

OXIDATION OF PM ALLOY Al-10Ti DURING SLIDING WEAR^①

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ABSTRACT Sliding wear behaviors of PM alloy Al-10Ti have been investigated. The compositions and structures of worn surface layer and wear debris have been studied using XPS and X-ray diffraction. The results show that iron transfers from the steel counterface to the surface of Al-Ti alloy sample. And Fe₂O₃ is formed during sliding wear process. The dark worn surface layer formed in sliding wear is determined to be an oxide layer consisting of Al₂O₃ and Fe₂O₃, which is rich in oxygen and aluminum, but depleted of titanium. The oxide layer can reduce wear of aluminum alloy.

Key words oxidation sliding wear Al-Ti alloy

1 INTRODUCTION

Dark surface layers are often found during sliding of aluminum alloys against the hardened steel counter-faces^[1-6]. The composition and structure of the dark worn layer have significant influence on wear behavior of aluminum alloy. It has been suggested that the dark layers are mainly composed of aluminum oxides^[1, 5, 6]. And SiO₂ as well as intermetallic compound AlFe^[6] are also found on the worn surface of Al-Si alloys. The presence of AlFe is attributed to transfer of iron from steel counter-face. Consequently, Al₂O₃ is present in wear debris detached from worn surface^[4, 7, 8]. However, Antoniou *et al*^[2, 3] have proposed that the dark layers which result from material transferring across the interface of friction couples contain only α -Fe and the original phases (such as aluminum and silicon) instead of oxide.

An understanding of the dark worn layer is important in clarifying sliding wear mechanism of aluminum alloy and developing wear-resistant aluminum alloy. Razavizadeh *et al*^[1, 5] have suggested that wear of aluminum alloy during sliding process occurs via a process of oxidation, de-

formation and fracture, producing the oxide layers on the worn surface. While other paper^[3] has emphasized material transfer between the friction couples, and in this case, oxidation has not been considered as a prevalent mechanism. Pramila Bai *et al*^[9] have proposed that delamination is the only wear mode, no oxidation is observed both under low load and under high load.

So far the microstructure of dark worn layer is still not adequately understood. This paper deals with this problem. The Al-Ti alloy is chosen as test material also due to its potential tribological applications.

2 EXPERIMENTAL

The Al-10% Ti alloy powders were atomized with argon gas. Powders whose size range is 60 ~ 90 μ m were sealed in the aluminum cans in vacuum and compacted into 80 mm diameter round rods at room temperature. The rods were then extruded into bars with rectangular section of 20 mm \times 10 mm at 400 $^{\circ}$ C. The as-extruded material contained 89.78% Al, 10.10% Ti and 0.12% Fe.

Dry sliding wear test was performed on the

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as-extruded Al-10Ti alloy using a block-on-ring wear tester of type M1S-23. The counter ring was normalized AISI 1045 steel with hardness of HRC 57. The block sample and counter ring were first ground and then polished with 1 μm alumina. They were cleaned in acetone prior to wear test. The test was carried out in air with relative humidity of 40% ~ 50% at 25 $^{\circ}\text{C}$. The block slid against steel at a relative speed of 1.7 m/s with the load of 40N. Weight loss was measured with an accuracy of 0.1 mg. In order to compare the dark worn-layer with natural oxide film, another Al-10Ti alloy samples was left in air for 30 d to form a natural oxide film. The pre-treatment and environment of this sample were as same as that of the worn sample.

