be ascribed to the high normal loads employed in the

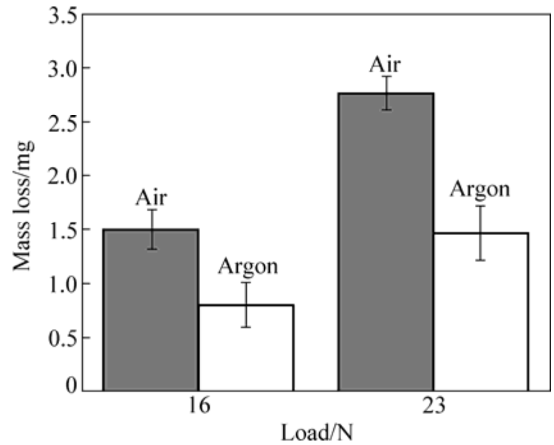

Fig. 1 Wear loss (mean value of mass loss) of BMG specimens after 1 km-sliding tests in air and argon at different loads (Error bars signify standard deviations)

Table 1 Wear loss of pins tested in air and argon at different loads (m denotes mean mass loss, V denotes volumetric loss, and μ denotes friction coefficient)

Load/N	Air			Argon		
	m/mg	V/mm^3	μ	m/mg	V/mm^3	μ
16	1.5	0.23	0.28	0.8	0.12	0.2
23	2.77	0.42	0.22	1.47	0.22	0.15

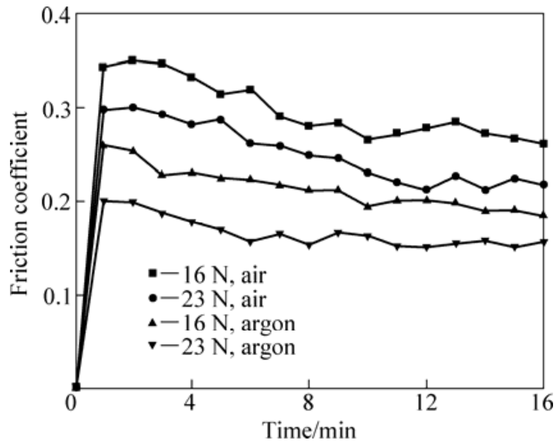

Fig. 2 Friction coefficients as function of time during wear tests run for 1 km in air and argon under different loads

present study. In addition, as there is no specific relationship between the friction coefficient and the wear loss [16], the friction coefficient cannot directly be used to be indicative of wear resistance for the BMG.

XRD patterns of the pins before and after wear tests conducted in two different environments at a load of 23 N are shown in Fig. 3. A typical pattern of an amorphous structure with only a broad diffraction halo, and without any detectable sharp Bragg peaks corresponding to crystalline phases is present for as-cast BMG. For the pin wear-tested in air, several sharp Bragg diffraction peaks corresponding to three different crystal structures of ZrO_2, i.e., cubic-ZrO_2, tetragonal-ZrO_2, and monoclinic-ZrO_2, superimpose on a broad diffraction halo which corresponds to the remaining glassy matrix. These signify the coexistence of various crystalline phases and residual amorphous phase on the worn surface after sliding. However, there are still a few peaks that are difficult to be determined due to limited number of diffraction peaks. Based on the investigation of phases on the same composition BMG after annealing at temperature from 400 °C up to 550 °C reported by HE et al [17], there could be either $Zr_2Ni_{0.67}O_{0.33}$, Zr_2Cu, or ZrAl phases, but this needs to be confirmed by further study.

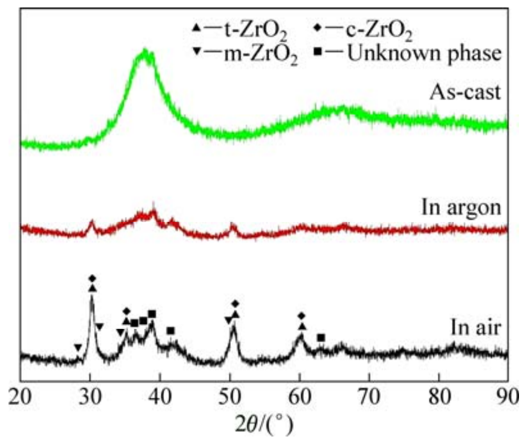

Fig. 3 XRD patterns of pins before and after wear tests in different environments at load of 23 N

DSC curves of the pins after wear tests in both environments at a load of 23 N are shown in Fig. 4. The DSC curve of as-cast BMG is included for comparison. No significant difference between the tested specimens and the untested specimen can be detected, indicating that there is no appreciable structural change in the pins after wear tests. FU and RIGNEY [12] compared the DSC curves of the wear debris generated in air and vacuum using different loads with the untested BMG specimen, and found a series of difference, including the absence of low temperature peaks, variation in shape for high temperature peak, and peak shifting with both load and environment. They conjectured that the potential reasons may be the further homogenization of the alloy and the redistribution of oxygen caused by sliding [12]. The decrease in the crystallization temperature of debris may be due to considerably increased surface [14]. However, similar examinations are not possible to be performed in the present study due to the insignificant amount of debris in all tests.

