Fretting Fatigue Properties of Zr-Based Bulk Amorphous Alloy in Phosphate-Buffered Saline Solution

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A fretting fatigue test was carried out with commercially available Zr-based amorphous alloy (7.6Ni-12.3Cu-3.5Al-76.6Zr in mass%) in air and in a pseudo-body fluid, PBS(-). The fracture behaviors were investigated. The fretting fatigue test was performed under load control using a sinusoidal wave with a stress ratio of 0.1, a frequency of 20 Hz in air or 2 Hz in PBS(-) and a fretting contact pressure of 30 MPa. The 10⁷-cycle fretting fatigue strength in air was one-third the 10⁷-cycle plain fatigue strength. On the other hand, the 2 × 10⁶-cycle fretting fatigue strength in PBS(-) was approximately two times the fretting fatigue strength in air. However, there was little difference between the friction coefficients in air and PBS(-). SEM observations showed that the actual contact area damaged by fretting in air due to the roughness of the surfaces became smaller than that in PBS(-). Thus, it can be considered that the fretting fatigue strength was decreased since in air the actual contact pressure caused by the roughness became higher than the apparent contact pressure. Also, based on the observation that film-forming elements in PBS(-) were different from those in air, it is believed that the surface film can affect the frictional wear characteristics and contribute to the suppression of fretting fatigue crack initiation.

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1. Introduction

Since an amorphous metallic alloy was first developed in 1960,¹ interesting characteristics of many amorphous alloys have been reported. In addition to having a low Young’s Modulus, amorphous alloys have superior tensile strength and corrosion resistance due to a lack of grain boundaries and slip planes compared with the crystalline alloy of the same chemical composition.²,³ Thus, such amorphous alloys are expected to be used as metallic implant biomaterials such as bone plates or spina fixators, which are required to have small size and excellent durability.⁴–⁸

Since such implant devices suffer from cyclic loading during walking, it is important to understand the fatigue behaviors of the amorphous alloys in human body fluid. So far, the authors have reported the following findings: (1) The plain fatigue characteristics of pure Ti for industrial use, Ti alloys and SUS316L, stainless steel in air are almost the same as those in PBS(-). (2) The fretting fatigue strength in air is lowered to one-half to one-third the 10⁷-cycle plain fatigue strength and is further lowered in PBS(-). (3) For Co-Cr alloys, there is little difference between the fatigue strength and the fretting fatigue strength in air and PBS(-).⁹–¹²

There are few papers, however, regarding the fatigue properties of bulk amorphous metallic alloys;¹³–¹⁷ in particular, very few papers on fatigue and fretting fatigue in pseudo-body fluid have been published.¹⁸,¹⁹ In this study, the fatigue and fretting fatigue behaviors of commercially available Zr-based bulk amorphous alloy in air and in pseudo-body fluid, which is expected to be used in the human body, were investigated and compared.

2. Experimental Methods

The material used in this study was commercially available Zr-based bulk amorphous alloy in 3-mm-thick plates. The plates were obtained by pressing 15-mm-diameter rods and consolidated by dry-pressing fine powders of the amorphous alloy. Their chemical composition and mechanical properties are shown in Tables 1 and 2. Before the experiment, the plates were confirmed to be composed of 100% amorphous phase by X-ray diffraction. The fatigue and fretting fatigue tests were performed using a 20-kN-capacity closed-loop electro-hydraulic fatigue testing machine.

Figure 1 shows the shape of the fretting fatigue specimens and fretting pads. Figure 2 shows a schematic diagram for the fatigue test in a pseudo-body fluid environment. When the fretting fatigue specimen whose parallel gauge part is pressed by a pair of bridge-type pads at a constant normal pressure is cyclically loaded, a small relative slip occurs at the contact area between the specimen and pad. This slip, caused by the expansion and contraction of the pad, is small compared with that of the specimen, and the specimen surface is damaged. In the fretting fatigue test, the material for the pad and for the rod that pushes the pad was the same as that of the specimen. After the specimen surface and contact surface of the pad were mirror-finished by buffing, they were degreased with acetone before testing.

Normal pressure was applied by a small actuator utilizing
oil pressure from the testing machine. The fretting fatigue test was carried out under load control using a sinusoidal wave at a stress ratio of $R = 0.1$ under the tension-tension mode and a load frequency of 20 Hz in air or 2 Hz, close to walking velocity, in a pseudo-body fluid and at a contact pressure of 30 MPa. The friction coefficients between the specimens and pads were measured using strain gauges bonded to the inner surface of the central part of the pad. The fatigue test was also carried out under the same conditions as those for the fretting fatigue test.

