Open Journal of Metal, 2014, 4, 56-64
Published Online September 2014 in SciRes. http://www.scirp.org/journal/ojmetal
http://dx.doi.org/10.4236/ojmetal.2014.43007

Scientific Research

Ultrasonic Fatigue of $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ Glassy Alloy

Shin-ichi Yamaura[1], Shengli Zhu[2], Katsuhiro Abe[1], Guoqiang Xie[1]

[1]Institute for Materials Research, Tohoku University, Sendai, Japan
[2]School of Materials Science and Engineering, Tianjin University, Tianjin, China
Email: yamaura@imr.tohoku.ac.jp

Received 20 June 2014; revised 18 July 2014; accepted 19 August 2014

Abstract

In this work, ultrasonic fatigue behavior of the $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ glassy alloy was investigated at 20 kHz at a stress ratio of R = −1. The number of cycles to failure in the S-N curve obtained in this work did not decrease again even after 10^7 - 10^8 cycles unlike previous findings for some steels. The fatigue endurance limit and the fatigue rate were σ_w = 762 MPa and σ_w/σ_B = 0.37, respectively. Fish-eye type inertial crack initiation, reported in many papers on giga-cycle fatigue testing, was not observed. A tendency for the fatigue strength of the $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ glassy alloy specimens to be divided into two groups was observed, that is, specimens with a short fatigue lifetime (<10^6 cycles) with distinct cast defects as crack initiation sites and the other specimens with a long fatigue lifetime (>10^6 cycles). This may have been caused by accidental nucleation of micro-defects such as impurities, voids and precipitates in the glassy rod specimens during the casting.

Keywords

Ultrasonic Fatigue, Metallic Glass, Fracture, Casting, Biomaterial

1. Introduction

Glassy alloys are promising materials that have various significantly different characteristics than crystalline materials because of their random atomic arrangement in a non-equilibrium state. Glassy alloys have attracted interest in basic science and are now mainly of interest for engineering applications, due to their very high mechanical strength [1], good corrosion resistance [2] and excellent soft-magnetic properties [3]. The present authors have studied mechanical and chemical properties of glassy alloys for their application as bio-medical materials, focusing on their good corrosion resistance and relatively low Young's modulus. Recently, various materials have been proposed for use as bio-medical materials. In particular, Ti-based alloys are recognized as strong

How to cite this paper: Yamaura, S.-I., Zhu, S.L., Abe, K. and Xie, G.Q. (2014) Ultrasonic Fatigue of $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ Glassy Alloy. *Open Journal of Metal*, **4**, 56-64. http://dx.doi.org/10.4236/ojmetal.2014.43007

candidates for biomedical material, because they are characterized by light weight, low magnetization, high mechanical strength, good corrosion resistance and good affinity to the human body. There have been many reports on the bio-medical applicability of Ti-based alloys such as Ti-Ni [4], Ti-Al-V [5] [6] and Ti-Nb-Ta-Zr [7] [8] alloys. The use of Ni, V and Cr should be avoided when bio-materials are developed since those metal elements are harmful to human cells, being severely carcinogenic. Recently, we have proposed a newly developed Ti-Zr-Cu-Pd-Sn glassy alloy as a candidate for bio-medical material [9] [10]. In this alloy system, the $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ glassy alloy can be formed in a rod of 10 mm in diameter. This glassy alloy does not include Ni, V, or Cr. Furthermore, its relatively low Young's modulus of 87 GPa indicates that it is applicable as implant material.

A lower Young's modulus is preferable when replacing bones and joints with artificial implant materials. Moreover, mechanical reliability such as fatigue strength is also important. Fatigue behaviors of the Ti-Al-V [5] [6] and Ti-Ni-Ta-Zr [7] [8] alloys have been well-investigated and reported by many papers. However, to the present authors' knowledge, fatigue behavior of the Ti-Zr-Cu-Pd-Sn glassy alloy has not yet been investigated. Thus, the objective of this work was to investigate the fatigue behavior of the Ti-Zr-Cu-Pd-Sn glassy alloy.

In materials science, the fatigue fracture phenomenon of metallic materials is progressive, localized structural damage that occurs when a material is subjected to cyclic stress change. It is important to obtain the S-N curve indicating the relation between the stress and the number of cycles to failure. In general, the greater the applied stress range, the shorter the life. It is well-known that some materials exhibit a theoretical fatigue limit below which continued cyclic loading does not lead to failure. Moreover, it is also well-known that fatigue life is influenced by a variety of factors, such as temperature, surface finish, microstructure, existence of defects, residual stress and so on. The fatigue strength (the maximum stress value) is less than the ultimate tensile stress and may be below the yield stress of the material. In general, the study of the fatigue behavior of materials is time-consuming.