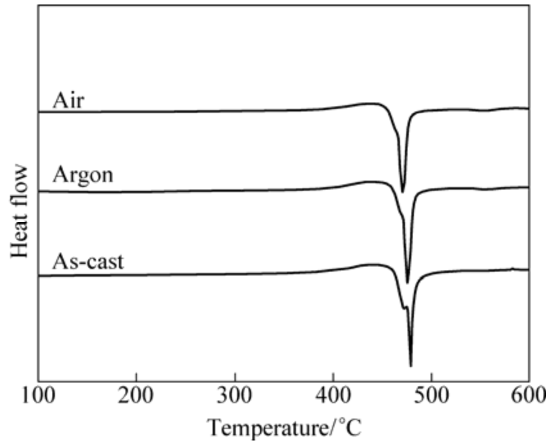

Fig. 4 DSC curves of pins before and after wear tests in different environments at load of 23 N

Worn surfaces of the pins wear tested in air and argon under different loads are shown in Fig. 5. Parallel grooves and abrasive particles are clearly observable in the pins tested in air under both loads (Figures 5(a) and (c)), showing a typical abrasive manner. Local plastic deformation can be found at the edge of the grooves in Fig. 5(c), which may be attributed to the higher normal load. Increasing the load leads to more adhesive wear in the BMG [16]. In contrast, for the tests in argon, evident plastic flow appears on the worn surface, and no grooves can be observed (Fig. 5(b)). Thus, the adhesive wear becomes the main mechanism. At the load of 23 N, a relatively smooth worn surface is present after smearing of the wear tracks (Fig. 5(d)), implying a mainly adhesive manner.

The surface topographies produced in air and argon as determined by a non-contact optical surface profilometer are shown in Fig. 6. The average surface roughness, R_a, of the pin tested in air was 3.474 μm, with some grooves as deep as 20 μm, while the worn surface generated in argon was smoother with an R_a of 1.88 μm. This demonstrates once more that the worn surface of the pin tested in argon was smoother than that of the pin tested in air.

The frictional heating occuring during the sliding process can induce both oxidation and crystallization in a BMG if temperature rise is sufficiently high. For the tests in air, a couple of oxides, e.g., monoclinic ZrO_2 and tetragonal ZrO_2, formed as a result of oxidation, were caused by frictional heating on the wear surface of the pin (see in Fig. 3). TRIWIKANTORO et al [18] studied

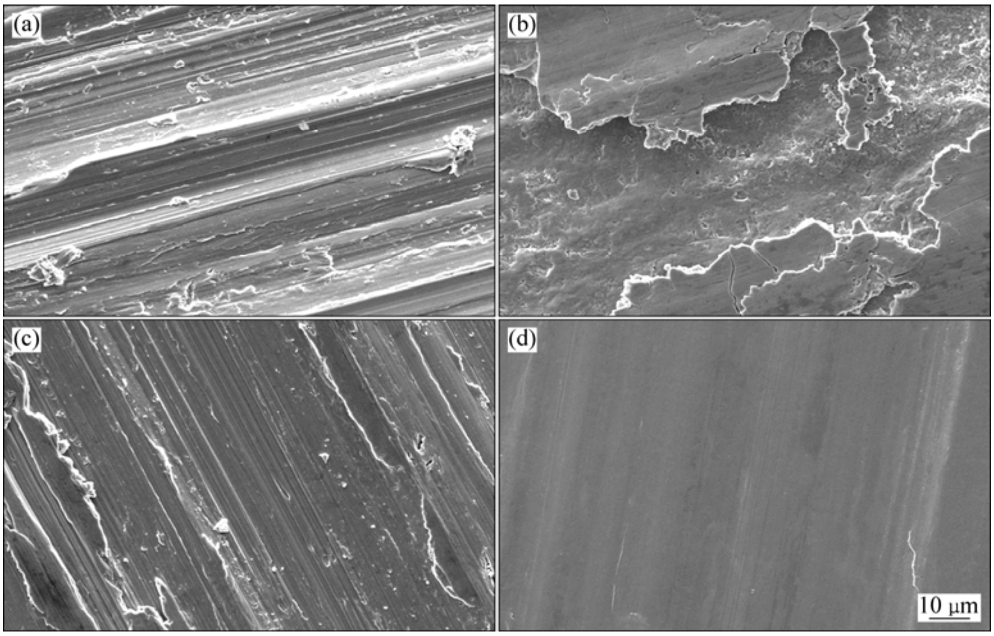

Fig. 5 Secondary electron images of worn surface of pins tested in air (a) and argon (b) at load of 16 N, and pins tested in air (c) and argon (d) at load of 23 N