The measurement of X-ray photoelectron spectrum(XPS) was performed on the dark worn layer of the sample with ESCLAB II electron spectrometer excited by Al K_{α} radiation ($h\nu = 1481.7 \text{ eV}$). The vacuum of sample chamber was maintained at $4 \times 10^{-8} \text{ Pa}$. The binding energies were calibrated against the binding energy of the C 1s electron(284.5 eV). An XPS depth profile analysis was carried out using sputtering of argon ion with bombing energy of 3 kV. The spectra were automatically analyzed with software. The element content was determined according to the following formula:

$$c_i = (I_i/S_i) / \sum_j I_j/S_j \quad (1)$$

where I_i is integrated intensity of peak, S_i is relative sensitivity factor of element. The relative sensitivity factors of elements are listed as following:

Peak	Al 2p	Fe 2p	O 1s	Ti 2p	C 1s
S_i	0.57	10.54	2.85	5.22	1.00

3 RESULTS AND DISCUSSION

Fig. 1 shows the microstructure of the as-extruded Al-10Ti alloy. It can be seen that the fine Al_3Ti particles are dispersed within the $\alpha\text{-Al}$ matrix. Visual examination had found that the dark surface layers were formed on the worn surface of Al-10Ti alloy during sliding process. SEM observation of the dark worn-layers shows

that many shear plates were present(Fig. 2(a)). At high magnification, it was found that wear scars were interspersed in the smooth dark surface(Fig. 2(b)).

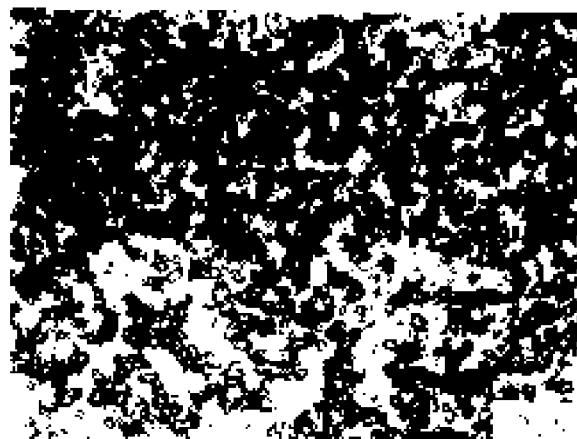


Fig. 1 Microstructure of Al-10Ti alloy

In order to investigate the composition of dark worn-layer. The XPS spectra were measured on both the worn layer and the natural oxide film. The results are shown in Fig. 3 and Table 1. The C 1s peaks in the XPS spectra are attributed to environmental contamination. The outer layers of both the worn layer and the natural oxide film were rich in oxygen and aluminum, but depleted of titanium. This indicates that aluminum oxide preferentially formed, because aluminum oxide is more stable thermodynamically than titanium oxide. No iron was observed within the natural oxide film. In contrast, it was found that iron content of the worn layer was much higher than that of base material. This can be ascribed to the fact that iron transferred from steel counter-face to the surface of aluminum alloy sample. The spectra of Al 2p level(Fig. 4) and Fe 2p level(Fig. 5) for the worn layer show that the binding energies of Al 2p, Fe 2p_{3/2} and Fe 2p_{1/2} were 74.8 eV, 710.5 eV and 724.0 eV, respectively. And the spectrum of O 1s from worn surface exhibits two distinguishable peaks, i. e., one with higher binding energy of 531.5 eV, the other with 529.9 eV (Fig. 6). Therefore, according to the XPS handbook^[10], there should exist Al_2O_3 and Fe_2O_3 in the worn-layer, and the outer natural oxide film contained only Al_2O_3 .



Fig. 2 Worn morphologies of Al-10Ti alloy

(a) —low magnification; (b) —high magnification

Both the worn layer and the natural oxide film were etched by argon ion in order to clarify depth profile variation of composition. After being etched for 35 min, the content of aluminum increased, and the content of oxygen decreased. It is visible that variation of the compositions of natural oxide film is more drastic than that of the worn layer. In addition, the iron content of worn layer remarkably decreased (Fig. 3 and Table 1). Since the atomic ratio of O to Al can imply oxidized degree of aluminum alloy, the O/Al ratio is plotted against etched time (Fig. 7). The O/Al ratio for the outer natural oxide film was determined to be 1.5. With prolonged etch time, the O/Al ratio rapidly decreased. But the O/Al ratio for the worn layer remained 1.2 after