Nowadays, there is a growing interest in clarifying the mechanism of very high cycle fatigue of metallic materials, because of the growing importance of using machinery and structural parts for a longer time and the need to evaluate the soundness of aged parts from the viewpoint of cost-efficiency and industrial waste reduction. In this situation, high cycle fatigue (giga-cycle fatigue) properties have been widely studied [11]. As a result, it has been found that failures can occur even below the theoretical fatigue limit obtained with conventional fatigue tests with a frequency around 10 - 100 Hz up to 10^7 - 10^8 cycles, after very high cycles (10^9 - 10^{10} cycles) tested with ultrasonic resonance vibration technique [12] [13]. An ultrasonic resonance technique is used in these experiments with frequencies around 10 - 20 kHz. Use of an ultrasonic resonance technique can drastically shorten the test period. For example, if fatigue strength is measured up to 10^9 cycles at a frequency of 100 Hz, it will take about 3 months. On the other hand, if an ultrasonic fatigue testing machine is used, it will take about 14 hours. This is a significant advantage of the ultrasonic resonance technique. It was clarified by ultrasonic fatigue tests that, in some cases, the number of cycles to failure in the S-N curve starts to decrease again even after 10^7 cycles, showing a modal shift of the fracture mechanism of crack initiation from around the side surface to inertial micro-defects, when fatigue tests are continued for more than 10^8 - 10^9 cycles for high-strength steels [12] [13].

In many cases, fatigue behavior of metallic glasses has been studied by using a conventional fatigue testing machine (e.g., servo-hydraulic type) at frequencies of 10 - 100 Hz up to about 10^7 cycles [14]-[19]. So, in this study, the fatigue behavior of the $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ glassy alloy, which is now under investigation for bio-medical applications [10], was studied by using an ultrasonic fatigue testing machine in order to obtain the S-N curve and to observe the fatigue fracture surfaces.

2. Experimental

Ingots of the $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ glassy alloy were prepared by arc-meting of high-purity raw materials of Ti (99.4%), Zr (99.9%), Cu (99.9%), Pd (99.9%) and Sn (99.999%) in a dilute Ar atmosphere. Ti raw material in sponge-type grains was purchased and melted twice prior to synthesizing mother alloy ingots. Rod-shaped glassy alloy samples were produced by tilt-casting in a dilute Ar atmosphere. The glassy rods were 6 mm in diameter.

One-millimeter-thick disc-shaped pieces were then cut from both ends of the rods and those discs were used for X-ray diffraction (XRD) analysis to identify a glassy single phase with Co-K*α* radiation. Moreover, thermal analysis of those pieces was conducted to investigate the thermal parameters such as the glass transition temperature, T_g, and the crystallization temperature, T_x.

Fatigue tests were conducted with an ultrasonic fatigue testing machine (Shimadzu, USF-2000) at a stress ratio ($R = \sigma_{min}/\sigma_{max}$) of −1 and a frequency of 20 kHz. A schematic of the ultrasonic fatigue test system is shown in **Figure 1**. A specimen was fixed to the end of the ultrasonic horn and was tested under ultrasonic resonant vibrations. The system has an air-compressor to cool the ultrasonic actuator. A part of the cooling air was used to decrease the specimen temperature. All the measurements were controlled by a personal computer.

Figure 2 shows the geometry of the hourglass-type specimen prepared in this work, the resonance frequency of which was determined to be 20 kHz by using the following Equations (1)-(3) [20].

$$L = \frac{c}{\omega} \cdot \tan^{-1}\left[\frac{c}{\omega}\left(\beta \cdot \coth \beta g - b \cdot \tanh bg\right)\right] \tag{1}$$

$$b = \frac{1}{g} \cdot \cosh^{-1}\left(\frac{R}{H}\right) \tag{2}$$

$$\beta = \sqrt{b^2 - \left(\frac{\omega}{c}\right)^2} \tag{3}$$

where c and ω are longitudinal wave velocity $\left(= \sqrt{(E/\rho)}\right)$, E: Young's modulus and ρ: density) and angular velocity ($= 2\pi f$, f: resonant frequency, 20 kHz), respectively. The specimen geometry was determined with the ordinary values of Young's modulus, E = 87 GPa, and density, $\rho = 7.10 \times 10^3\ \text{kg}\cdot\text{m}^{-3}$. As a result of calculation, the calculated parameters, H = 0.5 mm, R = 2.75 mm, g = 8 mm and L = 6.1 mm were obtained. The ultrasonic horn which was connected to a sample has a screw hole of M6. However, the diameter of sample glassy rods was 6 mm. It is impossible to tighten the samples to the horn. Therefore, L of the screw side was cut short by 1 mm and a stainless steel (SUS314) washer was used to fix the sample to the horn. Even in those cases, the samples were vibrated at 20 kHz. The stress concentration factor of this specimen was 1.014, so it was not necessary