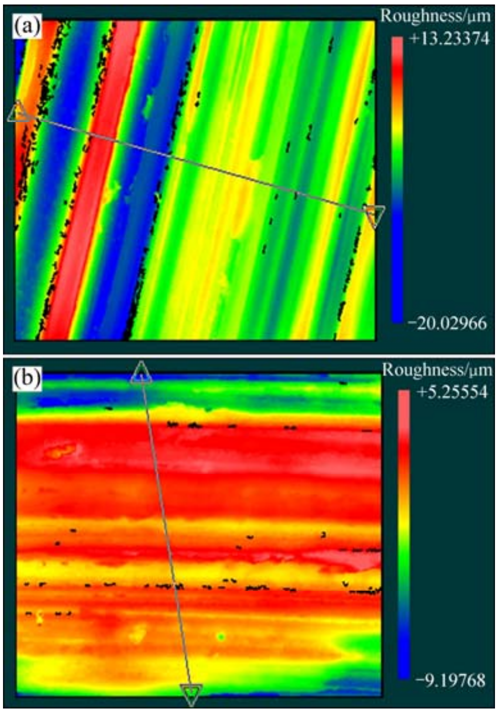

Fig. 6 Worn surface topographies of pins wear tested in air (a) and argon (b) at load of 23 N determined by optical surface profilometer (Color bands signify the relative height of the profile. Grey lines denote the moving direction of the profilometer)

the oxidation behavior in a series of Zr-based metallic glasses and found that the oxide scales formed during oxidation have a nanocrystalline microstructure consisting mainly of tetragonal and monoclinic ZrO_2. It is worth noting that the zirconia disk has been shown to have a cubic crystal structure [19]. Thus, the cubic ZrO_2 present on the worn surface of the pins supposed to be derived from the counterface. JIN et al [20] investigated the dry sliding wear characteristics of a Zr-based BMG at room temperature, and observed that the formation and subsequent peeling-off of oxygen-rich tribolayers during wear was the main wear mechanism in the as-cast and relaxed specimens. In the present study, the monoclinic ZrO_2 and tetragonal ZrO_2 formed on the pins were peeled off and subsequently acted as abrasive particles together with the cubic ZrO_2 that debonded from the counterface during the wear process, thus resulting in the presence of long parallel grooves in the pins tested in air (Figs. 5(a) and (c)).

For the tests in argon, the effect of oxidation can be ruled out owing to the removal of oxygen. Surface softening presumably occurred due to the combination of frictional heating and plastic deformation [16], and led to the appearance of plastic flow and smeared surface (Figs. 5(b) and (d)). LEE and EVETTS [14] noted that the development of the surface morphology of metallic glasses during sliding started at an initial stage, including low contact area, gradually increasing contact area occurring at asperities, and surface smoothing by a “smear-like” plastic deformation process, which allowed material to fill in the pits and holes between asperities, hence showing little wear debris. These features are quite similar to the observations of the pins tested in argon, implying that such initial stage during the wear process could be maintained by the exclusion of oxygen in the test environment.

4 Conclusions

1) The wear of a Zr-based BMG against an yttria-stabilized zirconia counterface was studied using pin-on-disk wear tests in two different environments, i.e., air and argon, at two different loads of 16 N and 23 N. The results obtained are summarized as follows.

2) The wear rate of the BMG pins was reduced significantly by the removal of oxygen from the test environment at both loads.

3) A number of abrasive particles and grooves were presented on the worn surface of the pin tested in air, thus implying an abrasive wear controlled manner.

4) A relatively smooth worn surface was observed in the specimens after tests conducted in argon, a feature attributed to the occurrence of adhesive wear.

References

[1] JOHNSON W L. Bulk glass-forming metallic alloys: Science and technology [J]. MRS Bull, 1999, 24: 42−56.

[2] PARLAR Z, BAKKAL M, SHIH A H. Sliding tribological characteristics of Zr-based bulk metallic glass [J]. Intermetallics, 2008, 16: 34−41.

[3] GLORIANT T. Microhardness and abrasive wear resistance of metallic glasses and nanostructured composite materials [J]. J Non-cryst Solids, 2003, 316: 96−103.