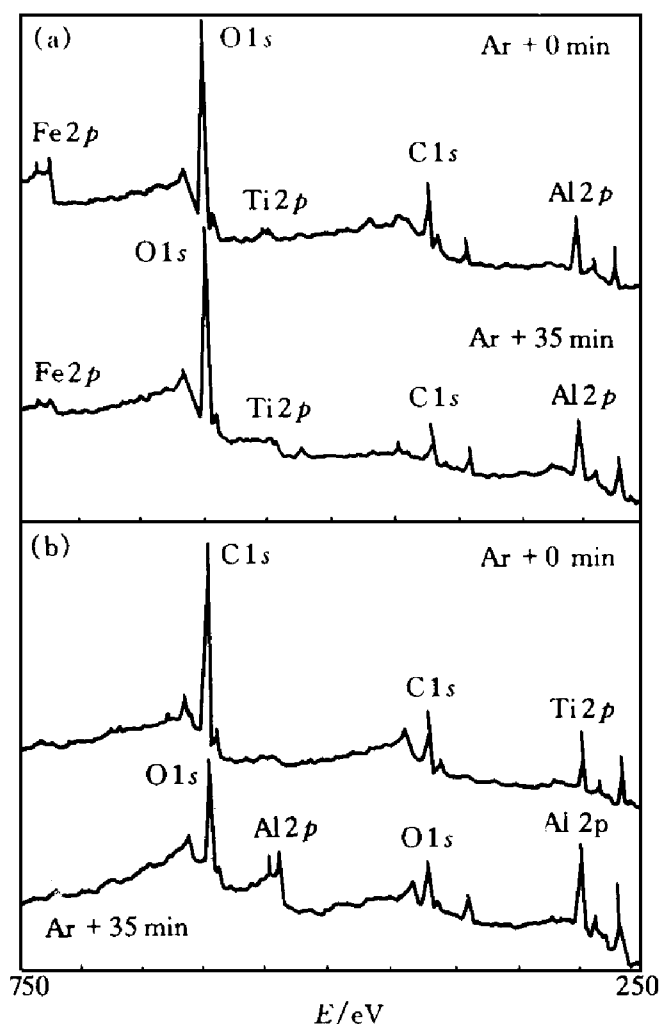


Fig. 3 XPS spectra at typical sections of worn surface and natural oxide film

(a) —worn layer; (b) —natural oxide film

Table 1 Composition at two typical sections of layers under different sputtering time (%)

Layer	<i>t</i> /min	Al	O	Ti	Fe
Worn layer	0	32.0	58.2	2.7	7.2
Worn layer	35	44.1	53.1	2.1	0.7
Natural oxide film	0	39.1	58.4	2.5	0.0
Natural oxide film	35	76.8	17.2	5.91	0.0

being etched for 35 min. In addition, the spectra of Al 2*p* (Fig. 4) show that the Al 2*p* peaks shifted lower binding energy with increase in etched time. This indicates that proportion of oxidized state of Al decreased with increase in depth from surface. After sputtering for 20 min,

it was found that the spectra of Al 2*p* for natural oxide film showed both oxidized state with binding energy of 74.8 eV and metallic state with 72.7 eV. The molar fraction of the latter reached to 42% (Fig. 4(b)). After sputtering for 35 min, no oxidized Al 2*p* was detected in the natural oxidized samples. In contrast, even after sputtering for 35 min, metallic Al 2*p* level for worn layer remained little (Fig. 4(a)). This shows that the worn layer is much thicker than the natural oxide film.