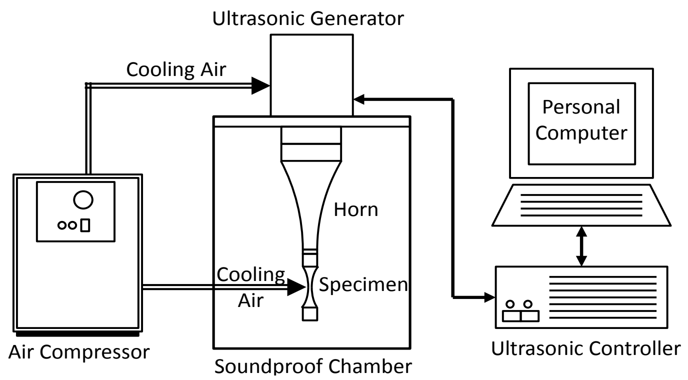

Figure 1. Schematic illustration of ultrasonic fatigue test system.

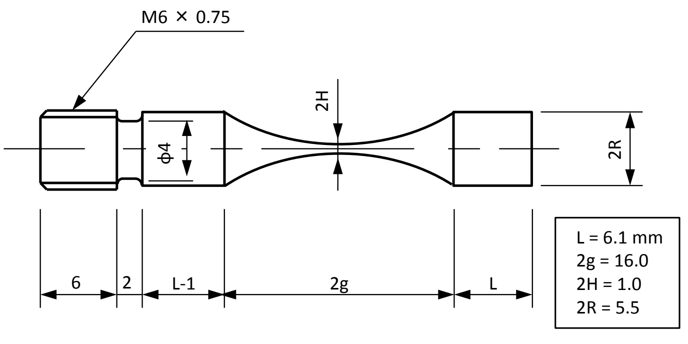

Figure 2. Specimen geometry for fatigue test.

to correct the practical stress with the stress concentration factor in this work. The stress was controlled by the operating software during the tests.

The specimens were machined with cooling water/oil so as not to increase the temperature. Before the tests, the specimens were polished manually with #1500 emery paper in the longitudinal direction, followed by the use of polishing paste.

The stress amplitude, σ_a, of the fatigue test was determined by the following equation [20].

$$\sigma_a = aE\beta \cdot \cos\left(\frac{\omega L}{c}\right) \cdot \cosh bg \cdot \left(\frac{1}{\sinh \beta g}\right) \quad (4)$$

where a is displacement amplitude at the free end of the specimen. Prior to the fatigue tests, the value was measured by an eddy current sensor to calibrate the output level of the ultrasonic actuator controller.

Furthermore, fracture surfaces of specimens were observed by using a scanning electron microscope (SEM) and fracture behaviors were studied in terms of the observation results.

3. Results and Discussion

Figure 3 shows an example of a glassy rod of φ6 in diameter, produced by tilt-casting. Small discs of about 1 mm in thickness were cut from both ends of a rod and were polished with #1500 emery paper and then used for XRD observation. In the case that XRD patterns obtained from both ends of the rod specimen showed a broad halo peak without any distinct peaks originating from the crystalline phase, the rod was recognized as a glassy one possessing only a single glassy pxase. Amorphicity of all the specimens was checked before the fatigue tests.

Figure 4 shows an example of the DSC curve for a $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ glassy alloy sample. As seen in the figure, it was found that the glass transition temperature, T_g, the crystallization temperature, T_x, of the $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ glassy alloy were 688 K and 730 K, respectively. The glass transition region, $\Delta T_x(= T_x - T_g)$, was 42 K. In the previous paper [10], it was reported that the glass transition region of this alloy was ΔT_x = 50 K with raw materials with purity higher than 99.9%. In this study, 2N-grade Ti was used, it may cause the decrease in ΔT_x.

Figure 5 shows the S-N curve of the $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ glassy alloy obtained by ultrasonic fatigue tests in this work. The fatigue test was terminated if the specimen did not show any fracture up to 10^9 cycles. The specimens were cooled by cold air during the tests, the temperature of them did not seem to increase above R.T. The ultimate tensile fracture strength, σ_B, of this alloy is 2050 MPa [10]. The number of cycles to failure in the S-N curve obtained in this study did not decrease again after 10^7 - 10^8 cycles unlike previously reported for some types of steel [12] [13]. The maximum stress amplitude, $\sigma_{a,\,max}$, under which a sample did not fracture up