[4] MA M Z, LIU R P, XIAO Y, LOU D C, LIU L, WANG Q, WANG W K. Wear resistance of Zr-based bulk metallic glass applied in bearing rollers [J]. Mater Sci Eng A, 2004, 386: 326−330.

[5] ISHIDA M, TAKEDA H, NISHIYAMA N, KITA K, SHIMIZU Y, SAOTOME Y, INOUE A. Wear resistivity of super-precision microgear made of Ni-based metallic glass [J]. Mater Sci Eng A, 2007, 449−451: 149−154.

[6] TAM C Y, SHEK C H. Abrasive wear of $Cu_{60}Zr_{30}Ti_{10}$ bulk metallic glass [J]. Mater Sci Eng A, 2004, 384: 138−142.

[7] BLAU P J. Friction and wear of a Zr-based amorphous metal alloy under dry and lubricated conditions [J]. Wear, 2001, 250: 431−434.

[8] LI G, WANG Y Q, WANG L M, GAO Y P, ZHANG R J, ZHAN Z J, SUN L L, ZHANG J. Wear behavior of bulk $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ metallic glasses [J]. J Mater Res 2002, 17: 1877−1880.

[9] GEBERT A, ECKERT J, SCHULTZ L. Effect of oxygen on phase formation and thermal stability of slowly cooled $Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$ metallic glass [J]. Acta Mater, 1998, 46: 5475−5482.

[10] LU Z P, BEI H, WU Y, CHEN G L, GEORGE E P, LIU C T. Oxygen effects on plastic deformation of a Zr-based bulk metallic glass [J]. Appl Phys Lett, 2008, 92: 011915-1−011915-3.

[11] FU X, KASAI T, FALK M L, RIGNEY D A. Sliding behavior of metallic glass: Part I. Experimental investigations [J]. Wear, 2001, 250: 409−419.

[12] FU X, RIGNEY D A. Tribological characteristics of $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ bulk metallic glass [J]. Mater Res Soc Symp Proc, 1998, 554: 437−442.

[13] MIYOSHI K, BUCKLEY D H. Microstructure and surface chemistry of amorphous alloys important to their friction and wear behavior [J]. Wear, 1986, 110: 295−313.

[14] LEE D H, EVETTS J E. Sliding friction and structural relaxation of metallic glasses [J]. Acta Metall, 1984, 32: 1035−1043.

[15] JOHNSON B J, KENNEDY F E, BAKER I. Dry sliding wear of NiAl [J]. Wear, 1996, 192: 241−247.

[16] LIU Y, YITIAN Z, XUEKUN L, LIU Z. Wear behavior of a Zr-based bulk metallic glass and its composites [J]. J Alloys Compd, 2010, 503: 138−144.

[17] HE G, BIAN Z, CHEN G L. Investigation of phases on a Zr-based bulk glass alloy [J]. Mater Sci Eng A, 2000, 279, 237−243.

[18] TRIWIKANTOR O, TOMA D, MEURIS M, KOSTER U. Oxidation of Zr-based metallic glasses in air [J]. J Non-cryst Solids, 1999, 250−252: 719−723.

[19] BAKER I, SUN Y, KENNEDY F E, MUNROE P R. Dry sliding wear of eutectic Al−Si [J]. J Mater Sci, 2010, 45: 969−978.

[20] JIN H W, AYER R, KOO J Y, RAGHAVAN R, RAMAMURTY U. Reciprocating wear mechanisms in a Zr-based bulk metallic glass [J]. J Mater Res, 2007, 22: 264−273.

Zr 基块体非晶合金的摩擦磨损行为

吴 宏[1,2]，Ian BAKER[2]，刘 咏[1]，吴晓蓝[2]

1. 中南大学 粉末冶金国家重点实验室，长沙 410083；
2. Thayer School of Engineering, Dartmouth College, Hanover, NH 03755-8000, U.S.A.

摘　要：采用销盘式摩擦实验研究 Zr 基块体非晶合金分别在空气与氩气环境中的摩擦磨损行为。结果表明，在 16 N 和 23 N 2 种不同载荷下，非晶试样在氩气中的磨损量都比在空气中的低 45%以上。通过 X 射线衍射仪、差示扫描量热分析仪、扫描电子显微镜和光学表面轮廓仪等检测分析手段对磨损试样摩擦面的形貌和微观结构进行表征，发现在空气中磨损试样的表面存在大量摩擦颗粒和犁沟，而氩气中的试样表面相对平滑；非晶试样的磨损机理在空气中以磨粒磨损为主，而在氩气中则为粘着磨损。

关键词：块体非晶合金；摩擦磨损；氧化；磨损机理

(Edited by YANG Hua)