As a pseudo-body fluid, phosphate buffered saline (PBS(-)) with pH 7.5 was used. After the fluid was filtered using a membrane filter with a pore size of 0.22 μm, 50 kIU of penicillin and 50 mg of streptomycin were added to 1 L of the pseudo-body as antibiotics. The temperature of the fluid in the chamber was kept at $310 \pm 1 \degree C$. To keep the concentration of dissolved oxygen low, close to that of the human body, a mixture of gases containing 4% O$_2$ and 96% N$_2$ was bubbled into PBS(-) at a flow rate of 10 mL/min. As the pseudo-fluid evaporated with time during testing, ultrapure water filtered with the 0.22 μm membrane filter was supplied appropriately. For the test in air, dry air with a relative humidity of 0.005% was flowed into the chamber during the test.

After the tests were finished, the fracture surfaces and fretted surfaces of the specimens were analyzed using a scanning electron microscope (SEM), micro X-ray diffraction (XRD) and an X-ray photoelectron spectrooscope (XPS).

### 3. Results

#### 3.1 Fatigue and fretting fatigue strength

The S-N curves of plain fatigue and fretting fatigue for the Zr-based amorphous alloy in air and PBS(-) are shown in Fig. 3. There was no difference between the S-N curves of the plain fatigue in air and PBS(-). The plain fatigue limits were detected in both environments, and the plain fatigue strengths at $10^7$ cycles were approximately 150 MPa in both environments.

The S-N curves of the fretting fatigue were different from those of the plain fatigue. At large stress amplitudes, the lives in air and PBS(-) were the same, while at small stress amplitudes, the life in PBS(-) was one order longer than that in air. The fretting fatigue strength at $10^7$ cycles in air was approximately 50 MPa, and that at $10^6$ cycles in PBS(-) was approximately 90 MPa.

#### 3.2 Two-stage fretting fatigue test

To examine the effect of fretting damage on the fatigue life or the behavior of crack initiation due to fretting, the fretting pad was taken off after carrying out the fretting fatigue test at a certain number of cycles, and subsequently the plain fatigue test was continued with the same stress amplitude. The stress amplitude ($\sigma_a$) in air and PBS(-) was 100 MPa. Figures 4(a) and (b) show the results in air and PBS(-), respectively. The abscissa indicates the total number of fretting fatigue cycles and plain fatigue cycles performed subsequently, ($N_t$), and the ordinate indicates the number of fretting fatigue cycles ($N_f$).

The plots on the $N_t = N_f$ line indicate the results of the fretting fatigue test. For the plain fatigue test, the specimens were not broken within $10^7$ cycles under the stress amplitudes used in both environments. On the other hand, for the fretting fatigue test, the specimens were broken at $1 \times 10^5$ cycles in air and $6 \times 10^5 - 1 \times 10^6$ cycles in PBS(-). In air, the minimum number of fretting fatigue cycles required for the initiation of the crack propagated by plain fatigue without fretting was $1.5 \times 10^5$, which was less than 15% of the fretting fatigue life.

In PBS(-), the frequency for the fretting fatigue cycle number $N_f$ was 2 Hz. However, in the plain fatigue test after
removing the fretting pad, the frequency was set at 20 Hz, at which point the crack propagation could scarcely be influenced by the environment. In PBS(-), the minimum number of fretting fatigue cycles required for the crack initiation was $3 \times 10^5$, which was 30-50% of the fretting fatigue life.

3.3 Friction coefficients

The relationship between the friction coefficients ($\mu$) and stress amplitude in air or PBS(-), measured during the fretting fatigue test, is shown in Fig. 5. The friction coefficients, $\mu$, were obtained from the equation

$$\mu = \frac{F}{P},$$

where $F$ is the amplitude of tangential force (frictional force) and $P$ is the normal pressure. The friction coefficients in both environments increased to be proportional to $\sigma_a$. The friction coefficient $\mu$ in PBS(-) was lower by 10% than that in air.

4. Discussion

Plain fatigue and fretting fatigue are the same phenomenon from the standpoint that they are fatigue failures occurring under cyclic loading. In fretting fatigue, the initiation and the early stage of propagation of the crack are influenced by fretting, and this is a different point that is not involved in plain fatigue. As shown in Fig. 3, the plain fatigue was scarcely affected by the PBS(-) environment. However, the fretting fatigue strength in PBS(-) showed a larger value than that in air. As previously reported, the fretting fatigue strengths of pure Ti for industrial use, Ti-6Al-4V alloy and SUS316L stainless steel in PBS(-) showed smaller values than those in air at high cycles.\cite{9-12} Next, we discuss why the fretting fatigue strength of the amorphous alloy increased in PBS(-).