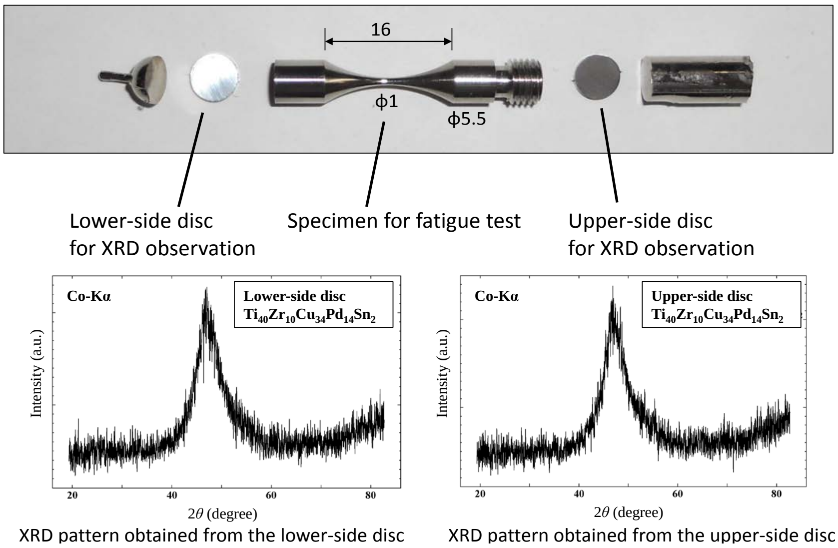

Figure 3. An example of the XRD patterns obtained from an as-cast rod.

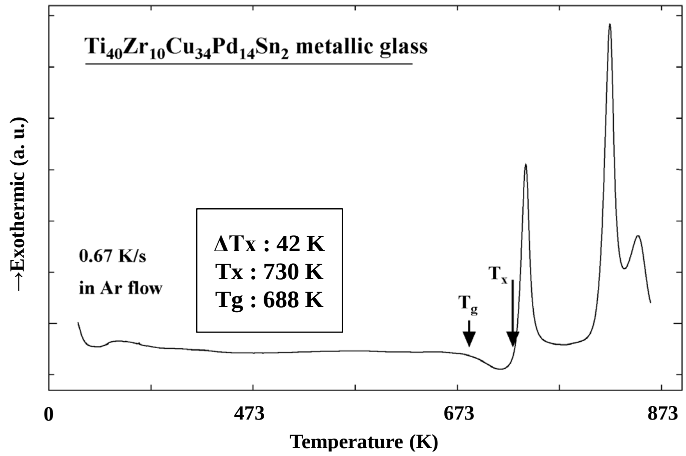

Figure 4. An example of the DSC curve obtained from an as-cast rod.

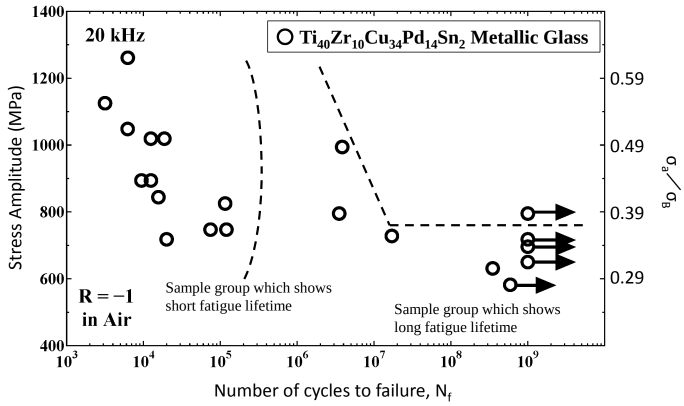

Figure 5. S-N curve of $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ metallic glass.

to 10^9 cycles, was 795 MPa and the maximum stress ratio, $\sigma_{a,\ max}/\sigma_B$, was 0.39. The fatigue endurance limit, σ_w, was defined as a medium value between the maximum stress under which a specimen did not fracture up to 10^9 cycles and the stress just below the maximum stress at which a specimen fractured. The fatigue endurance limit, σ_w, and fatigue ratio, σ_w/σ_B, obtained in this study were 762 MPa and 0.37, respectively. A tendency was observed for the fatigue strength of the $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ glassy alloy specimens to be divided into two groups, that is, some specimens with a short fatigue lifetime ($<10^6$ cycles) and other specimens with a long fatigue lifetime ($>10^6$ cycles).

Figure 6 shows a fractograph of the specimen fractured under the stress σ = 728 MPa (σ_a/σ_B = 0.36) at N_f = 1.702 × 10^7 cycles. This figure shows the fractograph of a specimen with a relatively long lifetime. The crack initiation site and its growth region are seen in Region A and some facets were observed, those are typical morphology of fatigue fracture surface of metallic glasses. Fish-eye type inertial crack initiation, reported in many papers on giga-cycle fatigue testing [12] [13], was not observed. The area outside Region A is the unstable fast fracture region. The unstable fracture region occupies most of the fracture surface, the fracture groove morphology radiates from the crack initiation site. In the magnified image around Region B, a flow-like patterninherent in the unstable fracture region can be seen. However, a melting region with a vein-like pattern [16] usually appears subsequently after the unstable fracture region was not observed in this work.

