SELF-LUBRICATING BEHAVIOR OF

Fe-Re BINARY ALLOYS[①]

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ABSTRACT   The temperature dependences of the coefficients of friction and the wear rates of several Fe-Re alloys containing various Re contents were determined with a pin-on-disc high-temperature wear device. The examination, analysis and determination of the debris, the wear scars and the load-bearing oxide films were performed using SEM, X-ray diffractometer, electron probe and microhardness tester. The results showed that after high-temperature sliding, there were formed surface glaze layers in the studied Fe-Re alloys, and the sub-surface layers were composed of ductile oxides and deformed matrix alloys. The presence of large amounts of iron oxides on the load-bearing oxide layers resulted in the high hardness platforms and the good high-temperature wear resistance of the alloys. The oxides of Re and $Fe(ReO_4)_3$ present in the skeletons of iron oxides play the role of lubricating at high temperatures.
Key words: lubrication   Re   oxide film   glaze

1 INTRODUCTION

The iron-based alloys are the most popular structural materials used in machine equipments. At the early days of the 1960s, the anti-friction effect of oxides was recognized; in recent years, the development of the alloys with self-lubricating behaviors at high temperatures using the antifriction behaviors of the naturally occurring oxide films was tried on the Ni-Cu-Re and Co-Cu-Re alloy systems[1-3], and their lubrication mechanisms at high temperatures were discussed. However, no systematic examinations on the friction and wear behaviors at elevated temperatures have been made yet. In this paper, the friction and wear behaviors under high-loads and high-speeds of several Fe-Re alloys were studied, and the optimum composition was determined. By measuring the composition and hardness distributions of the surface deformed layer being frictioned at high temperatures, the mechanisms of anti-friction and wear resistance of the Fe-Re alloys were discussed.

2 EXPERIMENTAL

The melting procedure of the alloy was the same as that described in Ref. [1].

The friction and wear tests were conducted on a pin-on-disc high temperature wear device. Test conditions: Al_2O_3 ceramic disc with surface roughness $= 3.5\ \mu m$, alloy pin sample diameter $= 4\ mm$, rotating rate $= 8.5\ m/min$, load $= 48\ N$. After the friction tester had been run for 1 h, the weight change of the sample was measured using a balance with a sensitivity of 0.1 mg, then the wear rate was calculated using the following equation:

$$K = \Delta V/(L \cdot S) \tag{1}$$

where ΔV is wear volume ($=$ weight loss/density), L is load, and S is slide distance.

The coefficients of friction and the wear rates at various temperatures are the means of three tests, respectively.

The structures of the alloys, the debris, the oxide films and the volatile products were determined using X-ray diffractometer; the metallographic examinations of the wear scars, the debris and the surface deformed layers were carried out using a stereo-microscope and a SEM; the composition and the hardness distributions of the deformed layers were determined using electron probe and a hardness tester.

3 RESULTS AND DISCUSSION

3. 1 *Variations of Coefficients of Friction and Wear Rates with Re Content and Temperature*

Fig. 1 shows the variations of the coefficients of friction(μ) and the wear rates(K) with Re content. When the Re contents are in the range of 0 to 50%, the coefficients of friction decrease significantly with Re content at all test temperatures; when the Re contents vary from 50% to 70%, the variations of the coefficients of friction are not evident, and the μ-values increase slightly at room temperature. The wear rates decrease with increasing Re content at all test temperatures except 600 ℃. When the Re contents vary from 25% to 50%, there are transition effects of wear at room temperature, namely from severe wear to mild wear. At 600 ℃, the wear rate of the Fe-25Re alloy is the lowest.

Based on a synthetic study of the friction and wear results of the Fe-Re alloys at elevated temperatures, it can be concluded that the Fe-50Re alloy has better comprehensive anti-friction and wear resistance properties, therefore it may become the base for developing high-temperature self-lubricating alloys.

