Research Article

Wear Behaviour of Nanocrystalline $\text{Fe}_{88}\text{Si}_{12}$ Alloy in Water Environment

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Wear behaviour of nanocrystalline $\text{Fe}_{88}\text{Si}_{12}$ alloy has been investigated in water environment compared with the coarse grained counterpart. The friction coefficient of the $\text{Fe}_{88}\text{Si}_{12}$ alloy changes slightly with the grain size. The wear resistance is enhanced as the grain size decreases first and then reduces when the grain size continues to decrease, although the hardness of the $\text{Fe}_{88}\text{Si}_{12}$ alloy decreases monotonically with the grain size. It is contrary to the predications of Archard's formula. The best wear resistance of $\text{Fe}_{88}\text{Si}_{12}$ alloy with grain size of 40 nm in our present work is attributed to the proper grain boundary volume fraction and composite phase structures of disordered B2 and ordered D0_3 .

1. Introduction

In recent decades, how to improve the wear resistance of engineering materials with lubricant has received much attention. Fretting is often an origin of catastrophic failures or loss of functionality in many engineering applications, such as bolted mechanical joints, stacks of objects in transport, and electrical connectors in vibrating machinery and so on. Lots of researchers tried to develop novel wear resistance materials for application in water environment because of pollution caused by oil hydraulic systems [1–3]. Since water has low viscosity and poor lubricity, many conventional materials used in oil hydraulics cannot be used in water condition.

The nanocrystalline materials are of great scientific importance because of the small grain size and significant grain boundaries (GB) volume fraction. Correspondingly, their physical and chemical properties, which are highly sensitive to their microstructure, suggest various potential structure and engineering applications [4–6]. The friction and wear properties of the nanocrystalline materials also have received considerable interest due to the high hardness compared with the coarse grained counterparts [7–10]. Takagi et al. [11], Jeong et al. [12], and Han et al. [13] indicated that the friction coefficient and wear rate of the nanostructured metals and alloys were not only decided by grain size, but also influenced by morphology, phase structure. Although some

studies had been undertaken to investigate the tribological behaviour of the nanocrystalline metals and alloys, there seem to be only a few reports on the tribological properties of the nanocrystalline metals and alloys in water condition.

In the present work, the wear behaviour of the bulk nanocrystalline $\text{Fe}_{88}\text{Si}_{12}$ alloy, which was successfully prepared by combustion synthesis technique [14], was comparatively studied using a conventional tribological tester in water environment.

2. Experimental Procedures

The $\text{Fe}_{88}\text{Si}_{12}$ alloy has been prepared by combustion synthesis technique [14]. Different grain sizes of the $\text{Fe}_{88}\text{Si}_{12}$ alloy were obtained by annealing at different temperatures in air. The grain sizes of the prepared and annealed $\text{Fe}_{88}\text{Si}_{12}$ alloy are 10 nm, 20 nm, 40 nm, and 30 μm , which were designated as NC_{10} , NC_{20} , NC_{40} , and CG, respectively. The hardness increases monotonically with the grain size. According to statistics of XRD and TEM images and corresponding selected area electronic diffraction patterns, the phase structures of the $\text{Fe}_{88}\text{Si}_{12}$ alloys are shown in Table 1. CG is fully composed of relative disordered B2 structure. The phase structure changes from relative disordered B2 to ordered D0_3 when the grain size decreases. And the B2 structure is only about

TABLE 1: Hardness and phase structures of the $\text{Fe}_{88}\text{Si}_{12}$ alloys.

Sample	Grain size	B2 at.%	D_{03} at.%	Hardness GPa	GB vol. %
NC_{10}	10 nm	9	91	10	27.3
NC_{20}	20 nm	38	62	5.5	14.3
NC_{40}	40 nm	79	21	5.3	7.3
CG	$30\ \mu\text{m}$	100	0	5.1	0.005

FIGURE 1: Average friction coefficients (a) and wear rates (b) of the $\text{Fe}_{88}\text{Si}_{12}$ alloys as a function of speed; inset of (a) is evolution of friction coefficient of NC_{10} as function of time.

9 at.% for NC_{10} . The GB volume fractions were calculated by equation $3\delta/(d+\delta)$ [15], where δ is width of GB and d is grain size. In this case, we supposed that δ is 1 nm. The GB volume fraction dramatically increases as the grain size decreases to nanoscale size (Table 1). In particular, the GB volume fraction of NC_{20} is about eighth of total volume of alloys. The relative ordered phase structure and the huge GB volume fraction would affect the properties of $\text{Fe}_{88}\text{Si}_{12}$ alloy with nanoscale size.