Figure 7(a) and Figure 7(b) show fractographs of the specimens fractured under (a) the stress σ = 718 MPa (σ_a/σ_B = 0.35) at N_f = 2 × 10^4 cycles and under (b) the stress σ = 747 MPa (σ_a/σ_B = 0.36) at N_f = 7.45 × 10^4 cycles, respectively. As shown in the figures, a distinct micro-inclusion was observed at the crack initiation site. Metallic glasses possess extremely high mechanical strength, so their fatigue strength is significantly sensitive to the existence of micro-defects such as precipitates, voids and inclusions. Therefore, the existence of micro-inclusions or precipitates as shown in Figure 7 can play the role of a crack initiation site, leading to a severe decrease

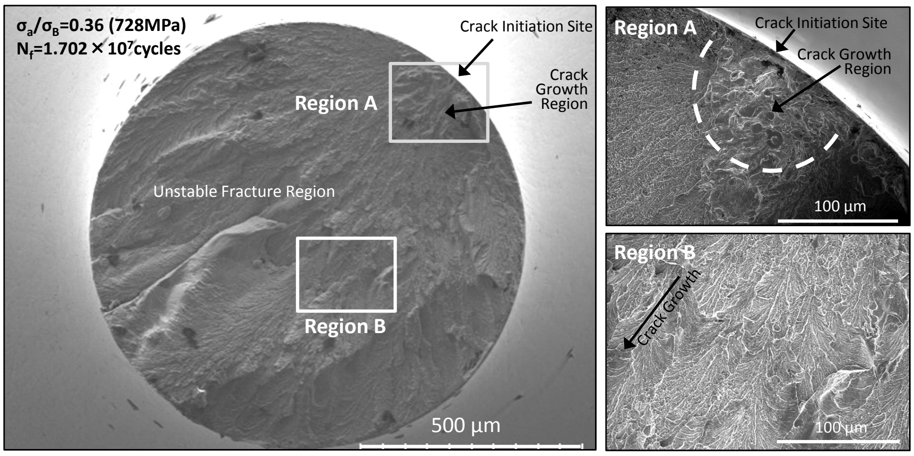

Figure 6. Fatigue fractography of the $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ metallic glass specimen tested at σ_a = 728 MPa (σ_a/σ_B = 0.36) and fractured after $N_f = 1.702 \times 10^7$ cycles.

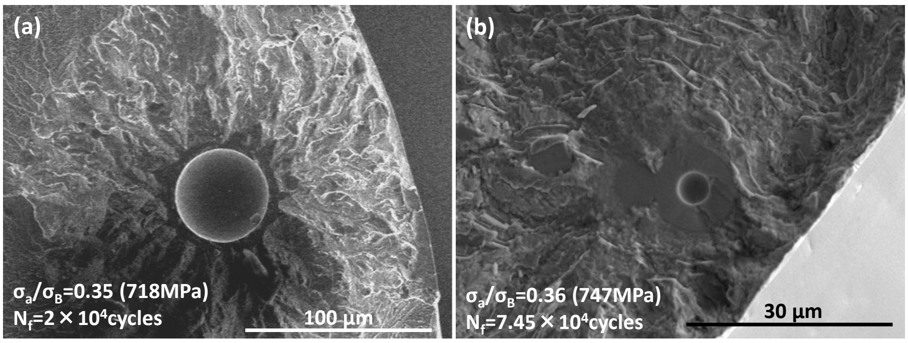

Figure 7. Examples of SEM images of the crack initiation site of the $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ glassy alloy specimens fractured before $N_f = 1 \times 10^5$ cycles. (a) fractured at 718 MPa after 2×10^4 cycles; (b) at 747 MPa after 7.45×10^4 cycles.

in fatigue lifetime. Examination of the fractographs of all the specimens with poor fatigue lifetime, *i.e.*, those described in **Figure 5**, revealed a distinct micro-defect at the crack initiation site in most of the specimens. As a result of alloy composition analysis by SEM-EDX, it was found that the composition of the micro-particle shown in **Figure 7** corresponded to the alloy composition of the glassy matrix phase. It was thus presumed that these micro-particles were casting defects trapped during the tilt-casting. It will be necessary to produce a perfect cast rod of glassy alloy without any micro-defects when glassy alloys with high reliability, *i.e.*, long fatigue lifetime, will be used for engineering applications in practice as structural materials in future.

Figure 8 shows the S-N curves obtained in this study (**Figure 5**) with the result of ultrasonic fatigue tests for the $Zr_{55}Al_{10}Ni_5Cu_{30}$ glassy alloy previously conducted by one of the present authors (S.Y.) [21]. The fatigue endurance limit, σ_w of the $Zr_{55}Al_{10}Ni_5Cu_{30}$ glassy alloy were 893 MPa. Its fatigue endurance limit, σ_w, is higher than that of the $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ glassy alloy (762 MPa). The tensile strength of the Ti-Zr-Cu-Pd-Sn glassy alloy is higher than that of the Zr-Al-Ni-Cu glassy alloy, ideally the fatigue strength of the former could be higher than that of the latter. However, the Ti-Zr-Cu-Pd-Sn glassy alloy did not show higher fatigue strength than the Zr-Al-Ni-Cu glassy alloy in this study although it is believed in general that the higher the mechanical strength, the more sensitive to micro-defects.