3. 2 *Examinations of Morphologies of Wear Scars and Debris*

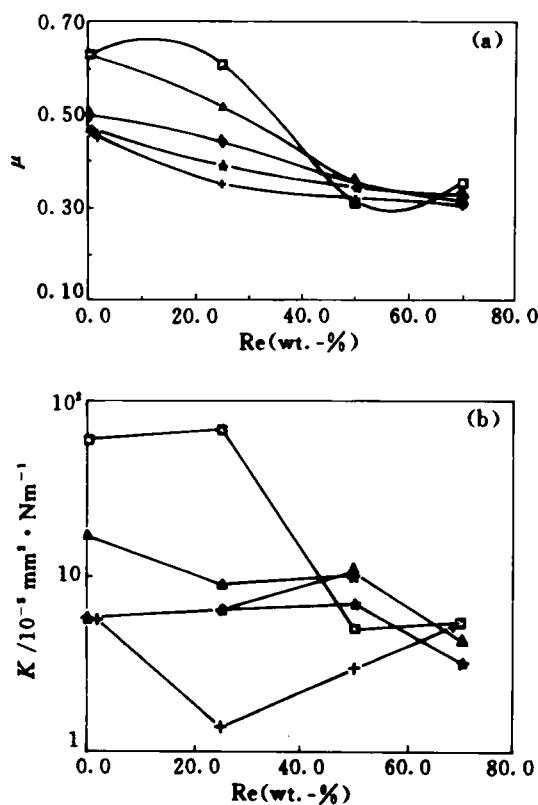After being weared, the samples were taken out from the furnace for the examina -

Fig. 1 Variations of coefficients of friction and wear rates with Re content
■—RT; ▲—200 ℃; ◆—400 ℃;
★—500 ℃; +—600 ℃

tions of the wear scars using a stereo-microscope. It was seen that there were distributed grooves on the weared surfaces at room temperature, which were produced by the plowing of the hard Al_2O_3 asperity.

Fig. 2 (a) shows the morphology of the wear scars of the Fe-50Re alloy at 600 ℃. It can be seen that there is a layer of bright oxides (generally termed glaze layer[4]). There are grooves on the glaze layer, and there are loose oxides adhering to the two sides of the grooves. Except for pure Fe and Fe-70Re alloy, there were formed bright glaze layers on the Fe-Re alloys studied after high temperature friction, and the brightness increased with increasing Re content. Fig. 2(b) shows the SEM photograph of the wear scars in the Fe-50Re alloy, from which it can be seen that
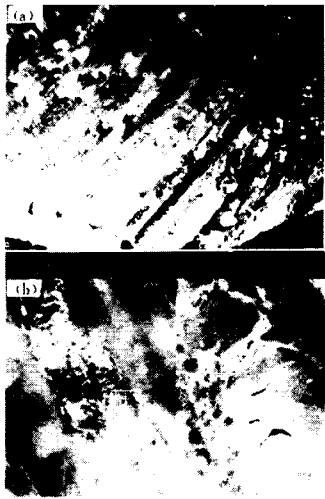
Fig. 2 Morphologies of wear scars of Fe-50Re alloy after weared at 600 ℃

there exist obvious cracks on the glaze layer, and the brown debris on the wearing disc surface is composed of edged oxide films with varying sizes.

The above experimental results showed that for the Fe-Re alloys, the damage was caused by the abrasive wear at lower temperatures; and the damage was mainly caused by the fatigue wear accompanied by plowing at higher temperatures.

3. 3 *Structures of Debris, Composition and Hardness Distributions of Surface Deformed Layer*

The debris and oxides produced by wearing at various temperatures of the Fe-Re alloys were collected for X-ray diffraction analyses, and the results are given in Table 1. Above 600 ℃, the debris is composed of major hexagonal Fe_2O_3 and minor a- Al_2O_3. At room temperature, the debris is composed of major a- $Fe(Re)$ and trace Fe_2O_3 produced by friction heat. With the increasing of temperature, the amount of Fe_2O_3 in the debris increased, and in particular there was found micro $Fe(ReO_4)_3$ in the debris produced at 550 ℃. The $Fe(ReO_4)_3$ possesses good high - temperature

Table 1   X-ray diffraction identification of debris wear scars

Alloy	$T/℃$	Color of Debris	Types of Debris
Fe-8Re	650	Brown	Fe_2O_3-Maj; Al_2O_3-Mic
Fe-15Re	650	Brown	Fe_2O_3-Maj; Al_2O_3-Mic
Fe-25Re	550	Brown	Fe_2O_3-Maj; FeOOH-Min; $Fe_{0.98}O$-Min; Al_2O_3-Min; $Fe(ReO_4)_3$-Tra
Fe-50Re	RT	Black-Light	a- $Fe(Re)$-Maj; Fe_2O_3-Tra
	300	Black-Light	a- $Fe(Re)$-Maj; Fe_2O_3-Mic; Al_2O_3-Tra
	400	Black-Light	a- $Fe(Re)$-Maj; Fe_2O_3-Min; Al_2O_3-Mic
	500	Brown-Black	Fe_2O_3-Maj; a- $Fe(Re)$-Min; Al_2O_3-Tra
	550	Brown-Black	Fe_2O_3-Maj; a- $Fe(Re)$-Min; FeOOH-Min; $Fe_{0.98}O$-Min; $Fe(ReO_4)_3$-Mic
	700	Brown	Fe_2O_3-Maj; Al_2O_3-Tra
Fe-70Re	300	Brown-Black	Fe_2O_3-Maj; a- $Fe(Re)$-Mic
	500	Brown	Fe_2O_3-Maj; FeOOH-Min; ReO_2-Mic; ReO_3-Mic; Al_2O_3-Mic
	600	Brown	Fe_2O_3-Maj; Al_2O_3-Tra