The wear behaviour of the $\text{Fe}_{88}\text{Si}_{12}$ alloys was evaluated on an Optimol SRV oscillating friction and wear tester at room temperature (about 25°C) and humidity of 30% in water environment. The surfaces of the discs were polished with 600-grit SiC emery paper. The counterpart is a Si_3N_4 ceramic ball with a diameter of 9.53 mm, Vicker's microhardness of 19 GPa, and surface roughness of $0.01\ \mu\text{m}$. The oscillating speed ranges from 0.02 to 0.08 m/s. The applied load is 30 N. The profiles of worn scars were measured using a micro-XAM surface mapping microscope to determine the wear volume V . The wear rate W was determined as $W = V/s$, where s is total sliding distance. At least three tests were conducted for each set of testing parameters and the average values were calculated from the data of the three tests. The relative error for the friction and wear tests was below $\pm 10\%$. Morphologies and compositions of the worn surfaces of the $\text{Fe}_{88}\text{Si}_{12}$ alloys at different wear conditions were examined by using a JSM-5600LV scanning electron microscope (SEM) and a PHI-5702

multifunctional X-ray photoelectron spectroscope (XPS). The XPS analysis was conducted at 400 W and a pass energy of 29.4 eV, using Al $K\alpha$ radiation as the exciting source and the binding energy of contaminated carbon (C1s: 284.6) as the reference.

3. Results and Discussion

A representative curve of the evolution of friction coefficient of NC_{10} indicates that the friction coefficient becomes steady after the initial transient running time (inset of Figure 1(a)). The average friction coefficients in the steady state of all the $\text{Fe}_{88}\text{Si}_{12}$ alloys increase at a low speed and basically keep stable at high speed in error range (Figure 1(a)). The average friction coefficients of all the $\text{Fe}_{88}\text{Si}_{12}$ alloys with identical speed are very close. This means that the friction coefficient of the $\text{Fe}_{88}\text{Si}_{12}$ alloy changes slightly with grain size in water condition.

The wear rate of the $\text{Fe}_{88}\text{Si}_{12}$ alloy decreases as the grain size reduces to 40 nm (Figure 1(b)), while the wear rate increases when the grain size decreases from 40 nm to 10 nm. In other words, the $\text{Fe}_{88}\text{Si}_{12}$ alloy with grain size of 40 nm has the best wear resistance in water environment for these samples. However, the best wear resistance may occur with grain size of between 20 nm and $30\ \mu\text{m}$, because limited grain sizes of the $\text{Fe}_{88}\text{Si}_{12}$ alloy have been examined in this paper.

FIGURE 2: SEM micrographs of the worn surfaces of NC₁₀ (a) and (b); NC₂₀ (c) and (d); NC₄₀ (e) and (f); CG (g) and (h) under speed of 0.02 m/s and 0.08 m/s, respectively.

We will test the wear rate of this alloy with other grain sizes of follow-up studies. The wear resistance of the Fe₈₈Si₁₂ alloy with nanoscale grain size varied with the speed is opposite to CG. The wear rates of NC₁₀, NC₂₀, and NC₄₀ increase at low speed and retain unchanged at high speed. On the contrary, the wear rate of CG decreases at low speed (Figure 1(b)). These facts demonstrate that the wear behaviour of the Fe₈₈Si₁₂ alloy markedly changes near the grain size of 40 nm.

The SEM micrographs show severe microgrooves and mild delamination on the worn surfaces of all the Fe₈₈Si₁₂ alloys at speed of 0.02 m/s (Figure 2). The wear mechanism of all the Fe₈₈Si₁₂ alloys is dominated by microgrooves and delamination at low speed. However, the plough on the worn surfaces of NC₁₀, NC₂₀, and NC₄₀ becomes mild as speed increases, whereas the plough changes severely with increasing speed for CG. Some microcracks are observed on the worn surfaces of all the NC₁₀, NC₂₀, and NC₄₀ under high speed. Severe delamination and some oxides can be found on the worn surface of CG.