Table 1 shows the ultimate tensile strength, fatigue endurance limit, fatigue ratio, test frequency and stress ratio of some metallic glasses [16] [19] [21] and Ti-Al-V alloy [5]. The stress ratio R is defined as the maximum stress amplitude divided by the minimum stress amplitude. AX stands for “axial loading”. As seen in the table, the fatigue ratio of the Zr-based glassy alloys is around 0.5 tested at 10 Hz [16] or 20 kHz [21]. However, the effect of frequency on fatigue strength of metallic glass is not yet clear and remains to be studied in the future. The fatigue ratio of other glassy alloys such as Co-, Fe- and Cu-based alloys [19] is also around 0.5 - 0.6. In

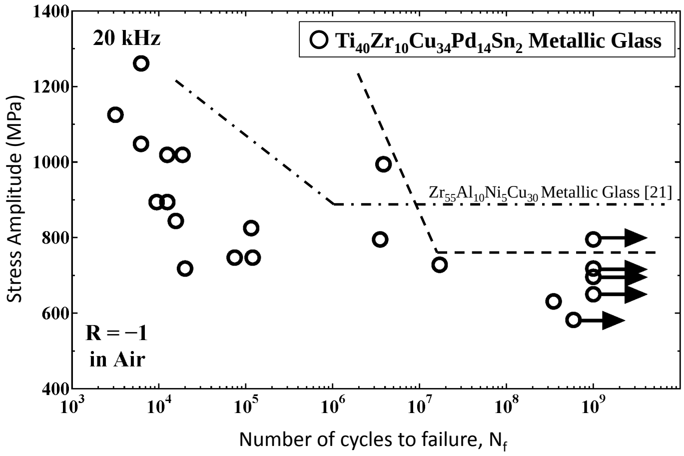

Figure 8. S-N curves of $Ti_{40}Zr_{10}Cu_{30}Pd_{14}Sn_2$ and $Zr_{55}Al_{10}Ni_5Cu_{30}$ metallic glasses obtained by using an ultrasonic fatigue testing machine.

Table 1. Fatigue-endurance limits and fatigue ratios of present metallic glass and others previously reported in the literatures.

Material BMG: Bulk Metallic Glass NCP: Nano-Cryastalline Particle Dispersed BMG	Ultimate Tensile Strength σ_B (MPa)	Fatigue Endurance Limit σ_w (MPa)	Fatigue Ratio σ_w/σ_B	Frequency (Hz)	R AX: Axial Loading
$Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ BMG (present study)	2050	762	0.37	20000	AX −1
$Zr_{55}Al_{10}Ni_5Cu_{30}$ BMG [21]	1700	893	0.53	20000	AX −1
$Zr_{50}Al_{10}Cu_{40}$ BMG [16]	1821	752	0.41	10	AX 0.1
$Zr_{50}Al_{10}Cu_{30}Ni_{10}$ BMG [16]	1900	865	0.46	10	AX 0.1
$Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG [16]	1850	703	0.38	10	AX 0.1
$Ti_{41.5}Zr_{2.5}Hf_5Cu_{42.5}Ni_{7.5}Si_1$ NCP [19]	2040	1610	0.79	10	AX 0.1
$[(Co_{0.6}Fe_{0.4})_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$ BMG [19]	4170	2370	0.57	10	AX 0.1
$(Fe_{0.5}Co_{0.5})_{72}B_{20}Si_4Nb_4$ BMG [19]	4200	2280	0.54	10	AX 0.1
$Ni_{60}Zr_{20}Nb_{15}Al_5$ BMG [19]	2900	1680	0.58	10	AX 0.1
$Cu_{60}Zr_{30}Ti_{10}$ NCP [19]	2000	980	0.49	10	AX 0.1
Ti-6AL-4V crystalline alloy [5]	960	535	0.56	20000	AX −1

particular, the Co- and Fe-based glassy alloys showed extremely excellent fatigue strength higher than 2 GPa. The Ti- and Ni-based glassy alloys also showed good fatigue strength higher than 1.6 GPa [19]. The $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ glassy alloy prepared in this work showed high fatigue strength over 750 MPa, tested at 20 kHz. These observations proved the potential of the metallic glass as a structural material. Furthermore, the $Ti_{41.5}Zr_{2.5}Hf_5Cu_{42.5}Ni_{7.5}Si_1$ NCP glassy alloy showed a significantly high fatigue ratio σ_w/σ_B of 0.79 though its tensile strength was almost same as that of the $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ glassy alloy. NCP stands for "nano-crystalline particle dispersed material". Dispersion of nano-scaled crystalline particles in the glassy alloy matrix may contribute to such an extremely high fatigue ratio. The reason for the extremely high fatigue ratio of this alloy is still unclear. It is also necessary to study the effects of frequency, stress ratio and purity of raw materials used to synthesize specimen alloys on the fatigue strength.