remarks: Maj—Major; Min—Minor; Mic Micro; Tra—Trace

lubricating behavior[5], and plays an impor-
tant role in the high-temperature self-lubricat-
ing behaviors of the Fe-Re alloys.

　　The surface static oxides and the volatile
products of the Fe-50Re alloy formed at 550 ℃
were analysed by X-ray diffraction. It was
known that the static oxides were composed of
major Fe_2O_3 and minor FeOOH, and no Fe
$(ReO_4)_3$ and Re oxides were found; and that
there were monoclic ReO_2, orthogonal ReO_2
and FeOOH in the volatile products. Because
the temperature at the monocrystalline silicon
film for collecting volatile products was
250 ℃, the most common volatile oxide Re_2O_7
in the Re was not found.

　　Fig. 3 shows the SEM photograph of the
structures of the surface and sub-surface lay-
ers after weared at 600 ℃ for 0. 5h on the ver-
tical cross-section along the slide direction. In
the sub-surface layer, there is evident plastic
flow along the slide direction and this de-
formed layer is a mixture of oxides and matrix
alloy. There are tearings and plastic flow in
the pure-Fe sample, but no dark oxide films
are seen. The Fe-70Re alloy is hard and brit-
tle, there is no plastic flow and dark oxide
layer near the wearing surface.

　　The composition analyses of the Fe-
15Re, Fe-25Re and Fe-50Re alloys were car-
ried out on the cross-sections along the depth
using electron probe. The results showed that
the composition changes follow a same law:
the surface glaze layers have high contents of
oxygen and the oxygen decreases with increas-
ing depth. The oxygen content in the oxida-
tion layer increases with increasing Re con-
tent. This means that the affinity of Re for
oxygen is stronger than the affinity of Fe for
oxygen. Figs. 4(a) and (b) show the composi-
tion distributions of the surface layer of the
Fe-50Re alloy after weared at 600 ℃ for 0. 5h
and 1h, respectively. By comparison it can be
known that longer time wearing can increase
the oxygen content in the oxidation layer, es-
pecially in the internal oxidation layer.

　　After weared at 600 ℃ for 0. 5 h, there
occurred hardness platforms in the Fe-Re al-
loys except for pure Fe and Fe-70Re alloy.

Fig. 5(a) shows the microhardness distrbution
of the Fe-50Re alloy along depth. Fig. 5(b)
shows the corresponding metallography, in

**Fig. 3　Morphology of ductile sub-surface
layer of Fe-25Re alloy after
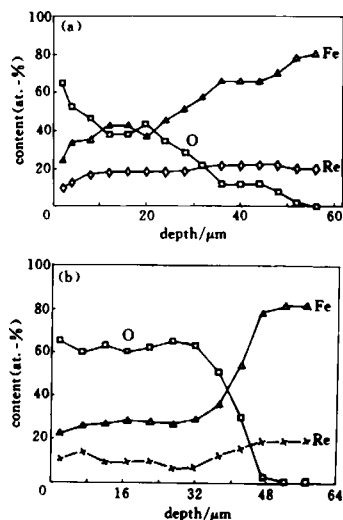weared at 600 ℃ for 0. 5 h**

**Fig. 4　Elemental distributions of sub-surface
layer of Fe-50Re alloy after weared
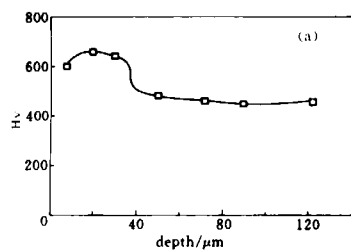at 600 ℃ for 0. 5 h(a) and 1 h(b)**

Fig. 5 Hardness distribution of sub-surface layer of Fe-50Re alloy after weered at 600 ℃ for 0. 5 h

which the dark layer consists of oxides with evident plastic flow, the bright part is the matrix.