Vickers' microhardness of the Fe₈₈Si₁₂ alloy increases from 5.1 GPa to 10 GPa when the grain size decreases from 30 µm to 10 nm. Generally, the wear loss is inversely proportional to the hardness of the material according to Archard's equation [16]. The high hardness indicates that lesser debris

could detach from the sample. It restrains both crack propagation and wear fragments formation. So the wear resistance of the Fe₈₈Si₁₂ alloy should improve as the grain size decreases to 10 nm. However, it is difficult to depict why the NC₄₀ just with hardness 5.3 GPa has better wear resistance in these samples. The previous researches indicated that tribological chemical reaction might play an important role in the dry wear, especially for nanocrystalline metals and alloys [13], because the interface of nanocrystalline metals and alloys has become an important structural component in addition to the grains, which results in producing some anomalous properties. For example, fast diffusion behaviour of nanocrystalline material has been reported [17]. The tribological chemical reactions on the worn surfaces may be different for the Fe₈₈Si₁₂ alloys with different grain sizes. So, in this case, the chemical states on the worn surfaces of all the Fe₈₈Si₁₂ alloys have been investigated by XPS.

The Fe and Si XPS spectra of worn surfaces of the Fe₈₈Si₁₂ alloys are shown as in Figures 3 and 4. The Fe2p peaks including Fe2p_{3/2} and Fe2p_{1/2} peaks of all the Fe₈₈Si₁₂ alloys can be systematically decomposed into Fe₂O₃, FeO(OH), and Fe₂SiO₄ compounds on the basis of references data published elsewhere [18, 19]. An additional weak peak of Fe₃O₄ can be detected on the worn surface of CG. The intensity of both

FIGURE 3: XPS spectra of Fe_{2p} of Fe₈₈Si₁₂ alloy on the worn surfaces at a sliding speed of 0.08 m/s.

FeO(OH) and Fe₂SiO₄ peaks increases as the grain size increases from 10 nm to 40 nm and then markedly decreases when the grain size increases to 30 μm. On the contrary, the strong Fe_{2p}_{1/2} peak of Fe₂O₃ is observed on the worn surfaces of NC₁₀, NC₂₀, and CG, while it is not found on the worn surface of NC₄₀. It demonstrates that FeO(OH) and Fe₂SiO₄ layers can be formed easier onto the worn surface of NC₄₀ than other samples in water environment.

Similarly, the Si_{2p} spectra of the Fe₈₈Si₁₂ alloys with nanoscale grain sizes can be divided into Fe₂SiO₄, Fe₃Si, and SiO₂ peaks (Figures 4(a), 4(b), and 4(c)) [19, 20]. However the SiO₂ cannot be observed on the worn surface of CG (Figure 4(d)). The intensity of Fe₂SiO₄ peak decreases as the grain size increases, while it increases for Fe₃Si. The Si₃N₄ may originate from the detached debris of the Si₃N₄ ball between contacted zones of friction pair and has not been fully oxidized on the worn surface of CG. According to the analysis of Figures 3 and 4, it is concluded that the Fe₂SiO₄,

SiO₂, and FeO(OH) composite films form easier on the worn surface of NC₄₀ than NC₁₀, NC₂₀, and CG.

There are large numbers of high-energy defects in nanocrystalline metals and alloys, such as GB, microvoids, lattice distortion, crystal defect, and internal stress. The GB volume fraction increases from about 0.005 vol.% to 7.3 vol.% as the grain size reduces to 40 nm (Table 1). So Fe and Si elements in Fe-Si alloy with nanoscale grain size exhibit strong inclination to segregate to the defects [21]. Meanwhile, a large amount of Si will accumulate on the worn surface of sample with small grain size because of the fast diffusion effect compared with CG. The accumulated Si is preferentially oxidized to form continuous SiO₂ and Fe₂SiO₄ composite film in water environment, which significantly prevent further oxidation and wear.

On the other hand, the specific phase structure of Fe₈₈Si₁₂ alloys also influences the oxides formation on the surface of the Fe-Si alloy. Lots of reports indicated that the oxide

FIGURE 4: XPS spectra of Si2p of $\text{Fe}_{88}\text{Si}_{12}$ alloys on the worn surfaces at a sliding speed of 0.08 m/s.