If there are casting defects in the glassy specimens, those defects can easily lead to initiation of microcracks, resulting in severe degradation of fatigue strength. So, it is significantly important to avoid casting defects during the fabrication of metallic glasses in the viewpoint of the mass-production for their engineering use. Tilt casting is thought to be a better casting method than conventional Cu-mold injection casting for suppression of nucleation of micro-defects, because the surface area of the molten alloy does not change rapidly during the tilt-casting which does not need nozzle tubes. However, metallic glass is a non-equilibrium solid. So, it may be difficult to avoid micro-defects which are nucleated by accident in glassy phase during the quenching. It is also difficult to produce a large quantity of glassy alloy rods manually in a laboratory whose quality and reliability are guaranteed at the mass-production level. Metallic glasses have been developed from the beginning of 1990s and their basic scientific studies have been conducted for about two decades. Thus, it is about time metallic glasses should be applied for engineering purposes in practice. Thus, in the near future, it will be necessary to standardize the properties and the production methods of some typical metallic glasses selected to meet engineering demands. Thereof, development of instrumentation techniques such as temperature control of molten alloys and an automatic casting operation is essential to stabilize and guarantee the quality and reliability of the metallic glasses by suppressing the nucleation of micro-defects.

4. Conclusions

In this study, ultrasonic fatigue behavior of the $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ glassy alloy which has a potential for biomedical applications was investigated at 20 kHz at the stress ratio of R = −1. The results are summarized below.

(1) The number of cycles to failure in the S-N curve obtained in this work did not decrease again after 10^7 - 10^8 cycles unlike previously reported for some types of steel. The fatigue endurance limit and the fatigue rate were σ_w = 762 MPa and σ_w/σ_B = 0.37, respectively. Fish-eye type inertial crack initiation, reported in many papers on giga-cycle fatigue testing, was not observed in this work.

(2) A tendency was observed for the fatigue strength of the $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ glassy alloy specimens to be divided into two groups, that is, some specimens with a short fatigue lifetime (<10^6 cycles) and other specimens with a long fatigue lifetime (>10^6 cycles). This may be caused by accidental nucleation of micro-defects such as impurities, voids and precipitates in the glassy rod specimens during the casting manually by hand. Indeed, distinct micro-defects at around the crack initiation site were observed on the fractured surfaces in most of the specimens fractured before 10^6 cycles. Therefore, it will be critically important to avoid micro-defects by careful control of the synthesizing process of metallic glasses in the future.

References

[1] Inoue, A., Shen, B.L., Koshiba, H., Kato, H. and Yavari, A.R. (2003) Cobalt-Based Bulk Glassy Alloy with Ultrahigh Strength and Soft Magnetic Properties. *Nature Materials*, **2**, 661-663. http://dx.doi.org/10.1038/nmat982

[2] Yoshioka, H., Asami, K., Kawashima, A. and Hashimoto, K. (1987) Laser-Processed Corrosion-Resistant Amorphous Ni-Cr-P-B Surface Alloys on a Mild Steel. *Corrosion Science*, **27**, 981-995. http://dx.doi.org/10.1016/0010-938X(87)90064-3

[3] Fujimori, H., Masumoto, T., Obi, Y. and Kikuchi, M. (1974) On the Magnetization Process in an Iron-Phosphorus-Carbon amorphous Ferromagnet. *Japanese Journal of Applied Physics*, **13**, 1889-1890. http://dx.doi.org/10.1143/JJAP.13.1889

[4] Oshida, Y. and Miyazaki, S. (1991) Corrosion and Biocompatibility of Shape Memory Alloys. *Zairyo-to-Kankyo*, **40**, 834-844. (in Japanese)

[5] (2010) Data Sheet on Giga-Cycle Fatigue Properties of Ti-6Al-4V (900 MPa CLASS) Titanium Alloy at High Stress Ratios, NIMS Fatigue Data Sheet, No. 111.

[6] Oguma, H. and Nakamura, T. (2010) The Effect of Microstructure on Very High Cycle Fatigue Properties in Ti-6Al-4V. *Scripta Materialia*, **63**, 32-34. http://dx.doi.org/10.1016/j.scriptamat.2010.02.043

[7] Tsutsumi, H., Niinomi, M., Akahori, T., Nakai, M., Takeuchi, T. and Katsura, S. (2010) Mechanical Properties of a β-Type Titanium Alloy Cast Using a Calcia Mold for Biomedical Applications. *Materials Transactions*, **51**, 136-142. http://dx.doi.org/10.2320/matertrans.L-M2009828

[8] Nakai, M., Niinomi, M. and Oneda, T. (2012) Improvement in Fatigue Strength of Biomedical β-Type Ti-Nb-Ta-Zr Alloy While Maintaining Low Young's Modulus through Optimizing ω-Phase Precipitation. *Metallurgical and Materials Transactions A*, **43A**, 294-302.