By comparing the composition and hardness distribution curves of the Fe-15Re, Fe-25Re and Fe-50Re alloys, it is known that the width of the hardness platforms corresponds to the thickness of the load-bearing oxide layers on the whole. Therefore, it is the oxidation of the surface deformed layers mainly contributing to the higher hardness of the load-bearing oxide layers than the matrixes.

3. 4 *Formation of Glaze Layer and Oxidation Layer and Their Antifriction and Antiwear Effects*

After weared at high temperatures for a period of time, except for pure Fe and Fe-70Re alloys, there were formed bright glaze layers on the friction surfaces of the studied Fe-Re alloys.

At the initial stages of the high temperature friction of the Fe-Re alloys, the preformed oxide films are worn away rapidly, and the fresh surfaces are exposed and the wearing processes are accelerated, thus leading to increasing amounts of debris and increasing friction heat. Under the combined actions of the friction heat and the ambient temperature, the contact points of friction surfaces are softened or even melted. The debris between the friction surfaces are pressured and milled repeatedly, thus being refined to adhere to the wearing surfaces to form a mixed oxide layer, namely glaze layer. The brightness of the glaze layers is in the sequence of Fe-50Re, Fe-25Re and Fe-15Re, which may be due to the fact that higher Re content can produce more soft Re-containing oxides. The antifriction and polishing effect of the soft oxides can make the friction surface brighter. After the glaze layer has been formed, the wearing is reduced, and the stable wearing stage begins.

The glaze layer is supported by subsurface consisting of ductile oxides. Under the glaze layer is the mixed layer of oxides and deformed matrix alloy. After weared at 600 ℃ for 1 h, in the range from the surface to 32 μm depth, the distributions of O, Fe and Re are basically stable and their proportions are 62%, 25% and 13%, respectively. This means that the glaze layer is composed of stable stoichiometric oxides. Based on analysis of X-ray diffraction of debris, static oxides and volatile products, it may be calculated that the layer consists of a large amount of $Fe_{0.98}O$, some amounts of ReO_2, a little $Fe(ReO_4)_3$ produced and so on in wearing process.

The load-bearing oxide film is much thicker than the static oxide film. After weared at 600 ℃ for 1 h, the load-bearing oxide film is 50 μm thickness; at unweared places the oxide film is only 8 μm thickness. The thickness of the load-bearing oxide film is related to the depth of the plastically deformed

Table 5　J_c values after repeated sintering　　(A/cm^2)

Direction	First	Second	Third
Parallel MFS	326	1 300	1 250
Vertical MFS	116	1 000	1 250

tion, so the J_c values along different directions are similar or same at last.

4　CONCLUSIONS

(1) The repeated sintering is useful for the superconductors' grains to crystallize more perfectly and raise the sample's body density in REBa$_2$Cu$_3$O$_{7-\delta}$(RE＝Y, Ho) systems.

(2) Within the temperature range 900 to 960 ℃, the higher the sintering temperature is, the higher the sample's body density and J_c values are.

(3) The magnetic field treatment can raise the HoBa$_2$Cu$_3$O$_{7-\delta}$'s body density and improving the superconductor crystallizing perfectibility.

(4) After the magnetic field treatment, HoBa$_2$Cu$_3$O$_{7-\delta}$ superconductor shows preferred orientation in [110], and its J_c values are different along different directions; but the YBa$_2$Cu$_3$O$_{7-\delta}$ superconductor does not have these phenomenon.

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layer. The plastic deformation can produce more defects such as dislocations and cracks in the matrix, which speed up the diffusion of the oxygen into the matrix, thus bringing about deep oxidation. The thickness of the oxide film is also related to whether there exist elements with strong affinities for oxygen. In addition, the bonding strength between the oxide film and the matrix and the wear rate also affect the thickness of the load-bearing oxide film. The thicker the load-bearing oxide film, the better the high-temperature wear resistance. At 600 ℃, the wear resistance of the Fe-25Re alloy with the maximum thickness of oxide film is better than that of the Fe-50Re alloy with relatively thicker oxide film; the wear resistances of the pure Fe and Fe-70Re alloy without appreciable thickness of oxide films are relatively poor.

The high-temperature wear of the Fe-Re alloys is a dynamic equilibrium process. After a long time of wearing, an oxide layer with stable thickness, composition, oxide types and corresponding proportions is obtained, thus the Fe-Re alloys can self-lubricate in a long term.

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