behaviour of the Fe-Si alloy depended on the Si content. Low-Si alloys have a reducible Fe oxide layer, while Si-rich alloys form thick and stable SiO_2 layers. For instance, Wolff et al. showed that the stable SiO_2 layer formed on the surface of Fe-24 at.% Si alloy in borate solution [22]. Atkinson [23] predicted that the Fe-Si alloy surface would form SiO_2 and Fe_2SiO_4 films in water when the Si content was larger than 5 at.% Si, but form Fe_3O_4 with Fe_2SiO_4 films as the Si content was less than 5 at.%. As the Si content in Fe-Si alloy increases, three different phases of α -Fe, Fe_3Si , and FeSi form in turn. The ordered D0_3 Fe_3Si easily forms Fe_2SiO_4 and SiO_2 layers, and disordered B2 $\text{Fe}(\text{Si})$ generates Fe_2O_3 , which transforms $\text{FeO}(\text{OH})$ in water environment. The phase structures of the $\text{Fe}_{88}\text{Si}_{12}$ alloy change from D0_3 and B2 to B2 as the grain size increases. The B2 structure almost disappears for NC_{10} , which suggests that there should form few $\text{FeO}(\text{OH})$ and Fe_2O_3 on the worn surface of NC_{10} in the water environment. So the NC_{40} and NC_{20} with composite structure of D0_3 and B2 would be in favor of forming $\text{FeO}(\text{OH})/\text{Fe}_2\text{O}_3$, SiO_2 ,

and Fe_2SiO_4 composite films. The Fe_2SiO_4 content on worn surface of NC_{20} is equivalent to NC_{10} , which is less than NC_{40} (Figure 3). As GB volume fraction increase above 14.3% (Table 1), the oxidation films may become loose and easy to delaminate when lots of oxide form on the Fe-Si alloy worn surface. Thus, oxidation films on NC_{20} worn surface have been removed in wear. Thus, some of the composite films loosen on the worn surface of NC_{20} and have been removed in wear. However, the different phase structures of the $\text{Fe}_{88}\text{Si}_{12}$ alloy originate from the different grain sizes rather than with identical grain size. It is still difficult to judge which factor is playing more roles during wear. The relation of oxidation and disordered and ordered composite structures should be further examined in the future.

The above discussions demonstrate that the wear behaviour exhibited significantly different characters for the $\text{Fe}_{88}\text{Si}_{12}$ alloys with different grain sizes. The hardness of the $\text{Fe}_{88}\text{Si}_{12}$ alloy increases with decrease of the grain size. So the wear resistance of $\text{Fe}_{88}\text{Si}_{12}$ alloys with grain size of nanoscale

is better than CG. The SEM and XPS of the worn surfaces of the $\text{Fe}_{88}\text{Si}_{12}$ alloys show that the tribochemistry reaction plays an important role during wear in water condition. The worn surface presents protected films and less microplough for NC_{40} . Because the $\text{FeO}(\text{OH})$, Fe_2SiO_4 , and SiO_2 composite films form easier on the worn surface of the NC_{40} than other $\text{Fe}_{88}\text{Si}_{12}$ alloys, so the best wear resistance is obtained for the $\text{Fe}_{88}\text{Si}_{12}$ alloy with grain size of 40 nm in the present work.

4. Conclusions

- (1) The friction coefficient of the $\text{Fe}_{88}\text{Si}_{12}$ alloy changes slightly with grain in water environment.
- (2) The hardness of the $\text{Fe}_{88}\text{Si}_{12}$ alloy increases with decrease of the grain size. The wear resistance of the $\text{Fe}_{88}\text{Si}_{12}$ alloy does not show monotonic improvement as the grain size decreases according to Archard's equation, while it improves as the grain size decreases to 40 nm, and then decreases when the grain size continues to decrease to 10 nm.
- (3) The best wear resistance of the $\text{Fe}_{88}\text{Si}_{12}$ alloy with grain size of 40 nm in our present work is attributed to the specific microstructure. First, the high-energy interfaces of the $\text{Fe}_{88}\text{Si}_{12}$ alloy increase rapidly as the grain size decreases to nanoscale, which can improve the tribochemical reactions of the $\text{Fe}_{88}\text{Si}_{12}$ alloy in water environment. Second, the composite ordered D0_3 and disordered B2 structures are beneficial to forming Fe_2SiO_4 and $\text{FeO}(\text{OH})$ composite films. It possesses excellent wear resistance comparing with the $\text{FeO}(\text{OH})/\text{Fe}_2\text{O}_3$ film, which results from the disordered B2 structure $\text{Fe}(\text{Si})$ phase. In summary, the $\text{Fe}_{88}\text{Si}_{12}$ alloy with proper grain boundary volume fraction and composite phase structures has the best resistance in these samples.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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