Fig. 8 reveals the X-ray diffraction spectra

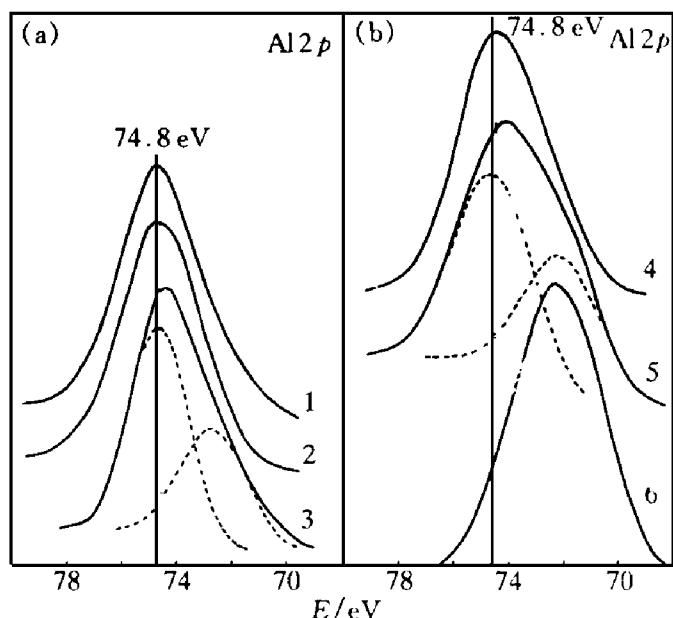


Fig. 4 Al 2*p* spectra at typical sections

(a)—worn layer; (b)—natural oxide film

1—Ar + 0 min; 2—Ar + 20 min;
3—Ar + 35 min; 4—Ar + 0 min;
5—Ar + 20 min; 6—Ar + 35 min

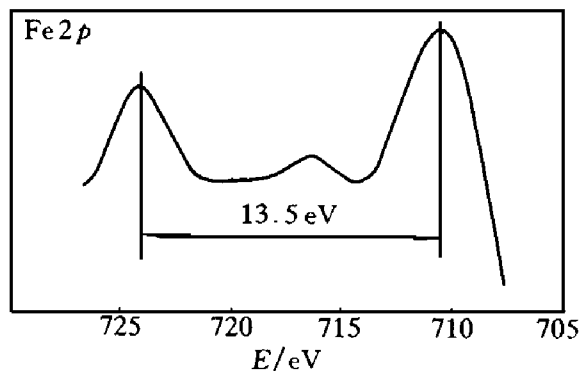


Fig. 5 Spectrum of Fe 2*p* for worn layer(not etched)

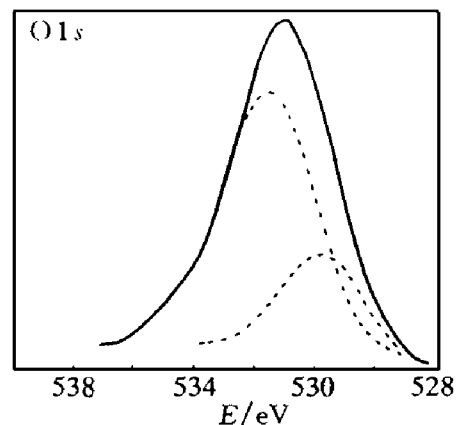


Fig. 6 Spectrum of O 1*s* for worn layer(not etched)

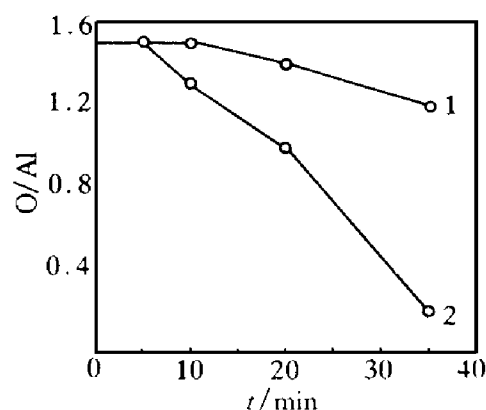


Fig. 7 Change in O/Al ratio with depth from surface

1 —worn layer;
2 —natural oxide film

of the unworn specimen (Fig. 8(a)) and the wear debris (Fig. 8(b)). Trace of α -Al₂O₃ was detected in the wear particles (Fig. 8(b)). Since the oxide layer is normally quite thin, the peaks of α -Al₂O₃ are weak. It should be noted that very weak Al₃Ti peak was found as compared to the diffraction spectrum of the unworn alloy. This indicates that pronounced chemical disordering was caused by repeated shear and compression during sliding wear process.