[9] Zhu, S.L., Wang, X.M., Qin, F.X., Yoshimura, M. and Inoue, A. (2007) New TiZrCuPd Quaternary Bulk Glassy Alloys with Potential of Biomedical Applications. *Materials Transactions*, **48**, 2445-2448. http://dx.doi.org/10.2320/matertrans.MRA2007086

[10] Zhu, S.L., Wang, X.M. and Inoue, A. (2008) Glass-Forming Ability and Mechanical Properties of Ti-Based Bulk Glassy Alloys with Large Diameters of up to 1 cm. *Intermetallics*, **16**, 1031-1035.

http://dx.doi.org/10.1016/j.intermet.2008.05.006

[11] Takahashi, K. and Ogawa, T. (2008) Evaluation of Giga-Cycle Fatigue Properties of Austenitic Stainless Steels Using Ultrasonic Fatigue Test. *Journal of Solid Mechanics and Materials Engineering*, **2**, 366-373. http://dx.doi.org/10.1299/jmmp.2.366

[12] Shiozawa, K., Morii, Y., Nishino, S. and Liu, L.T. (2006) Subsurface Crack Initiation and Propagation Mechanism in High-Strength Steel in a Very High Cycle Fatigue Regime. *International Journal of Fatigue*, **28**, 1520-1532. http://dx.doi.org/10.1016/j.ijfatigue.2005.08.015

[13] Murakami, Y., Takada, M. and Toriyama, T. (1998) Super-Long Life Tension-Compression Fatigue Properties of Quenched and Tempered 0.46% Carbon Steel. *International Journal of Fatigue*, **16**, 661-667. http://dx.doi.org/10.1016/S0142-1123(98)00028-0

[14] Gilbert, C.J., Lippmann, J.M. and Ritchie, R.O. (1998) Fatigue of a Zr-Ti-Cu-Ni-Be Bulk Amorphous Metal: Stress/ Life and Crack-Growth Behavior. *Scripta Materialia*, **38**, 537-542. http://dx.doi.org/10.1016/S1359-6462(97)00522-8

[15] Yokoyama, Y., Nishiyama, N., Fukaura, K., Sunada, H. and Inoue, A. (1999) Rotating-Beam Fatigue Strength of $Pd_{40}Cu_{30}Ni_{10}P_{20}$ Bulk Amorphous Alloy. *Materials Transactions, JIM*, **40**, 696-699.

[16] Wang, G.Y., Liaw, P.K., Peker, A., Yang, B., Benson, M.L., Yuan, W., Peter, W.H., Huang, L., Freels, M., Buchanan, R.A., Liu, C.T. and Brooks, C.R. (2005) Fatigue Behavior of Zr-Ti-Ni-Cu-Be Bulk-Metallic Glasses. *Intermetallics*, **13**, 429-435. http://dx.doi.org/10.1016/j.intermet.2004.07.037

[17] Wang, G.Y., Liaw, P.K., Yokoyama, Y., Inoue, A. and Liu, C.T. (2008) Fatigue Behavior of Zr-Based Bulk-Metallic Glasses. *Materials Science and Engineering A*, **494**, 314-323. http://dx.doi.org/10.1016/j.msea.2008.04.034

[18] Menzel, B.C. and Dauskardt, R.H. (2008) Fatigue Damage Initiation and Growth from Artificial Defects in Zr-Based Metallic Glass. *Acta Materialia*, **56**, 2955-2965. http://dx.doi.org/10.1016/j.actamat.2008.02.029

[19] Fujita, K., Zhang, W., Shen, B.L., Amiya, K., Ma, C.L. and Nishiyama, N. (2012) Fatigue Properties in High Strength Bulk Metallic Glasses. *Intermetallics*, **30**, 12-18. http://dx.doi.org/10.1016/j.intermet.2012.03.021

[20] Salama, K. and Lamerand, R.K. (1981) The Prediction of Fatigue Life Using Ultrasound Testing. *Proceedings of the first International Conference on Fatigue and Corrosion Fatigue up to Ultrasonic Frequencies*, Pennsylvania, 25-30 October 1981, 109-118.

[21] Yamaura, S. and Fujita, K. (2014) Ultra-High Cycle Fatigue Properties in $Zr_{55}Al_{10}Ni_5Cu_{30}$ Metallic Glassy Alloy Using Ultrasonic Fatigue Testing Machine. *Journal of the Society of Materials Science, Japan*, **63**, 473-479. http://dx.doi.org/10.2472/jsms.63.473