4.1 Effect of mechanical factors on fretting fatigue strength

At high cycles, the fretting fatigue strength of the amorphous alloy in PBS(-) is approximately twice that in air. The fretting fatigue life consists of crack initiation life and crack propagation life. At high-stress amplitudes, the ratio of the crack propagation life to the total life is high, and at low-stress amplitudes the ratio of the crack initiation life to the total life is high. Judging from the fact that for plain fatigue there is little difference between the S-N curves in air and PBS(-), as shown in Fig. 3, the crack growth rate in both environments can be estimated to be almost the same. The friction coefficients which can influence the fretting fatigue are almost the same in PBS(-) and air, as shown in Fig. 5. Also, the initiation sites of the main cracks responsible for failure are closely related to the fretting fatigue life.\cite{20} The main crack initiation occurred at the outer edge of the fretted surface in both environments, suggesting that the fretting fatigue strength for the amorphous alloy depends little on the initiation sites of the main cracks.

Figures 6(a) and (b) show the cross-section profile of the fretted surface of the fretting fatigue test specimen observed by a surface roughness analyzer. There was little difference between the profiles in air and PBS(-), and their maximum roughness difference was less than 1 $\mu$m. However, the roughness in PBS(-) showed a more frequent variation than that in air. Figures 7(a) and (b) show SEM images of the fretted surfaces of fretting fatigue specimens tested in air and PBS(-), respectively. The surface tested in air had a small amount of protrusion locally but was mostly unfretted, indicating that the normal pressure was supported by a
contact area smaller than the given area (2 mm × 4 mm). This result suggests that the contact pressure became locally larger than the given pressure (30 MPa) in air and the fretting fatigue strength was reduced by the resultant high local stress concentration. It suggests that in PBS(-), the normal pressure was supported by the whole contact area. Fretting products probably were involved in this result, causing no occurrence of such a high local stress concentration as that in air. Thus, the fretting fatigue strength became higher than that in air.

4.2 Effects of crystallization

During the fretting fatigue test, a relative slip occurs at the fretted surface, and frictional heat is generated. As the load frequency in air is high, 20 Hz, crystallization can occur locally due to the frictional heat and the fretting fatigue strength is decreased due to the resultant embrittlement. On the other hand, as the load frequency in PBS(-) is low, 2 Hz, and the solution has a cooling effect, it is considered that crystallization due to the temperature increase can scarcely occur. To examine the possibility of crystallization, the fretted and unfretted surfaces were analyzed with micro XRD, as shown in Fig. 8. However, the crystallization at the fretted surface was not confirmed from the X-ray results.

The effect of frictional heat can be reduced by decreasing the frequency. Thus, the tests were carried out with the frequency being varied over two orders from 0.2 to 20 Hz. A stress amplitude $\sigma_a$ of 75 MPa was used at a region where the slope is high and the scatter in life is relatively low in the S-N curve of the fretting fatigue test in air, as shown in Fig. 3. Figure 9 shows the effect of frequency on the fretting fatigue life of the amorphous alloy in air, indicating that the life depends little on the frequency, in other words, no dependence of the fretting fatigue on the frictional heat which increases with the increment of frequency. Consequently, the results shown in Figs. 8 and 9 deny the idea that crystallization of the amorphous alloy can occur due to the frictional heat generated during the fretting fatigue test and can decrease the fretting fatigue strength due to the resultant embrittlement. Although the very small volume fraction of crystalline phase may not be detected by micro XRD, such small amount of crystalline phase seems to give only the small effect on the fretting fatigue strength.

4.3 Effects of surface film of the fretted surface

It has been reported that Zr-based alloys can have corrosion pits due to Cl- in PBS(-). However, there were no traces of the corrosion pits at the fretted surface and at the initiation sites of cracks on the fracture surface. In the fretting fatigue test in PBS(-), a surface oxide film which had formed on the contact surface was broken, and a newly formed surface was exposed during each load cycle. For Zr and its homologous series element Ti, the time required for re-passivation was several 10 ms, and the new surface caused...
by fretting was immediately re-oxidized. For Zr-based amorphous alloys, similar behavior was reported, and thus it can be considered that no corrosion pits appeared on the newly formed surface.