It is known that decrease in crystallite size and increase in heterogeneous strain leads to broadening of XRD peaks. Assuming that contributions of the grain size *d* and the strain ϵ to the integrated intensities follow Cauchy and Gaussian distribution, respectively, then *d* and

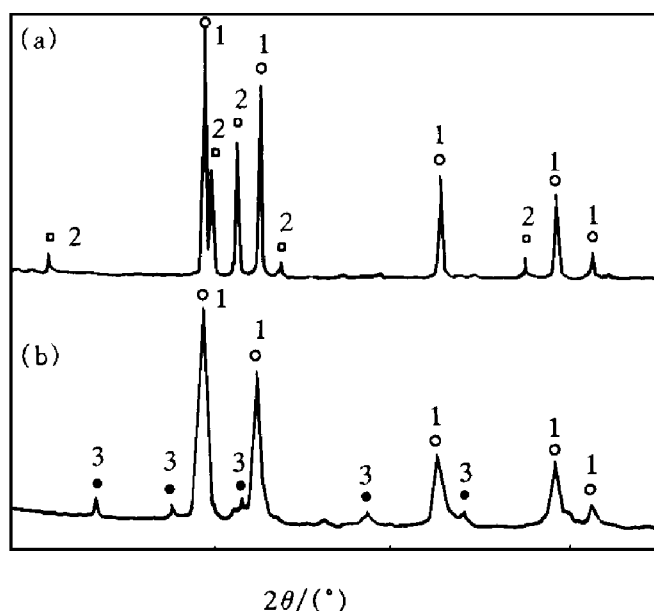


Fig. 8 X-ray diffraction for unworn sample(a) and wear particles(b)
1—Al; 2—Al₃Ti; 3—Al₂O₃

ε can be estimated from Cauchy β_c and Gaussian β_g integral breadth component of Voigt function by

$$d = \lambda / \beta_c \cos \theta \quad (2)$$

$$\varepsilon = \beta_g / 4 \tan \theta \quad (3)$$

where λ is wave length, θ is Bragg angle^[11]. The estimated crystallite and strain of wear particles were 25~60 nm and 5.5×10^{-3} , respectively.

The previous investigations^[2, 3] have shown that the grain sizes of wear debris and the worn layer range from 25 to 60 nm, providing large volume fraction of grain boundary. In addition, dislocations with density of $10^{14} \sim 10^{15} \text{ m}^{-2}$ were accumulated during sliding wear process. Dislocations and grain boundaries act as rapid diffusion ways, accelerating diffusion rate of reactant components^[12]. Moreover, severe lattice strain reduces activation energy of oxidation reaction^[13]. And temperature rise induced by friction increases rate of oxidation. In short, sliding wear promotes oxidation of AlTi alloy.

The oxide layers on the worn surface have

significant influence on the wear process. Firstly, they provide in-situ lubricants, reducing coefficient of friction. This can lead to the decrease of crack nucleation depth and crack growth rate. Secondly, the oxide layers reduce adhesion of aluminum alloy to steel counter-face.

4 CONCLUSIONS

(1) During sliding wear process, iron transferred from steel counter-face to surface of AlTi alloy sample, and Fe₂O₃ was formed.

(2) The dark worn layer was determined to be an oxide layer consisting of Al₂O₃ and Fe₂O₃, which was rich in oxygen and aluminum, but depleted of titanium.

(3) The oxide layer can reduce wear of aluminum alloy.

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