In fretting fatigue, crack initiation generally can be accelerated by mechanical factors such as frictional forces. As clearly seen from Figs. 4(a) and (b), the minimum number of fretting fatigue cycles for crack initiation due to fretting in PBS(-) ($3 \times 10^5$ cycles) was approximately 20 times higher than that in air ($1.5 \times 10^7$ cycles). As previously mentioned, mechanical factors such as frictional forces of the amorphous alloy in air are almost the same as those in PBS(-). However, as shown in Fig. 7, the morphology of the fretted surface in air was different from that in PBS(-). Thus, the compositions of oxide films formed on the fretted and unfretted surfaces of the amorphous alloys, after the fretting fatigue test in air and PBS(-), were measured with XPS. The measurement was done over a region that was 1000 μm in diameter, and the results are shown in Table 3. The differences between the compositions of the oxide films of the fretted and unfretted surfaces in air and PBS(-) were as follows:

a) In the results for the frequencies of 2 and 20 Hz in air, the difference between the analyzed values of the compositions of the fretted and unfretted surfaces was small. However, the Cu content of the fretted surface at 2 Hz was three times higher than that of the unfretted surface, and Cu was not detected on the fretted surface at 20 Hz. Also, the O content of the oxide films of the fretted surface was slightly higher.

b) The Zr contents of the fretted and unfretted surfaces in PBS(-) were less than half those in air, and their O contents in PBS(-) were higher than those in air. The Cu content in the oxide films of the fretted surface was one order higher than that of the unfretted surface. Also, the intake of $PO_4^{3-}$ was observed.

In air, from fact a) and the fact that the surface morphology was locally changed at the fretted surface, new surface formation and re-oxidization occurred less frequently at the

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Table 3 Composition of surface oxide film on unfretted area and fretted area of Zr-based bulk amorphous alloy.
fretted surface compared with the occurrence in PBS(-) since they can be induced by a reaction with oxygen in air. On the other hand, the fact that the morphology of the whole fretted surface was changed in PBS(-), as shown in Fig. 7(b), suggests that the formation and re-oxidization of the new surface, due to the reaction with water molecules, dissolved oxygen and phosphate, occurred frequently at the fretting surface, and thus the composition of the surface oxygen film was changed.

Furthermore, at the fretted surface in air, Cu was detected at 2 Hz but not at 20 Hz, possibly due to the preferential oxidization of Zr and Al, whose affinity to oxygen is higher than Cu. As the frictional heat at a frequency of 20 Hz is higher than that at 2 Hz, the oxidation reaction may be promoted. The composition of the surface oxide film and surface oxidization rate may be related to fretting fatigue, and further investigations regarding the oxide films are required.

5. Conclusions

Using commercially available Zr-based amorphous metallic alloy, its plain fatigue and fretting fatigue behaviors in air and PBS(-) were investigated and compared with each other. The results are as follows:

(1) There was no difference between the S-N curves of the fatigue in air and PBS(-), and the $10^7$-cycle fatigue strengths for the both environments were approximately 150 MPa.

(2) The fretting fatigue strength in air decreased to one-third of the plain fatigue strength, and the $10^7$-cycle fretting fatigue strength in air was approximately 50 MPa. However, from $10^6$ to $10^7$ cycles, the fretting fatigue strength in PBS(-) was approximately two times larger than that in air, and the $2 \times 10^8$-cycle fretting fatigue strength was approximately 90 MPa.

(3) In both environments, there was not a large difference in the friction coefficients. However, the actual contact area of the fretted surfaces in air was lowered by the presence of a local protrusion compared with that in PBS(-), suggesting that the actual contact pressure became locally larger than the given pressure and the fretting fatigue strength decreased by the resultant high local stress concentration.

(4) At a stress amplitude of 100 MPa, the minimum number of fretting fatigue cycles for the crack initiation in air was less than 15% of the fretting fatigue life, while that in PBS(-) was 30-50% of the life, and the crack initiation life due to fretting in PBS(-) was longer by more than one order.

(5) The fretting fatigue life in air was scarcely changed even by lowering the load frequency by two orders, and the fretted surface was scarcely influenced by fragility due to crystalization induced by the frictional heat.

(6) There was little difference between the compositions of the film-forming elements of the fretted and unfretted surfaces in air. However, the fretted surface was shown to have higher contents of Cu, O and PO$_4$$^{3-}$ in PBS(-), and this difference in the film-forming elements was suggested to be related to the fretting fatigue crack initiation.

REFERENCES